**Fig. 10 Primary components of a batch-type vacuum deposition system that can be used for plasma processing**

**Processing Chamber.** There are several chamber configurations for vacuum deposition systems (Fig. 11). The batch-type system is the most common but exposes the system to the ambient air with each deposition, which can introduce uncontrolled process variables. Load-lock systems allow the deposition chamber to be kept under a more controlled environment.

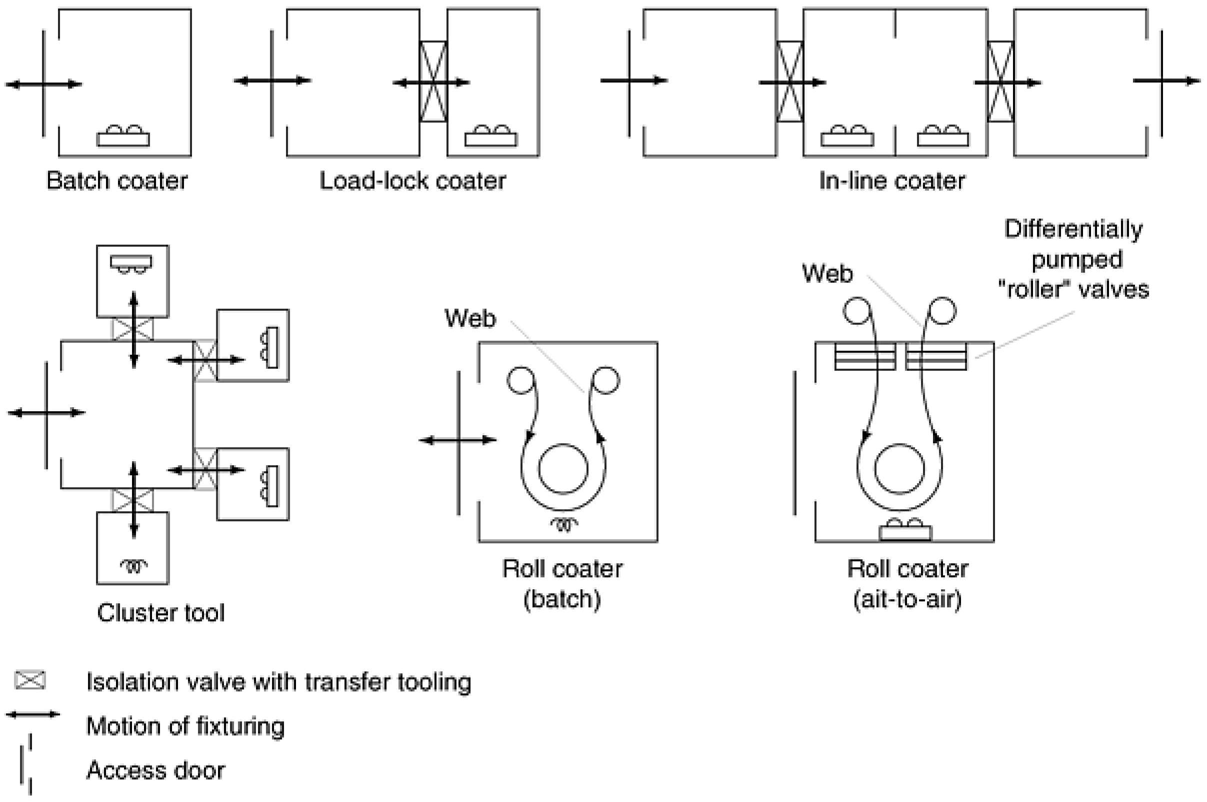

**Fig. 11 Chamber configurations employed in vacuum deposition systems**

Vacuum deposition systems need to be kept clean in order to operate efficiently. Deposit buildup results in increased pumpdown time because of slower desorption of adsorbed contaminants (for example, water). Deposit buildup also results in flaking from walls and fixtures, which can cause pinholes in coatings. Good vacuum practices should be used in all aspects of the use of deposition equipment. The design of the system should allow good access for cleaning and mounting of appropriate fixturing, sources, shutters, and so on.

Heating from the vaporization source can raise the system temperature to unacceptable levels, leading to desorption, outgassing, and the failure of organic seals. Heat is generally removed by water cooling the chamber walls or by using an internal heat sink, such as a water-cooled surface (Ref 128). The cooling channels in the chamber walls can be used to heat the surface using hot water when the system is opened to the ambient air. This heating minimizes water adsorption on the surface when the system is open to the ambient air.

**Pumping System.** Pumping in the vacuum deposition system is generally relatively simple because there are typically no high-gas loads. However, in some cases, the gas and vapor loads can be high from outgassing and desorption, and the system should be designed accordingly. An example is web (roll) coating, where trapped gases are released during unrolling of the plastic web in the deposition chamber. Where water vapor release is a problem, it is often desirable to have an in-chamber cryocondensation surface. These surfaces are cooled by refrigeration and "freeze out" the water vapor in the chamber at low temperatures (<-130 °C, or -202 °F).

In reactive deposition processes and gas evaporation, where the gas pressures are high, the vacuum pumping system can generate pressure differentials in the chamber. This can have a significant effect if the system has a great deal of fixturing in the processing volume. This problem has been noted at processing pressures as low as 0.13 Pa (10 mtorr).

**Fixturing and Tooling.** The definitions of *fixturing* and *tooling* are not universally accepted, but in general, *fixturing* is used to hold the substrates while *tooling* is used to move the fixtures. Fixturing and tooling should be constructed to minimize virtual leaks, particle generation by flaking, and shadowing effects on the deposition process. Fixtures and tooling should be easily removable for cleaning or rearrangement. Fixture surfaces often represent a major portion of the surface in the processing chamber and should be cleaned, handled, and stored with care.

Tooling is used to randomize the substrate position and angle with respect to the direction of the depositing flux. A common tooling in evaporation processing is a spherical dome-shaped (calotte) holder that maintains a constant line-of-sight distance between the source and substrates. Often this holder is rotated to randomize the position of the substrates. This results in improved surface coverage, a more uniform thickness distribution, and more consistent film properties (Ref 6, 129, 130). However, it should be realized that no amount of movement can completely overcome the angle-of-incidence and thickness variations on a complex surface. Angle-of-incidence differences can lead to significant film property variations.

**Mounting of Substrates.** Substrates should be mounted so that particles in the deposition ambient do not settle on the substrate surface. This requires mounting the substrates so that they face downward or to the side. Mechanical clamping is often used to secure the substrates, but this entails having a region that is uncoated. Mechanical clamping provides poor and variable thermal contact to the fixture surface and can result in variable substrate temperatures during the vaporization/deposition process.

**Substrate Heating and Cooling.** Substrates can be heated from a number of sources:

- Condensation of the depositing atoms
- Radiant heating from the vaporization source
- Separate radiant heaters (for example, quartz radiation lamps) in the system to heat the substrate directly
- Embedded heaters to heat the fixturing
- Accelerated electrons from a heated filament, used to heat conductive substrates or fixtures
- Laser radiation, used to provide local heating during the deposition process

Substrates can be cooled by being in contact with a cooled substrate fixture. Circulating chilled water or oil, a cooled water/ethylene glycol mixture (at -25 °C, or -13 °F), dry ice/acetone (at -78 °C, or -109 °F), or liquid nitrogen (at -196 °C, or -321 °F) can be used as coolants.

**Masks.** Because in vacuum deposition the vapor flux travels in a straight line to the substrate surface, physical masks can be used to intercept the flux to produce defined patterns of deposition on a surface. The effectiveness of masks depends on the mask-surface contact, mask thickness, edge effects, and mask alignment on the surface. Masks can be made by numerous methods (for example, etching or machining) (Ref 131) and can allow pattern resolutions as small as several microns. Masking allows the patterning of hard-to-etch materials and in situ patterning during deposition. Deposited masks are used in the lift-off patterning process (Ref 131). Programmed moving masks can also be used to control the film thickness distribution on a surface (Ref 14, 15, 132)

**Shutters.** The shutter is an important part of the vacuum deposition system. Shutters can be used to isolate the substrate from the source and to allow outgassing and wetting of the source without contaminating the substrate. Shutter design is limited only by the ingenuity of the designer. The shutter can be the moving part, or the substrate can be moved. Shutters can be in the form of fans, leaves, flaps, or sections of geometrical shapes (for example, cones, cylinders, and so on). In designing a shutter, care must be taken to keep the complexity to a minimum. Shutter design should provide for easy removal when cleaning is necessary. In some cases, it may be desirable to cool the shutter as an aid in pumping condensables.

**Source fixturing** involves making good electrical contact with the resistively heated vaporization source (for example, wire or sheet). Thermal expansion requires that the fixture be slightly flexible. If the fixture is too rigid, the vaporization source can be stressed and subsequently broken. If the source is flexible (for example, a wire or coil), the source can distort and thus produce changes in the flux distribution pattern on heating and in actual use. In some cases, the source and its electrical connections are moved during deposition to increase coverage uniformity over a large stationary substrate.

High current connections to the source should be of a high-conductivity material such as copper. Physical contact to boats and crucibles can be improved by using spring contacts of a material such as tungsten, along with graphite paper shimming materials, such as that known by the tradename Grafoil. In some cases, cooled clamps can be used to hold the source. Multiple evaporation sources can be arranged to produce large-area or linear vaporization patterns.

**In Situ Cleaning.** Many vacuum deposition systems, particularly optical coating systems, are equipped with the capability to establish a plasma discharge for cleaning substrate surfaces prior to film deposition (Ref 1). Pure air is often used as the cleaning plasma for oxide surfaces. Often a plasma ring is used as the cathode in the processing chamber. The plasma ring should be shielded to prevent sputtered material deposits on the substrate. The cathode can be cooled if the power to the cathode is high.

The effectiveness of plasma cleaning depends on the packing of surfaces in the volume. If there is a large volume of fixturing and close spacing of surfaces in the chamber, the effectiveness of plasma cleaning will vary throughout the volume of the system.

**Getter Pumping.** When reactive materials are deposited, the fixturing and shields in the deposition system can be arranged to provide getter pumping by the excess deposited film material. This gettering lowers the contamination level in the system and at the substrate.

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## Process Monitoring and Control

To provide a reproducible vacuum deposition process, the principal deposition parameters that need to be monitored and controlled are:

- Residual gas pressure and composition prior to and during deposition
- Substrate temperature and temperature variations over the substrate surface
- Deposition rate
- Angle of incidence of depositing flux
- Purity of source material

- Preprocessing, such as surface preparation and substrate heating

In the case of reactive evaporation, the following parameters also need to be monitored and controlled:

- Availability of reactive gases over the substrate surfaces
- Activation of reactive gases
- Gas density distribution in the processing chamber

**Substrate Temperature Monitoring.** The substrate loses heat by conduction and radiation, thus often making it difficult to monitor substrate temperature. Thermocouples embedded in the substrate fixture often give a poor indication of the substrate temperature, because the substrate often has poor thermal contact with the fixture. In some cases, thermocouples can be embedded in or attached directly to the substrate material. Optical (infrared) pyrometers can be used to determine the temperature if the surface emissivity and adsorption in the optics are constant and known.

Passive temperature monitors can record the maximum temperature a substrate has approached during processing. Passive temperature monitors register color changes, phase changes (for example, melting of indium), or crystallization of amorphous materials (Ref 133).

**Source Temperature Monitoring.** Generally, source temperatures are very difficult to monitor or control with precision. In molecular beam epitaxy, the deposition rate is controlled by carefully controlling the temperature of a well-shielded Knudsen cell source using embedded thermocouples (Ref 7).

**Deposition Rate and Deposited Mass Monitors.** Quartz crystal monitors measure the frequency of the oscillations as a function of the mass added to the crystal face. By calibrating the frequency change with the mass deposited, the quartz crystal output can measure deposition rate and total mass deposited (Ref 134). Ionization rate monitors compare the ionization currents in a reference chamber and a chamber through which the evaporant flux is passing. By calibration, the differential in gage outputs can be used as a deposition rate monitor (Ref 135). A vacuum microbalance can be used to measure the deposition rate and the total amount of material deposited. In electron-beam evaporation, the ions that are formed above the molten pool can be used to monitor the vaporization rate and the mass deposited.

The total amount of deposited material is sometimes controlled by evaporating to completion a specific amount of source material. This avoids the need for a deposition controller and is used where many repetitious depositions are to be made.

**Film Thickness Monitoring.** There is no easy way to measure the geometrical thickness of a film during deposition because the thickness depends on the density for a given mass deposited. In general, thickness is determined from the mass deposited, assuming a density so that the mass monitor is calibrated to give thickness.

**Optical Property Monitoring.** In optical coating systems, in situ monitoring of the optical properties of the films is used to monitor film deposition and provide feedback that controls the evaporators (Ref 136, 137). Generally, the optical transmittance, interference (constructive and destructive), or reflectance at a specific wavelength is used to monitor the optical properties. Ellipsometric measurements can be used to monitor the growth of oxides on semiconductor materials.

**Electrical Property Monitoring.** An electrically conducting path between electrodes can be deposited using a mask, and the electrical resistivity of the path can be used as a deposition monitor (Ref 138).

**Film Stress Monitoring.** There are several techniques for measuring the film stress during the deposition process. These techniques typically measure the movement of surfaces, as monitored by changes in capacitance between two plates, or they measure the deflection of a beam by optical interferometry (Ref 139) or an optical lever arm. X-ray diffraction measurements of the lattice spacing can be used to measure film stress due to lattice deformation (Ref 140).

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# Sputter Deposition

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## Introduction

SPUTTERING is a nonthermal vaporization process in which surface atoms are physically ejected from a surface by momentum transfer from an energetic bombarding species of atomic/molecular size. Typically, sputtering uses a glow discharge or an ion beam (Ref 1) to generate a flux of ions incident on the target surface. These ions cause atoms, and occasionally clusters of atoms, to be knocked free from the target surface by impact transfer, or sputtering. Sputtering is used in two principal applications: sputter etching, in which the primary objective is removal of material from the target surface (Ref 2); and sputter deposition, in which redeposition of these sputtered atoms onto another surface, or substrate, is the primary goal. The latter application is discussed in this article. The fundamentals of plasma formation and the interactions on the target surface are discussed first, followed by the differences between reactive and nonreactive sputtering, and several methods of process control. In the third section, the basic principles and relative advantages and disadvantages of the most common sputtering techniques are examined, specifically direct-current (dc) diode, radio-frequency (rf) diode, triode, magnetron sputtering, and a relatively new technique known as "unbalanced" magnetron sputtering.

Compared to other thin-film deposition methods, sputter deposition techniques have several distinct advantages:

- Use of an unlimited range of source and film materials (i.e., metals, semiconductors, insulators, alloys, and compounds)
- Small sputtering-yield variations from one material to another as compared to the relative variation in the evaporation rates at a given temperature
- Ease of low-temperature deposition of refractory materials
- Elimination of droplet emission from the source that can occur in thermal evaporation
- Absence of droplets, which are common in arc-deposited films
- Ease of forming multicomponent films
- Uniformity of film thickness over large areas
- High degree of film adhesion
- Environmentally friendly processing

Sputter deposition processes have several limitations as well:

- Target (source) materials must ordinarily be in sheet or tube form.
- Deposition rates are typically less than 300 nm/min (3000 Å/min).
- Setup costs are high because of the required vacuum environment.
- Line-of-sight process may not be suitable for three-dimensional components.
- Energy efficiency is low (70% or more of the input energy is expended in target heating).

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## Glow Discharge Sputtering

**Glow Discharge Formation.** The simplest case of a glow discharge, the dc diode discharge, is illustrated in Fig. 1. At the far left of Fig. 1(a) is the cathode and adjacent to it the cathode glow region, which is luminous because of positive and negative ion neutralization at the cathode surface. Next to the cathode glow region is the cathode dark space, or sheath, across which most of the voltage is dropped (Fig. 1b), providing the accelerating force driving the ions into the target. The net space charge (Fig. 1c) also changes dramatically across the cathode dark space. To the right of the cathode dark space are the negative glow, the Faraday dark space, the positive column, and the anode, as shown in Fig. 1(a).

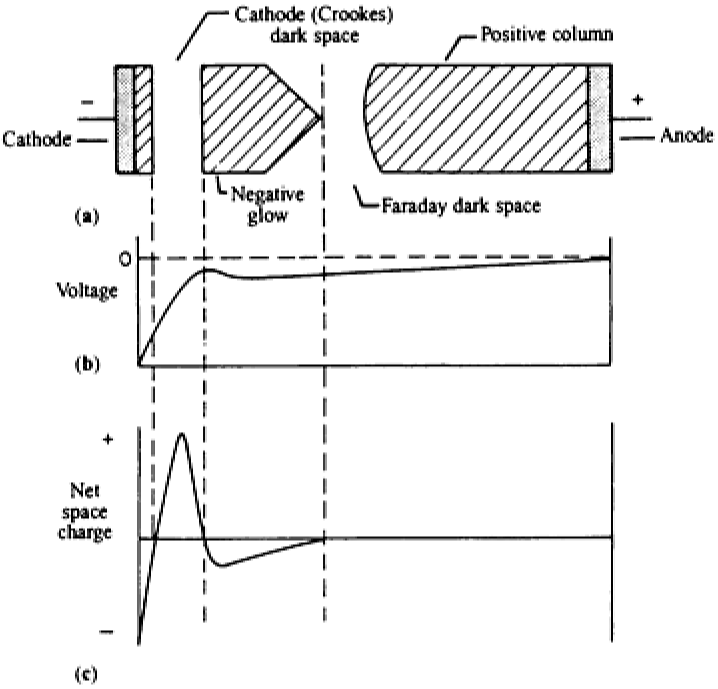

**Fig. 1 Schematic illustration of the (a) primary regions, (b) voltage characteristics, and (c) net space charges for a dc glow discharge. Source: Ref 32**

When an ion strikes the cathode, in addition to the generation of heat and the removal of neutral atoms and ions, there is about a 5 to 10% probability of secondary electron emission. These secondary electrons are then accelerated back across the dark space into the negative glow region where they expend most of their energy creating additional ions, approximately 10 to 20 ions/electron. It is these secondary electrons that are primarily responsible for sustaining the discharge, in this case, a cold cathode discharge. In the case of self-sustaining plasmas, the regions beyond the negative glow are less important, and in many cases the anode can be moved closer to the cathode, eliminating the positive column and shrinking the size of the negative glow region, without greatly affecting the discharge characteristics. Thus in sputter deposition, the substrates are often immersed in the negative glow region. In this case, an additional dark space will form surrounding the substrates, and the thickness of this dark space, as well as the type and energy of the charged carriers reaching the substrate surface, will depend on whether the substrates are at the anode potential or are externally biased relative to the plasma.

**Target Considerations.** A great variety of interactions can occur on the target surface because of the impinging positive ions, as illustrated in Fig. 2. These interactions include liberation of neutral atoms, ionized atoms, backscattering, x-ray emission, photon generation, secondary electron emission, and desorption of gas atoms from the target surface. In the target itself, several other processes can occur, including the generation of collisional cascades, the creation of point defects, local heating, amorphization, implantation, and compound formation. Within the plasma, the secondary electrons cause additional ionization, supporting the discharge. The color of the optical emission of the plasma is characteristic of the target material, gas species, pressure, excitation, and so on. Thus, it is often possible to detect the presence of certain components in the discharge simply by monitoring the characteristic spectral wavelengths, and, hence, this feature of glow discharges is often used in process control.

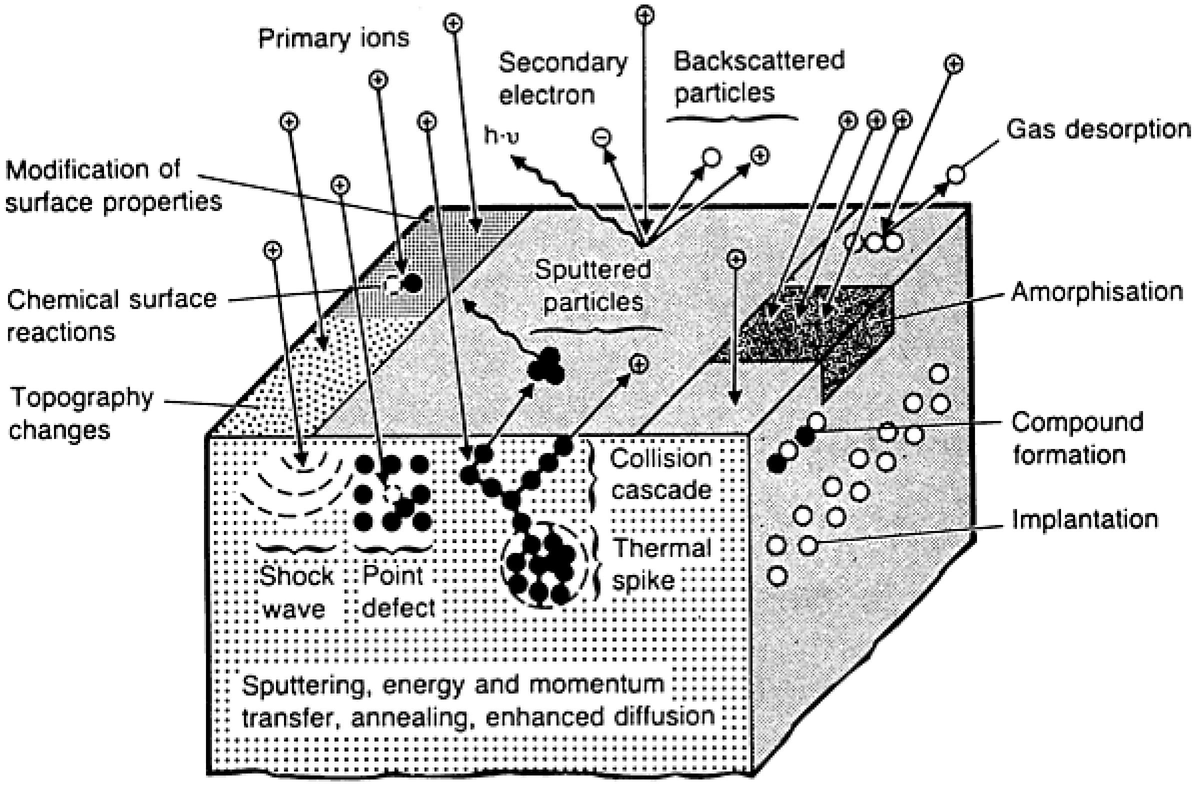

**Fig. 2 Synopsis of the interaction events occurring at and near the target surface during the sputtering process. Source: Ref 5**

One of the most important sputtering parameters is the sputtering yield, which is defined as the number of atoms ejected from the target surface per incident ion. The sputtering yield is dependent on the characteristics of the target material, incident ion energy, ion mass, and angle of incidence, as shown in Table 1. Detailed studies of sputtering yields for a large variety of materials can be found in the literature; see, for instance, Maissel (Ref 3) and Wehner (Ref 4). Although the variation in sputtering yields is as high as one order of magnitude, it is considerably lower than the rate variations that occur for evaporation from liquid sources at a specific temperature, which are often several orders of magnitude.

**Table 1 Elemental sputtering yields for 500 eV ions**

| Element | Ion |
|---|---|

|  | **He** | **Ne** | **Ar** | **Kr** | **Xe** |
|---|---|---|---|---|---|
| Be | 0.24 | 0.42 | 0.51 | 0.48 | 0.53 |
| C | 0.07 | . . . | 0.12 | 0.13 | 0.17 |
| Al | 0.16 | 0.73 | 1.05 | 0.96 | 0.82 |
| Si | 0.13 | 0.48 | 0.50 | 0.50 | 0.42 |
| Ti | 0.07 | 0.43 | 0.51 | 0.48 | 0.43 |
| V | 0.06 | 0.48 | 0.65 | 0.62 | 0.63 |
| Cr | 0.17 | 0.99 | 1.18 | 1.39 | 1.55 |
| Mn | . . . | . . . | . . . | 1.39 | 1.43 |
| Fe | 0.15 | 0.88 | 1.10 | 1.07 | 1.00 |
| Co | 0.13 | 0.90 | 1.22 | 1.08 | 1.08 |
| Ni | 0.16 | 1.10 | 1.45 | 1.30 | 1.22 |
| Cu | 0.24 | 1.80 | 2.35 | 2.35 | 2.05 |
| Ge | 0.08 | 0.68 | 1.10 | 1.12 | 1.04 |
| Y | 0.05 | 0.46 | 0.68 | 0.66 | 0.48 |
| Zr | 0.02 | 0.38 | 0.65 | 0.51 | 0.58 |
| Nb | 0.03 | 0.33 | 0.60 | 0.55 | 0.53 |
| Mo | 0.03 | 0.48 | 0.80 | 0.87 | 0.87 |
| Ru | . . . | 0.57 | 1.15 | 1.27 | 1.20 |
| Rh | 0.06 | 0.07 | 1.30 | 1.43 | 1.38 |
| Pb | 0.13 | 1.15 | 2.08 | 2.22 | 2.23 |

| | | | | | |
|---|---|---|---|---|---|
| Ag | 0.02 | 1.77 | 3.12 | 3.27 | 3.32 |
| Sm | 0.05 | 0.69 | 0.80 | 1.09 | 1.28 |
| Gd | 0.03 | 0.48 | 0.83 | 1.12 | 1.20 |
| Dy | 0.03 | 0.55 | 0.88 | 1.15 | 1.29 |
| Er | 0.03 | 0.52 | 0.77 | 1.07 | 1.07 |
| Hf | 0.01 | 0.32 | 0.70 | 0.80 | . . . |
| Ta | 0.01 | 0.28 | 0.57 | 0.87 | 0.88 |
| W | 0.01 | 0.28 | 0.57 | 0.91 | 1.01 |
| Re | 0.01 | 0.37 | 0.87 | 1.25 | . . . |
| Os | 0.01 | 0.37 | 0.87 | 1.27 | 1.33 |
| Ir | 0.01 | 0.43 | 1.01 | 1.35 | 1.56 |
| Pt | 0.03 | 0.63 | 1.40 | 1.82 | 1.93 |
| Au | 0.07 | 1.08 | 2.40 | 3.06 | 3.01 |
| Th | 0.00 | 0.28 | 0.62 | 0.96 | 1.05 |
| U | . . . | 0.45 | 0.85 | 1.30 | 0.81 |

Source: Ref 32

Sputtering processes are governed primarily by energy transfer, momentum transfer, annealing effects, and enhanced diffusion, which often limits the performance of targets and creates a need for process control (Ref 5). For example, adsorbed gases tend to desorb under the influence of ion bombardment and heating. This is an important consideration when using powder metallurgically prepared targets that can liberate water vapor and cause surface chemical reactions if not properly degassed. Additionally, chemical surface reactions occur in the presence of reactive or residual gases such as nitrogen, oxygen, or hydrocarbons and can cause compound formation on the target surface. These reactions usually result in decreased sputtering rates, and compound formation is further intensified by a low target heat conductivity and cooling rate.

Additionally, topographical changes in the target surface may occur over time, particularly in multiphase polycrystalline targets in which the crystallites have different sputtering yields, leading to cone formation and arcing on the target. It is essential to consider these interactions in the selection and operation of various targets. More detailed information on these aspects of sputter processes is provided in the general literature (Ref 6, 7, 8, 9, 10, 11).

**Process Parameter Effects on Film Microstructure.** Scattering within the discharge significantly affects the energy with which atoms impact the film surface and, hence, the microstructure and properties of the sputtered film. Ejected atom energies range from a few tenths of an electron volt up to nearly that of the ions impinging on the target, but because of intense scattering within the discharge, the atoms usually arrive at the substrate with energies of only a few electron volts. Scattering also causes the deposition rate to decrease as the target-to-substrate separation increases. Additionally, the incidence of scattering increases with increasing gas pressure, because the mean-free-path between collisions decreases as the pressure rises. Thermalization of these ejected atoms occurs after the ejected atoms suffer a sufficient number of energy-loss events that their energy is reduced to the thermal energy of the discharge. The distance required for thermalization depends on the pressure, initial atom energy, atomic mass, and several plasma characteristics and is typically a centimeter or less (Ref 12). In low-pressure, high-voltage discharges, the mean free path between collisions is long, and it is therefore possible for a statistically significant number of atoms to reach the substrate with energies in excess of the thermal energy; these atoms are termed ***energetic neutrals***. Energetic neutrals can cause additional bombardment of the growing film; however, their energy is difficult to determine and their effect on film properties is not easily understood.

In addition to neutral atom bombardment, auxiliary substrate heating and negative substrate bias voltages are often employed during deposition, and these parameters also influence the microstructure of the growing film. Thornton (Ref 13) and others have examined the influences of substrate temperature and discharge pressure on film microstructure. It has been shown that, in general, increasing substrate temperatures can be associated with a transition from an open columnar arrangement (zone I), to a dense columnar formation (T-zone), to a second dense columnar microstructure (zone II), and, finally, to dense equiaxed grain structure (zone III), as shown in Fig. 3. Thus, increasing the growth temperature causes the density of the films to increase, whereas increasing the pressure produces the opposite effect (Ref 13). Of course, changes in microstructure with pressure are closely related to changes in the thermalization distance and hence the ion/atom energy. Some caution should be exercised in applying such models, because these early models were developed using only scanning electron microscope investigations, and more recent studies using transmission electron microscopy have shown these models to be overly simplistic.

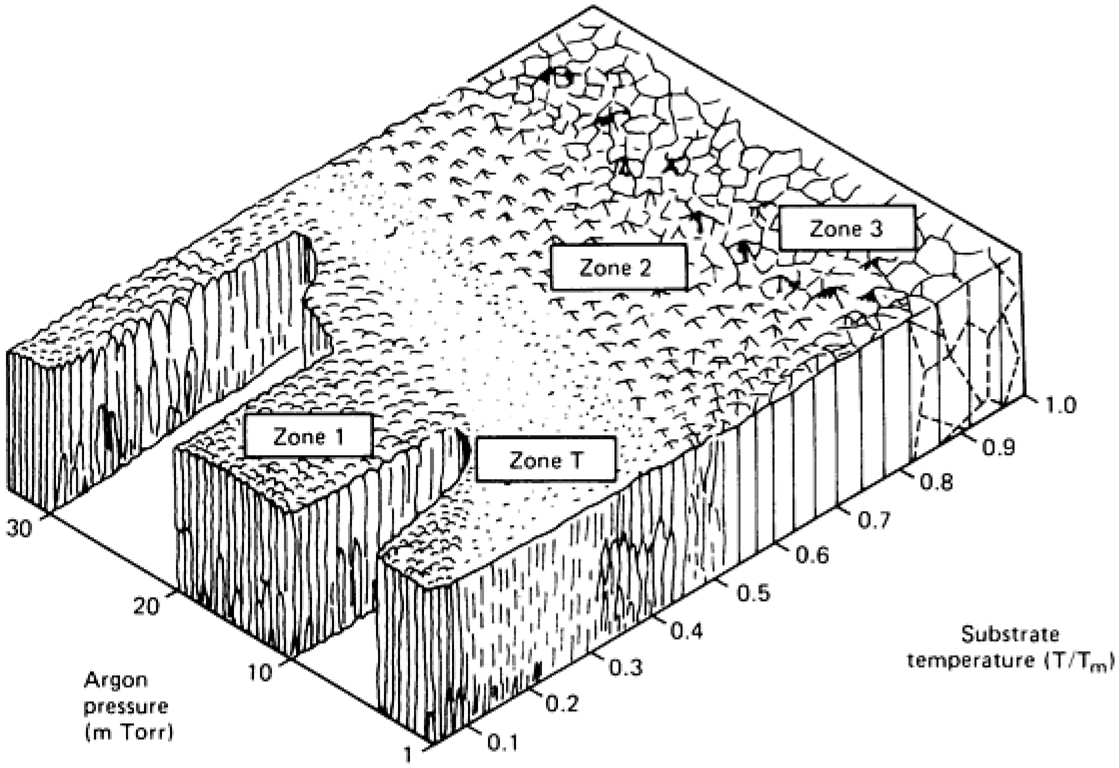

**Fig. 3 Microstructural dependence of sputtered thin films on argon pressure and substrate temperature**

Microstructural changes similar to those induced by temperature and pressure can be reproduced to some degree by applying a negative bias potential to the substrate during deposition. Under the influence of this negative potential, positively charged ions impact the substrate surface, resulting in increased adatom mobilities, substrate heating, point defect generation, and so on. In this case, the dense T-zone moves toward lower temperatures with increasing negative bias (Ref 14). This effect has also been shown experimentally; for example, Mattox showed that ion bombardment during the condensation process resulted in increased film density of sputter-deposited refractory tantalum with increasing negative bias (Ref 15, 16). The evolution of film morphology is covered in detail in the article "Growth and Growth-Related Properties of Films Formed by Physical Vapor Deposition Processes" in this Volume.

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## Reactive Sputtering and Process Control

**Reactive versus Nonreactive Processes.** Both reactive and nonreactive processes may be used in the formation of sputter-deposited films. For nonreactive sputtering, an inert gas, which does not participate directly in the formation of compounds on either the target or the substrate, is used to generate a plasma and sputter material from the target. The inert gas is also sometimes termed the *working gas*. Argon is used in most cases because its mass is high enough to ensure adequate sputtering yields and it is less expensive than xenon or krypton. Although inert gas ions and atoms are not incorporated as primary constituents, incorporation even in very small concentrations can have deleterious effects on film properties. For example, argon incorporation can cause lattice expansions, increasing the internal stress of the films (Ref 17). Additionally, inert-gas ion bombardment of the substrate/film couple using an applied negative-substrate bias can increase inert gas incorporation as well as alter the growth mode, stoichiometry, and properties of deposited films. Nonreactive sputtering processes are common in the deposition of thin metallic overlayers for electron microscopy, industrial-scale deposition of metals and metallic alloys, industrial-scale deposition of some insulators, and research-scale deposition of insulators and compounds. The primary advantage of this type of thin-film deposition is its simplicity.

Nonreactive processes can be used to directly sputter compound targets such as TiN, which is used in many decorative and wear-resistant applications. However, this use presents several difficulties: (a) the rate at which The pure metal (titanium) can be sputtered is about an order of magnitude lower than the rate at which pure titanium can be sputtered; (b) off-stoichiometry of the films can occur during deposition; and (c) the thermal conductivity of the compound is often much lower than that of the pure metallic species, and thus the target power must be reduced accordingly due to the heating and fracture of the target. These difficulties often preclude the cost-effective use of nonreactive processes in many applications. In these cases, use of reactive sputtering becomes a necessity.

Reactively sputtered films can be deposited using a variety of methods including dc diode, rf diode, triode, magnetron, and modified rf magnetron sputtering. In any case, there are only two basic reactive sputtering modes: compound-coated cathode and metallic cathode. Sputtering in the compound-coated cathode mode is straightforward: sufficient reactive gas is bled into the chamber during sputtering to form the desired compound on the target surface; this compound is then sputtered off and redeposited on the substrate. In many ways, there is little difference between reactive sputtering in the compound-coated cathode mode and nonreactive sputtering from a compound target. The sputtering rates are usually much lower for compounds because of a reduction in the sputtering yield and an increase in the secondary electron emission that is observed with most compound targets. Additionally, depending on the sputtering technique, materials, and deposition conditions, the film may not possess the same chemical composition as the target material. For these reasons, sputtering in the metallic cathode mode is often preferable.

In the metallic cathode mode, the target is maintained as a clean metallic surface and compound formation is limited to the deposited material. Although simple in concept, careful process control is necessary to avoid contamination of the target or deposition of substoichiometric films. Control of the reactive gas species is often costly, requiring at a minimum an automated feedback control and a sensor system to measure partial pressure of the reactive species. However, this is often the only cost-effective means of depositing compound thin-film materials on an industrial scale.

**Process Control.** The process control necessary for successful reactive sputtering in the metallic cathode mode is often quite difficult to achieve. When flow control is used, the reactive gas is bled into the chamber until there is sufficient gas to form the desired compound at the substrate. However, in most cases this also means that there is sufficient reactive gas present to form the compound on the target surface as well. This phenomenon is known as *poisoning of the target* and generally results in a several-fold decrease in the sputtering rate and, hence, the deposition rate.

During the early 1980s a number of gas-control methods were proposed based on timed or pulsed gas flows. Although they provided significant improvements in the film deposition rates, truly homogenous films are unlikely to result from this type of pulsing technique (Ref 18). The problem is that simple gas flow control does not permit direct control of the partial pressure of the reactive gas species in the chamber. This is illustrated in the hysteresis behavior observed in measuring the reactive gas partial pressure as a function of gas flow, shown for the case of TiN deposition in Fig. 4(a). In this case, stoichiometric TiN is formed under the partial-pressure conditions of point "B." Clearly this exact condition is difficult to maintain by manually pulsing the gas flow, and in the case of slow pulsing, it is likely that the full hysteresis is traveled with each pulse, creating nonstoichiometric layered films.

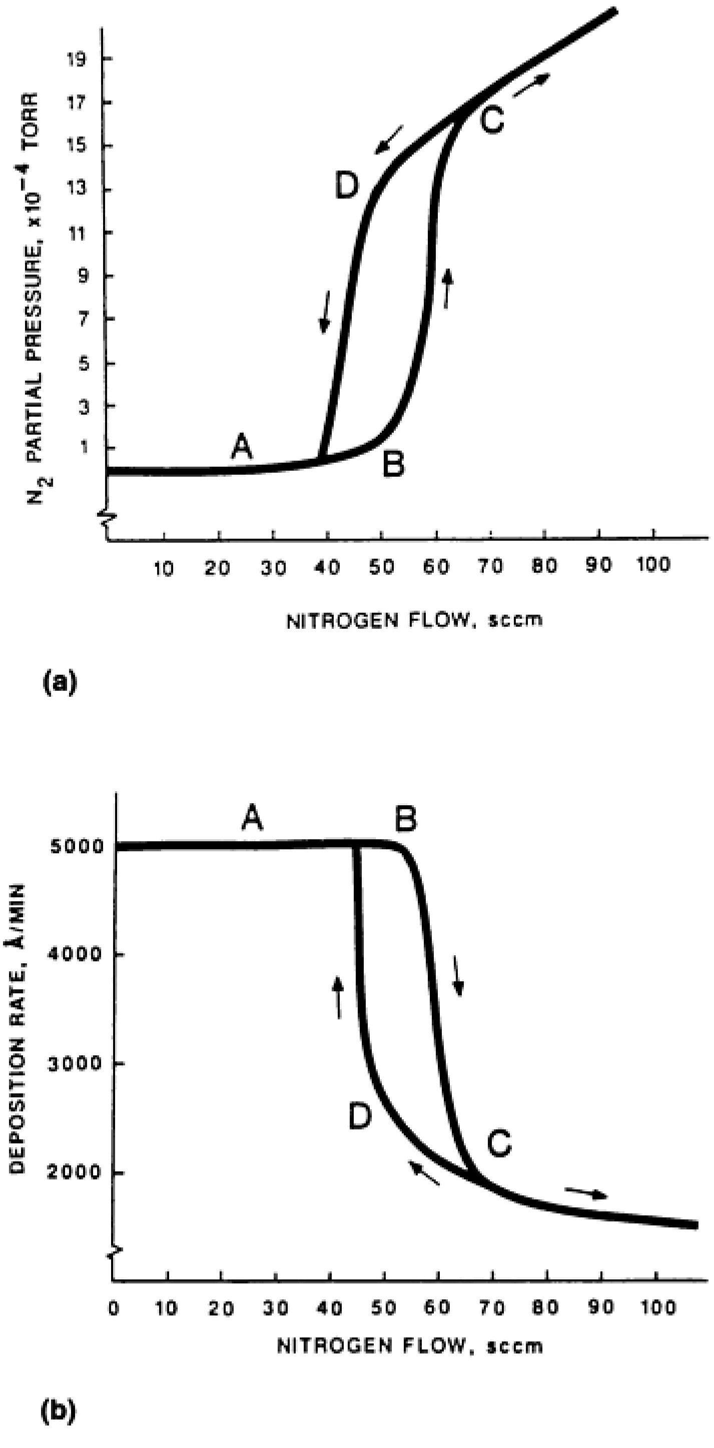

**Fig. 4 (a) Nitrogen partial pressure vs. reactive gas flow in a mixed Ar-$N_2$ discharge under mass flow control, at a target power of 10 kW. (b) Deposition rate vs. flow hysteresis behavior for $TiN_x$ deposition, at a target power of 10 kW, in a mixed Ar-$N_2$ discharge. Source: Ref 18**

As discussed, as the target surface becomes compound coated the deposition rate drops precipitously. This effect can be illustrated by plotting the deposition rate as a function of the reactive gas flow, as shown in Fig. 4(b); again the desired operating conditions are given by point "B." However, the problem of achieving stable operation at point "B," in both Fig. 4(a) and 4(b), is nontrivial because a relatively small increase in flow results in a large decrease in the deposition rate, which is then accompanied by a rapid increase in the partial pressure of the reactive species in front of the target.

This instability is influenced by several other factors. During film deposition at the optimum flow rate, the target can very quickly become completely poisoned if the partial pressure or flow increases slightly, as commonly occurs during slight arcing at the target surface. The consequent decrease in the sputtering rate in turn results in an excess partial pressure of the reactive gas species in front of the target, creating a circular chain of events that amplifies the initial instability. Another factor fueling this instability is the target power, because the current-voltage requirements of the target change as the target becomes poisoned. In order to avoid driving the process up or down the hysteresis curve, the input current and/or voltage must be adjusted to maintain a constant target power constant.

Associated with this hysteresis effect is the problem of maintaining film stoichiometry. It has been shown that for $Ti_xN_{1-x}$ film microhardness increases monotonically with increasing nitrogen flow rate until stoichiometric TiN is formed (i.e., point "B" in Fig. 4 a and b). Once this optimal nitrogen flow rate is exceeded, the microhardness drops precipitously and the target becomes poisoned (Ref 19). Before film growth can be resumed, intensive "presputtering" is required to return the target surface to a purely metallic state.

A significant advance in process control was the development of automated flow-control systems using a feedback control loop. Sproul and Tomashek introduced the first closed-loop feedback control system in 1984, which monitored the nitrogen peak height obtained from mass spectrometer analysis and generated a feedback signal for a gas flow controller (Ref 20). Because the peak height obtained from the mass spectrometer can be correlated to a certain gas partial pressure within the chamber, this type of automated flow control is, in effect, a partial pressure control system. Similarly, Affinito and Parsons developed a microprocessor-based system to monitor a number of discharge parameters and provide feedback control of the reactive gas. In this case, control of the reactive gas was possible for nitrogen, but not for oxygen (Ref 21). Both of these control systems work well, but in most cases it is necessary to differentially pump the mass spectrometer head, which adds to the cost and complexity of these systems and can also generate undesirable delays in the control process and signal distortions.

Schiller et al. developed a somewhat different control system, the plasma emission monitor (PEM), that uses the optical emission spectra from the target material to produce a feedback signal to control the reactive gas flow and more directly monitor the conditions at the target surface (Ref 22). The optical emission spectra from the plasma near the target is collected using a collimator connected to a quartz fiber. This signal is fed into a monochromator that is linked to a photomultiplier. The photomultiplier outputs an amplified electrical signal to a control unit where the incoming signal level is compared to a preset "optimum" signal level. A control signal is then sent from the control unit to a piezoelectric gas-control valve that is opened or closed in response to a change in the spectral signal. Typically, the optimum reactive gas level is set as some fraction of the spectral peak height of the metallic species. The spectral peak height of pure metal must be measured for each run just prior to the introduction of the reactive gas, and a thin metallic layer may be deposited before the reactive process attains stoichiometry. In some applications this thin metallic underlayer can create a problem; however, this difficulty can be overcome. The primary advantage of the PEM technique is that neither a mass spectrometer nor differential pumping of the sensor is required, so it is less expensive. This and several similar systems are now commercially available.

Another commercially available device for partial-pressure control is the optical gas controller (OGC), which uses the optical emission generated within the sensor from a gas sample drawn directly from the chamber to determine the partial pressure and drive the closed-loop control system at sputtering pressures (Ref 23, 24). Like the PEM system, no mass spectrometer or differential pumping is required. However, unlike the PEM system, the OGC is based on electron-impact ionization spectroscopy. This permits the process gases to be ionized under reproducible conditions within the sensor head, but it also adds the limitation that the sensor must be located very close to the target to provide accurate control (Ref 24, 25, 26, 27).

Alternatively, research by Penfold (Ref 28), Kadlec et al. (Ref 29), and others has shown that the hysteresis effect can be eliminated entirely by increasing the pumping speed of the system beyond a critical level. While successful, this technique is rather expensive in practice, resulting in reduced deposition rates, inefficient gas use, and very high pumping throughput requirements. Whatever the method, effective process control of sputtering is critical in the production of reproducible high-quality thin films at rates that allow them to be commercially competitive with other thin-film processes.

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## Sputtering Techniques

Since the discovery of sputtering by W.R. Grove in the mid-1800s, a number of sputter deposition techniques have been developed to deposit thin films of various materials, and much has been written about these techniques (Ref 6, 7, 8, 9, 10, 11, 30, 31). The following section provides a brief overview of several common techniques, including dc diode, rf diode, triode, magnetron, and unbalanced magnetron sputtering.

**Diode sputtering** is the oldest sputtering technique. A dc diode plasma may be formed by applying a relatively large potential (approximately 300 to 5000 V) between the cathode and anode electrodes in the presence of a sufficient gas density (approximately 10 to 500 μbar). Under a sufficiently large electric potential, the gas atoms between the electrodes become ionized and diffuse through the plasma. However, only the ions in the near-cathode region will "feel" the effect of the potential drop and thus be accelerated across the cathode dark space, impacting the target or cathode surface (see Fig. 1). It is these ions that are responsible for the sputtering.

A common application of dc diode sputtering is the deposition of thin conductive films on samples for electron microscopy. This has two notable advantages:

- A large variety of single- and multi-component target materials can be used.
- It is a simple process, perhaps its greatest advantage.

However, dc diode sputtering also has definite limitations:

- The target must be electrically conductive.
- Deposition rates are generally low.
- Electron bombardment heating of the substrate may be significant because the discharge is not confined.
- Energy efficiency is low because since 75 to 95% of the power supplied to the targets is dissipated through target heating (Ref 32, 33, 34).

**Radio-Frequency Sputtering.** The use of an oscillating power source to generate a sputtering plasma offers several advantages over dc methods. Principally, when the frequency of oscillation is greater than about 50 kHz, it is no longer necessary for both electrodes to be conductive because the electrode can be coupled though an impedance (Ref 35). The coupled electrode must be much smaller than the direct electrode in order to effectively sputter only the insulating or coupled electrode; this is usually accomplished by connecting the rf generator directly to the grounded chamber walls or substrate fixtures. An impedance matching network is integrated into the circuit between the rf generator and the load to introduce the inductance necessary to form a resonant circuit. It is important in rf systems to provide adequate grounding, minimize the lead lengths, and eliminate any unneeded flange projections to reduce excessive inductive and capacitive losses.

An additional benefit of using rf frequencies above 50 kHz is that the electrons in the negative glow region have sufficient energy to directly ionize the gas atoms; hence, the number of electrons required to sustain the discharge is substantially reduced (Ref 32). This, in turn, means that lower sputtering pressures can be used, reducing the potential for film contamination.

At frequencies above the low megahertz range, the ions, because of their relatively large mass, are no longer able to follow the oscillations of the potential, and, hence, there is little ion accumulation at the cathode (Ref 30). Thus, any frequency above about 5 MHz can be efficiently used for sputtering; however, the most commonly used frequencies are 13.56 and 27 MHz, because these are the FCC-specified frequencies for medical and industrial use (Ref 35). The applications of rf sputtering are quite varied and include deposition of metals, metallic alloys, oxides, nitrides, and carbides (Ref 36, 37, 38).

A number of comprehensive reviews and discussions of rf discharges are available in the literature (Ref 34, 35, 39, 40, 41). In general, the primary advantages of rf sputtering are:

- Ability to sputter insulators as well as almost any other material
- Accessibility of lower operating pressures

Unfortunately, the deposition rates in rf sputtering are often limited by the low thermal conductivity of the insulating target materials. This low thermal conductivity of the materials, leads to the formation of "hot spots" on the target; the hot spots generate stresses that cause fracture of the brittle target materials. For this reason, it may be preferable to deposit insulating films reactively from a metal source. Although compound materials can be readily sputtered in an rf discharge, the resulting films may not be representative of the initial target composition.

**Triode sputtering** uses a cathode separate from the sputtering target to sustain the plasma. The target electrode then extracts ions from the plasma. This additional electron source, typically either a simple biased conductor or a thermionic electron emitter, provides a means of sustaining the discharge that is independent of the secondary electron generation at the cathode. Thus, the discharge may be maintained at pressures as low as 0.001 Pa ($10^{-5}$ torr) or at discharge voltages as low as 40 V (Ref 42). By varying the emission of the electron source, the discharge current can be varied independently of the sputtering voltage, allowing high ion densities at the target and substrate while maintaining a low discharge potential.

Triode discharges, both dc and rf, have been used successfully to deposit films of a great variety of materials for semiconductor, wear-resistant, optical, and other coating applications (Ref 42, 43, 44, 45, 46, 47, 48, 49). The primary advantages of triode sputtering are:

- Lower discharge pressures
- Lower discharge voltages
- Higher deposition rates
- Independent control of the plasma density and the bombardment conditions of the sputtering target

The major weaknesses of triodes are that they:

- Are often more complicated to use

- Can increase film contamination from the electron source
- Are difficult to scale up for industrial processing
- May not be suitable in temperature-sensitive and reactive processes because of the electron source

**Magnetron sputtering** differs from other techniques in that most of the plasma is confined to the near-target region. This plasma confinement is achieved by establishing strong magnetic fields above the target surface that reshape the trajectories of the secondary electrons ejected from the target surface into convoluted spiral-like patterns skipping across the surface of the cathode (Fig. 4). In such a magnetic arrangement, the secondary electrons are trapped and most of their energy is expended in the near-target region, increasing ionization and, hence, greatly improving the sputtering and deposition rates. This method is quite successful in producing high-quality, low-impurity films at reasonable deposition rates, and it has seen widespread commercial use since its development in the mid-1970s.

In magnetron sputtering, as for all sputtering techniques, planar target geometries are the most commonly used sources, as illustrated in Fig. 5. Both circular and rectangular planar magnetrons are commercially available in sizes ranging from a 2.5 cm diameter magnetron gun configuration to rectangular cathodes as large as 2 m in length. However, all planar magnetrons tend to erode preferentially in the areas where the magnetic field is parallel to the target surface. This creates a racetrack-like erosion pattern that often leads to an annular distribution of sputtered atoms.

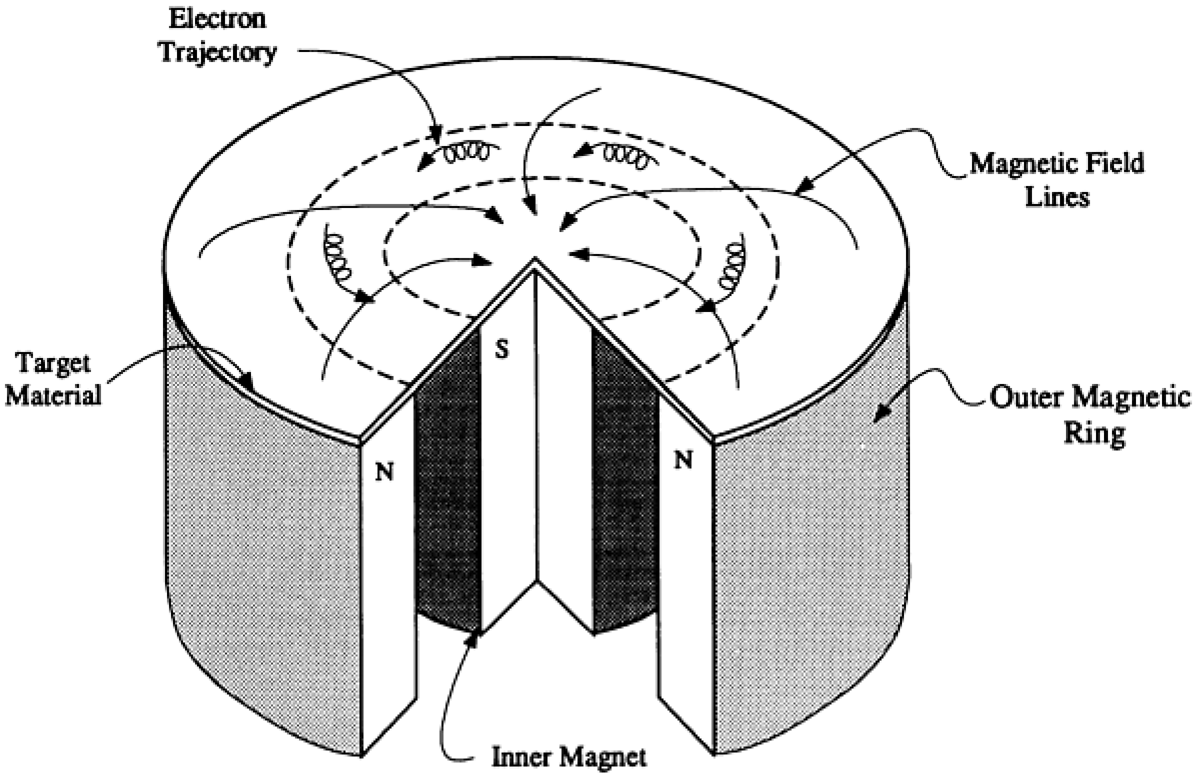

**Fig. 5 Circular, planar magnetron cathode schematic, illustrating the magnetic confinement and the resulting electron trajectories**

The issue of uneven target erosion has been studied in detail and a number of geometries have been developed to improve target use (Ref 50, 51, 52). For example, cylindrical magnetron geometries (Fig. 6) provide improved target use and typically yield higher sputtering rates, as do most other nonplanar geometries (Ref 53). However, the commercial applications of these magnetron systems has been hampered by the difficulties of producing nonplanar targets and the expense of creating large arrays of shaped magnets. Some of the most successful commercial nonplanar geometries are variations of the rotatable cylindrical cathode (Fig. 6 c, d).

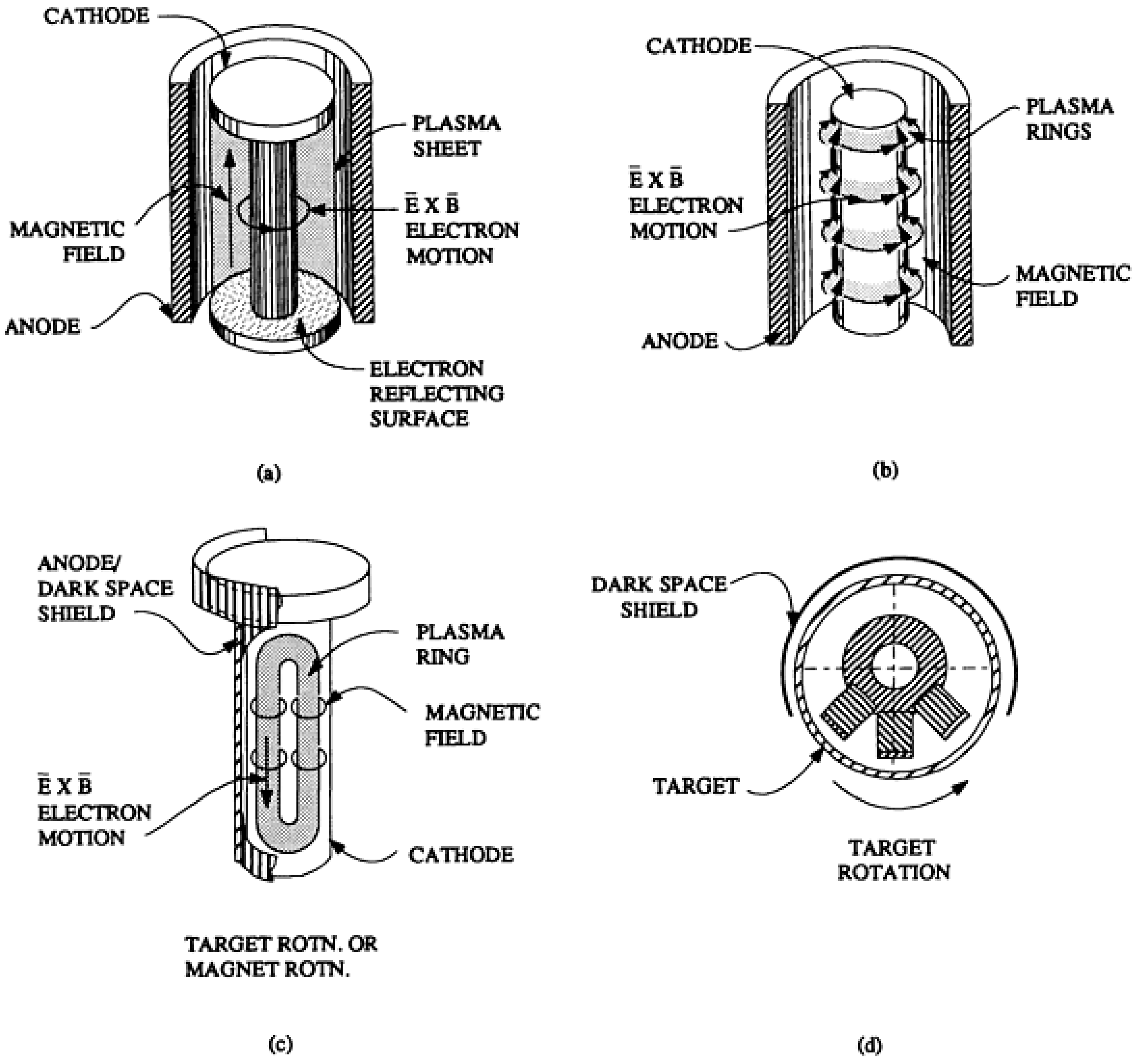

**Fig. 6 Schematic illustration of several cylindrical magnetron sources. (a) A cylindrical post magnetron with a longitudinal magnetic field. (b) A cylindrical magnetron with a radial magnetic field. Source: Ref 53. (c) A rotating cylindrical magnetron and (d) its cross section. Source: Ref 54**

Additionally, magnetron sources can be operated in triode mode or using an rf power source. For example, a hollow cathode discharge directly in front of the magnetron source can be used as the third electrode of a triode to increase ionization and enhance magnetron performance. However, this type of system suffers from many of the same scale-up difficulties as other triode systems (Ref 55). Additionally, when using an rf discharge voltage, it is important to realize that the magnetron source functions as a "true" magnetron only during a portion of the voltage oscillation. Because the electric field vector varies in amplitude and direction, the forces acting on the electrons in the plasma vary during the cycle, and thus the plasma is no longer confined to the vicinity of the target (Ref 56, 57, 58).

There are several advantages to magnetron sputtering:

- Increased deposition rates (i.e., higher sputtering rates)
- Reduced sputtering from the substrate and chamber walls
- Reduced substrate heating from electron bombardment during deposition
- Reduced "working" gas pressure requirements
- Ease of conversion to industrial-scale processing

Of course, there are also a number of limitations:

- Target use of planar geometries is usually less than 40%
- There may be annular distribution of sputtered atoms, particularly from planar magnetrons
- Porous films may result from large target-to-substrate separations because of reduced electron and ion bombardment at the substrate
- There is inherent nonuniformity in the plasma because of the magnetic fields of the cathode

To overcome some of the line-of-sight limitations that are typical of most sputter processes, a number of magnetron systems have been developed to coat three-dimensional components by sandwiching the components between a face-to-face pair of magnetrons. This technique is very successful as long as the target-to-substrate separation ($d_{t-s}$) is small; hence the components must also be fairly small. At large $d_{t-s}$ separations, the ion bombardment of the films is frequently insufficient to produce dense film microstructures, and matte, void-containing coatings result.

In general, ion bombardment during deposition can be used to alter favorably the nucleation behavior, growth kinetics, morphology, composition, and mechanical properties of thin films. These effects can be observed as changes in the residual stress, lattice parameter, resistivity, stoichiometry, orientation, film density, and apparent hardness of the resulting films (Ref 59). The extent to which a deposited film is affected by the ion bombardment is dependent on both the kinetic energy and the flux density of the impinging ions, or more correctly the ion-to-deposited-atom ratio and the mass ratio of the ions relative to the surface atoms.

Typically in magnetron sputtering, ions are extracted from the discharge surrounding the substrate by applying a negative potential of 50 to 500 V to the substrate. However, the current density incident on the film-substrate surface is generally quite low, 0.05 to 0.10 ions per deposited atom in conventional dc magnetrons (Ref 60). If this ratio can be increased without increasing the energy of the bombarding ions, denser film microstructures can be produced, while inducing minimal damage within the crystalline lattice. This is desirable because increasing the bias voltage typically results in the generation of defects within the grains and increased film stresses, resulting in poor adhesion and inferior film quality. To circumvent these limitations it would be preferable to increase the ion current density (i.e., the ion-to-deposited-atom ratio) while maintaining a reduced bias voltage, thus keeping the energy of the impinging ions low (Ref 92). In an effort to increase low-energy ion bombardment during film growth a new class of magnetron sources, known as ***unbalanced magnetrons***, has been developed.

**Unbalanced Magnetron Sputtering.** Window and Savvides (Ref 60) introduced the unbalanced magnetron in 1986 in an article that described seven different magnetic configurations and grouped them in three basic types (Fig. 7). The type I magnetron is characterized by a strong inner pole and weak outer pole, and the type II is the converse. The intermediate type is nearly balanced and is typical of most conventional magnetrons. With type I geometry, ion bombardment at the substrate is very limited, resulting in ion-to-deposited-atom ratios as low as 0.25:1. In comparison, the type II geometry gives strongly enhanced ion bombardment, resulting in ion-to-deposited-atom ratios of the order of 2:1 at low substrate bias potentials. Thus, in most applications, only type II unbalanced magnetrons are of commercial interest.

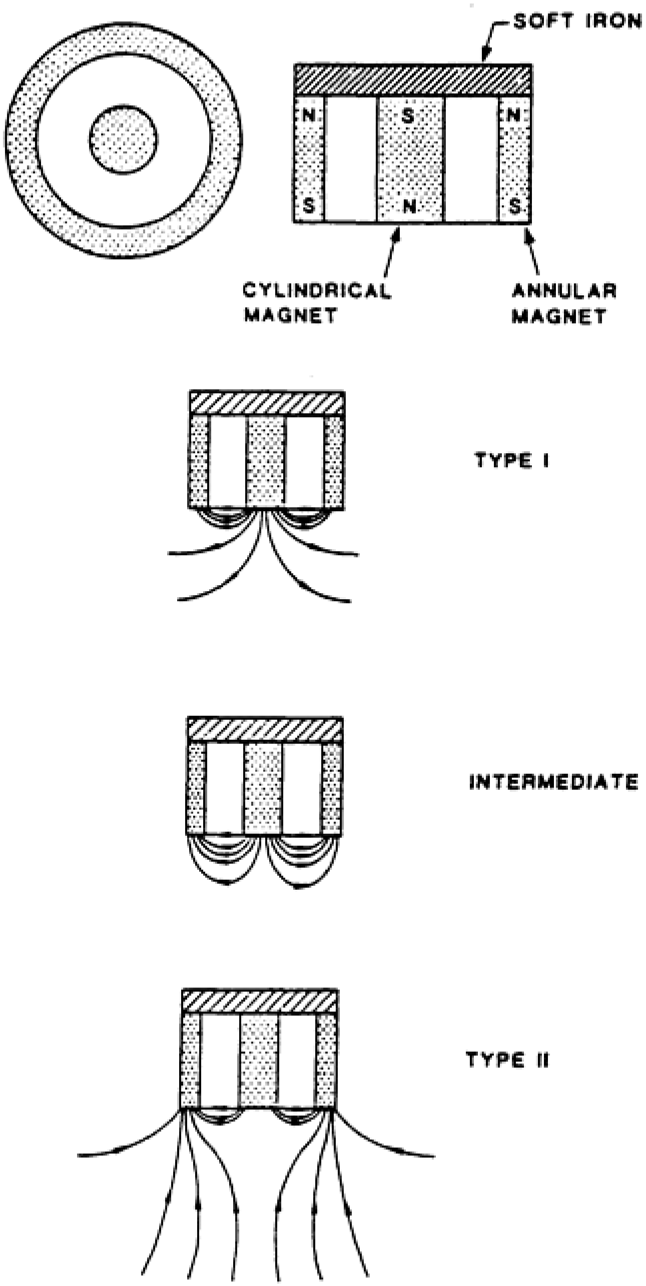

**Fig. 7 Three types of magnetron configurations: type I, intermediate, and type II. Source: Ref 60**

For unbalanced magnetrons, the ion current density has been shown to increase almost linearly with the discharge current and to be only weakly dependent on the gas pressure (Ref 61). In addition, the degree of "unbalance" and, hence, the ion current density, can be controlled independently of the discharge current by changing the magnetic field configuration (Ref 62, 93).

Several research groups have applied the unbalanced magnetron concept in a variety of sputtering applications, using both permanent magnets and electromagnets (Ref 33, 60, 61, 62, 63, 64, 65, 66, 67, 68, 69, 70). In contrast to the ion-to-deposited-atom ratios for conventional magnetrons, ratios as high as 10:1 have been reported for unbalanced magnetrons, a figure more akin to ion plating processes (Ref 63).

Using a single unbalanced planer magnetron with a pair of electromagnetic coils, Musil and Kadlec (Ref 69) were able to deposit TiN films with ion current densities as high as 6 mA/cm$^2$ and low substrate bias voltages ranging from -5 to -100 V at target-to-substrate distances of up to 200 mm. This work directly addressed the problem of decreasing substrate ion current density with increasing target-to-substrate distances. In many commercial applications, where it is more cost-effective to coat large batches of components, the increased ion current density at the substrate provides unbalanced magnetrons with a distinct advantage over conventional magnetrons.

By allowing greater $d_{t-s}$ separations, large multicathode unbalanced systems can be used to coat either large components or numerous smaller parts in a single run. Commercial multicathode systems as large as 1 m in diameter are currently available (Ref 71, 72). The primary restriction on these systems is that there must be an even number of cathodes so that the fields of each unbalanced magnetron cathode can be linked north pole to south pole with the adjacent cathodes. The interrelationship between cathodes is fairly complex because of the magnetic interactions and will differ according to the angle between cathodes (Ref 62). Hence, finite element modeling may be useful in modeling the magnetic interactions before building such systems.

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## Applications of Sputtered Films

In the fields of microelectronics and optoelectronics, sputtered thin films have been used extensively for:

- Metallization and diffusion barriers in microelectronic circuits (Ref 73, 74, 75)
- Insulating layers in microelectronic circuits
- Thin-film layers in compact disks
- Transparent conducting electrodes
- Thin-film resistors and capacitors
- Piezoelectric transducers
- Amorphous optical films in integrated circuits
- Thin-film lasers
- Memory devices
- High-temperature superconductors

A variety of sputtering techniques can be used in most applications, but rf and magnetron sputtering seem to be most prevalent. Magnetrons are fairly common because they allow very low substrate temperatures. Because most of the above applications are planar in nature, sufficient ion bombardment at the substrate is not an issue. Sputtered thin films are also used extensively in wear-resistant applications such as:

- Decorative coatings on eyeglass frames, watch cases, and other consumer goods (Ref 19, 76)
- Protective coatings on high-speed cutting tools (Ref 77, 78, 79)
- Tribological coatings on bearing surfaces (Ref 80, 81, 82)
- Heat-reflecting optical coatings on architectural glass panels (Ref 83)
- Multilayer dielectric coatings of laser mirrors and filters
- Chromium-base replacements for electrodeposited hard chrome (Ref 84, 85)

Transition metal nitrides, carbides, and oxides such as TiN, TiAlN, CrN, $Ta_2O_3$, and $Al_2O_3$ are frequently used in these applications because of their extreme hardness, corrosion resistance, attractive colors, and high spectral reflectance. In decorative applications, for instance, TiN-based films can be tailored to produce the color and brightness of gold but with superior scratch resistance at a reduced cost. With the previously described process control methods, various color values can be preselected and reproduced. In magnetron sputtering, substrate temperatures as low as 150 to 220 °C can be maintained throughout the deposition process, and, thus, temperature-sensitive materials such as electroplated brass, die-cast zinc, and bronze can be used as substrate materials for decorative coatings. Sputtered decorative coatings are usually deposited in thicknesses ranging from 0.2 to 2 μm.

Although electronic and wear-resistant coatings are the two broadest categories of commercially produced sputtered thin films, there are many other applications. For example, sputter-deposited metallic thin films are widely used as moisture and gas-diffusion barrier coatings on polymer films in the packaging industry. The applications for sputter-deposited thin films continue to broaden in scope each year.

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## Future Trends

In the future, there are certain to be new applications for sputtering technology and new thin-film coatings tailored to special needs. Recently there has been a move away from simple binary alloy coatings into multicomponent coatings to provide increased film "tailorability." This trend can be observed both in microelectronics, with investigations into ternary and quaternary II-V and II-VI systems, and in the area of hard, wear-resistant coatings of TiAlN, TiZrN, and TiVN (Ref 86). For example, for enhanced corrosion resistance for turbine blades, (Ti,Al)N alloys appear very promising as a replacement for the current TiN coatings (Ref 85), especially because the high-temperature oxidation resistance of (Ti,Al)N coatings is also superior.

Multilayer coatings are another area in which there is likely to be continued development in the next decade. These materials are already beginning to see commercial use in optical and wear-resistant applications. Very recently, work involving polycrystalline metal-nitride superlattice materials has produced films with hardness values in excess of 5000 HV.

It is foreseeable that sputtered chromium nitride coatings will also see increased use, because CrN has mechanical properties and color much like those of traditional electrodeposited hard chrome coatings and, in many applications, provides superior performance. In the past its cost has been prohibitively high, but with growing concern over process safety and environmentally hazardous wastes, sputter deposition processes are becoming increasingly attractive. Hence, the CrN sputter deposition process is an excellent candidate to replace traditional electroplating or chemical vapor deposition processes, at least in high-performance applications of hard chrome.

Improvements in the thermal stability of hard coatings for temperatures up to 800 °C and beyond seem possible in the near future. Development of more stable high-temperature coatings would open up a whole range of new applications.

In the area of decorative coating, there is a demand for distinctive new colors to supplement the well-known golden and black color tones that are currently available.

Although sputtered thin-film materials will continue to be developed, there will be some notable changes in the techniques used to deposit these films. One approach currently under investigation is to combine specific positive aspects from various deposition techniques. For instance, it has been shown that during the etching phase of the arc deposition process, titanium ions penetrate into regions below the substrate surface, forming intermetallic-like compounds and developing a gradually decreasing titanium atom density with depth into the steel substrate (Ref 87). This effect is thought to strengthen the adhesion performance of arc ion-plated coatings. On the other hand, unbalanced magnetron sputtering offers the possibility of depositing dense but rather low-stress coatings (Ref 88). A combination of arc etching and unbalanced magnetron sputter deposition may open new avenues (Ref 89, 90).

Another combined process, sputtering and plasma nitriding, can be used to increase the life of sputter-coated tools. $Ti_{0.5}Al_{0.5}N$ sputter coating of hobs has been shown to produce a sixfold improvement in tool life (Ref 91). After resharpening, however, the improvement decreased to a twofold increase in tool life when compared to the uncoated hobs. Instead of recoating the hobs by sputter deposition after each resharpening step, a simple plasma nitriding treatment was successful in restoring a fourfold increase in tool life. The $Ti_{0.5}Al_{0.5}N$ sputter-deposited coatings did not deteriorate appreciably under repeated plasma nitriding.

Examination of these trends suggests that sputtering processes should continue to hold a strong position among the competing deposition techniques. The environmentally friendly nature of sputtering processes should also make them increasingly attractive in the future.

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# Ion Plating

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## Introduction

ION PLATING is a generic term applied to film deposition processes in which the substrate surface and the growing film are subjected to a continuous or periodic flux of energetic massive bombarding particles (ions, radicals, atoms, or molecules--reactive or inert) sufficient to cause changes in the film formation process and the properties of the deposited film (Ref 1, 2, 3, 4). The bombarding species and the depositing species can be from a number of sources. Bombardment can take place in a plasma or vacuum environment. When a beam of energetic particles is used in vacuum, the process is often called ion-beam-assisted deposition (IBAD).

A vacuum can be defined as an environment where the gas density is low and the mean free path for collision is very long. In vacuum-barrel deposition processing, this means that the pressure is lower than about 1.3 mPa (1 × $10^{-5}$ torr). A plasma is a low-pressure gas that contains enough ions and electrons to have an appreciable electrical conductivity. This requires a gas pressure of greater than 13 mPa (1 × $10^{-4}$ torr). Plasmas can be low-pressure (less than about 0.4 Pa, or 3 mtorr) or higher-pressure (greater than about 0.4 Pa, or 3 mtorr), depending on whether or not collisions in the gas phase are sufficient to "thermalize" high-energy particles leaving a source (Ref 5, 6). This differentiation is important when using sputtering as a source for deposition because reflected high-energy neutrals from the target can have an important effect on the growing film. Figure 1 shows the distance traveled by particles of differing masses (12 and 400 atomic mass unit, or amu) and energies (5 eV, or 0.8 aJ, and 1 keV, or 160 aJ) in argon before becoming thermalized. It should be noted that the gas density in a plasma system can vary with position due to preferential gas motion and particle temperature distribution (Ref 7, 8, 9).

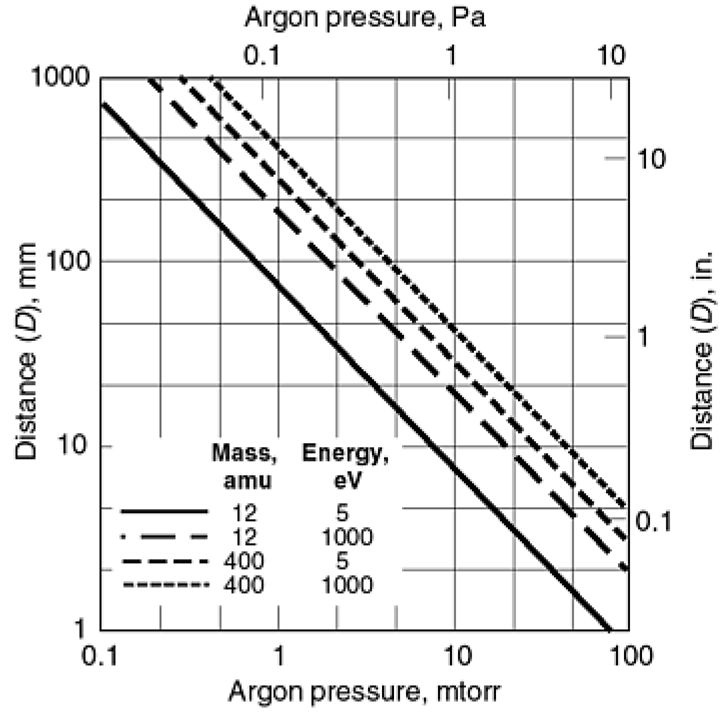

**Fig. 1 Plot of distance traveled vs. argon gas pressure to show effect of variations in mass and energy of particles before thermalization. Results calculated from test data obtained at room temperature. Source: Ref 5**

There are two basic versions of the ion plating process. In *plasma-based ion plating* the substrate is in contact with a plasma, and the ions are accelerated from the plasma and arrive at the surface with a spectrum of energies. In *vacuum-based ion plating* the film material is deposited in a vacuum and the bombardment is from an ion or plasma "gun." The plasma-based ion plating process was first described in the technical literature in 1963 (Ref 10, 11, 12), and the first reference to vacuum-based ion plating was in 1973 (Ref 13). In *reactive ion plating*, the plasma or ion/plasma gun can form ions of a reactive species to both bombard and react with the depositing material to form a compound film material. In some cases, such as when using low-voltage, high-current electron-beam evaporation or arc vaporization, an appreciable portion of the vaporized source material can be ionized to allow bombardment by "film ions." Often the term *ion plating* is accompanied by modifying terms such as *sputter ion plating*, *reactive ion plating*, *chemical ion plating*, *alternating ion plating*, *arc ion plating*, and so on, which indicate the source of depositing material, the method used to bombard the film, or other particular conditions of the deposition.

Figure 2(a) shows a simple plasma-based ion plating configuration using a resistively heated vaporization source, and Figure 2(b) shows a simple vacuum-based system using an electron-beam evaporation source. In plasma-based ion plating, the substrate can be positioned in the plasma generation region or in a remote or downstream location outside the active plasma generation region.

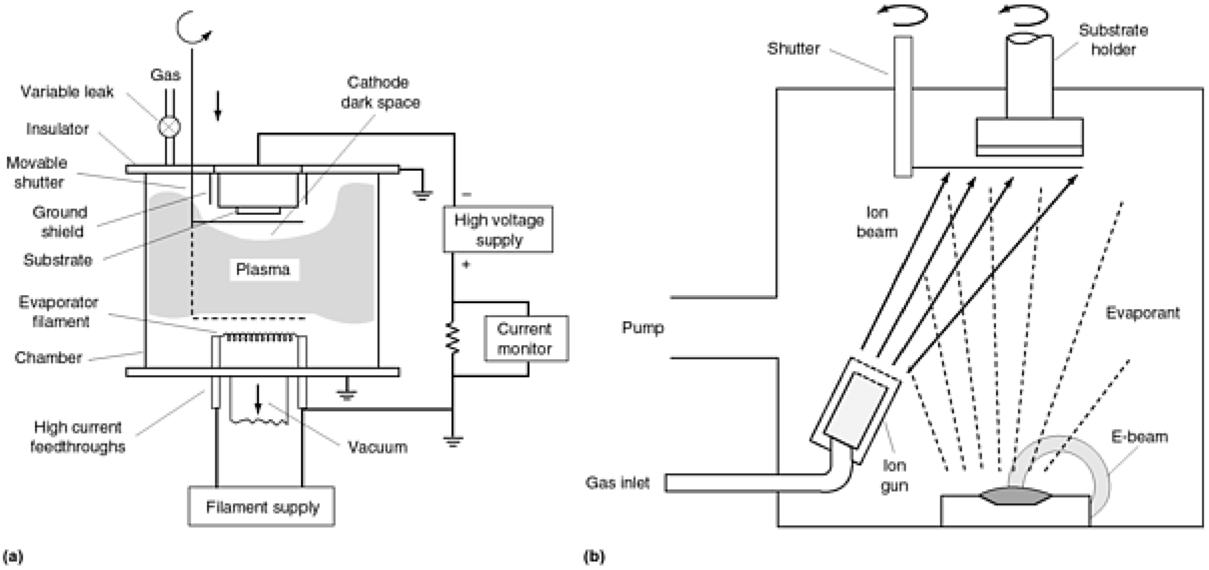

**Fig. 2 Schematic showing typical ion plating installations. (a) Plasma-based configuration with resistively heated vaporization source. (b) Vacuum-based configuration with electron-beam evaporation source**

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## Effects of Bombardment on Film Formation

**Film Properties.** The properties of a film of a material formed by any physical vapor deposition (PVD) process depend on four factors, namely:

- Substrate surface condition: morphology (roughness, inclusions, particulate contamination), surface chemistry (surface composition, contaminants), surface flaws, outgassing, and so on
- Details of the deposition process and system geometry: angle-of-incidence distribution of the depositing adatom flux, substrate temperature, deposition rate, gaseous contamination, and so on
- Details of film growth on the substrate surface: nucleation, interface formation, interfacial flaw generation, energy input to the growing film, surface mobility of the depositing adatoms, growth morphology of the film (i.e., roughness), gas entrapment, reaction with deposition ambient (including reactive deposition processes), lattice defects produced, grain size and orientation, recoil implantation (atomic peening), and so on
- Postdeposition processing and reactions: reaction of film surface with the ambient, thermal, or mechanical cycling; corrosion; interfacial degradation; burnishing of soft surfaces; shot peening; encapsulation ("topcoat"); and so on

In order to have reproducible film properties, each of these factors must be controlled. Figure 3 depicts the effect of energetic particle bombardment on surfaces and the near-surface region (Ref 14). The near-surface region is defined as the region of physical penetration by the bombarding species and is about 1 nm/keV (10 Å/keV). These effects include:

- Reflection of some of the impinging high-energy particles as high-energy neutrals
- Generation of collision cascades in the near-surface region
- Physical sputtering
- Generation of lattice defects
- Trapping of the bombarding species
- Stuffing of atoms into the lattice by recoil processes
- Recoil implantation of surface species
- Enhanced chemical reactivity (bombardment-enhanced chemical reactivity)
- Enhanced diffusion in the surface region
- Heating of the near-surface region

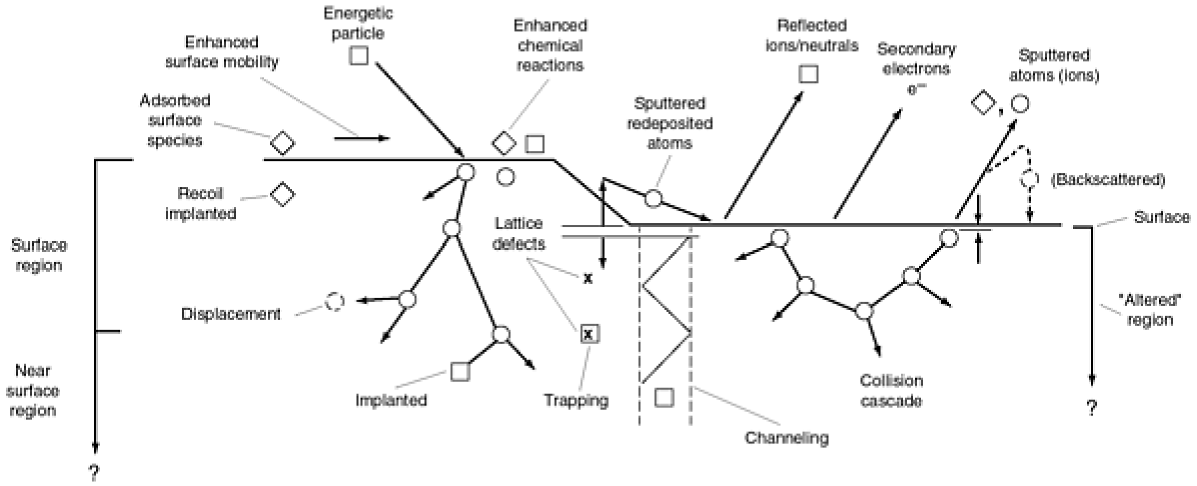

**Fig. 3 Schematic showing interactions in the near-surface region and on a surface during massive energetic**

**particle bombardment. Source: Ref 14**

Most of the bombarding energy is given up in the near-surface region in the form of heat. In a growing film that is being concurrently bombarded by energetic particles, the surface and near-surface region is continually being buried and bombardment effects are trapped in the growing film (Ref 14, 15).

**Surface Preparation.** Bombardment of the substrate surface by energetic particles prior to the deposition of the film material allows in situ cleaning of the surface (Ref 16). Any surface placed in contact with a plasma will assume a negative potential with respect to the plasma (self-bias), due to the more rapid loss of electrons to the surface compared to the loss of ions to the surface. This sheath potential will accelerate ions across the sheath to bombard the surface. The sheath potential that is developed depends on the flux and energy of the electrons striking the surface. For a weakly ionized direct current (dc) plasma, the sheath potential will be several volts. For a system where electrons are accelerated to the surface, the self-bias can be many tens of electron volts. When the surface is conductive, a dc potential can be applied directly to the surface (applied bias). If the surface is nonconductive, a radio frequency (rf) potential can be applied to the surface to give a periodic high negative potential (applied bias) to the surface.

For inert gas ions with less than about 25 eV (4 aJ) energy, cleaning by bombardment is in the form of desorption of volatile materials ("ion scrubbing"). For reactive gases such as hydrogen or oxygen, the cleaning is in the form of reaction with contaminants such as hydrocarbons and desorption of volatile reaction products such as CO or $CH_3$. Energetic reactive ions produce etching of the surface by reacting with the substrate surface material and producing a volatile compound ("plasma etching") (for example, $SiCl_4$ from bombardment of silicon with an energetic Cl-containing ion from a vapor such as $CCl_4$) (Ref 17, 18). More energetic inert particles produce physical sputtering ("sputter cleaning").

This in situ cleaning or surface preparation allows good interfacial contact for adhesion (Ref 19) and the generation of ohmic contacts to semiconductor materials. If done at low bombarding energies, the cleaning of semiconductor materials can be done without introducing surface defects that affect the electronic properties of the surface/interface (Ref 20). Bombardment can also make the surface more "active" by the generation of reactive sites and defects. For example, unbombarded silicon surfaces metallized with aluminum show no interdiffusion, but the bombarded surface gives rapid diffusion (Ref 21).

Bombardment can also be used to change the surface properties such as morphology (roughening) or chemical composition. For example, bombardment of a carbide surface by hydrogen ions results in the decarburization of a thin surface layer to produce a metallic surface on the carbide (Ref 22), and bombardment from a nitrogen plasma can be used to plasma nitride a steel surface prior to the deposition of a titanium nitride film (Ref 23, 24).

**Nucleation.** In ion plating, it is important that bombardment of the substrate surface during the surface preparation stage be continued into the deposition stage, where adatoms (atoms adsorbed on a surface so they will migrate over the surface) are continually being added to the surface. This prevents the surface from being recontaminated. Nucleation of adatoms on the surface is modified by concurrent energetic particle bombardment. This modification can be due to a number of factors, including cleaning of the surface, the formation of defects and reactive sites on the surface, recoil implantation of surface species, and the introduction of heat into the near-surface region (Ref 14, 25). Generally, this modification of nucleation increases the nucleation density. In addition, where there is high energy bombardment, sputtering and redeposition allow nucleation and film formation in areas that would not otherwise be reached by the depositing adatoms.

**Interface Formation.** Bombardment enhances the formation of a diffusion- or compound-type interface on the "clean" surface if the materials are mutually soluble, or it enhances the formation of a pseudodiffusion-type of interface, due to the energetic particle bombardment, if the materials are insoluble (Ref 14). Interface formation is aided by defect formation and the deposition of energy (heat) directly into the surface without the necessity for bulk heating (Ref 26, 27). In some cases, the temperature of the bulk of the material can be kept very low while the surface region is heated by the bombardment. This allows the development of a very high temperature gradient in the surface region, which limits diffusion into the surface (Ref 28). Ion bombardment along with a high surface temperature can cause all of the depositing material to be diffused into the surface, producing an alloy or compound coating.

**Film Growth.** Energetic particle bombardment during the growth of the film can modify a number of film properties, including (Ref 14):

- Density

- Bulk morphology
- Surface morphology
- Grain size
- Crystallographic orientation
- Electrical resistivity
- Porosity

The changes in film properties are due to a number of factors, including

- Input of energy into the surface region during deposition
- Forward sputtering and redeposition of deposited atoms that densify the film
- Bombardment-enhanced chemical reaction
- Sputtering of loosely bonded contaminants and unreacted reactive species

**Surface Coverage.** The macroscopic and microscopic surface coverage of a deposited film on a substrate surface can be improved by the use of concurrent bombardment during film deposition. The macroscopic ability to cover complex geometries depends mostly on scattering of the depositing material in the gas phase (Ref 29, 30). On a more microscopic scale, sputtering and redeposition of the depositing film material will lead to better coverage on micron-sized and submicron-sized features (Ref 31, 32, 33, 34, 35, 36) and to reduced pinhole formation. On the atomic scale, the increased surface mobility, increased nucleation density, and erosion/redeposition of the depositing adatoms will disrupt the columnar microstructure and eliminate the porosity along the columns. As a result, the use of gas scattering, along with concurrent bombardment, increases the surface-covering ability and decreases the microscopic porosity of the deposited film material as long as gas incorporation does not generate voids.

**Reactive Deposition.** In reactive ion plating, codepositing species, or depositing species and gaseous species, react to form a nonvolatile compound film material (Ref 37). For example, depositing titanium atoms can react with "activated" gaseous nitrogen to form TiN, with codeposited carbon (Ref 38, 39) to form TiC, or with a combination to form $TiC_xN_y$. In plasma-based ion plating, the plasma activates reactive species and creates new species in the gas phase. The concurrent bombardment of the surface enhances chemical reaction (bombardment-enhanced chemical reactions) (Ref 40, 41, 42, 43), desorbs unreacted adsorbed species (Ref 44), and densifies the film (Ref 45). In general, it has been found necessary to have concurrent bombardment in order to deposit hard and dense coatings of materials. Figure 4 shows the relative effects of heating and concurrent bombardment on the resistivity of ion plated and non-ion plated TiN films (Ref 46, 47).

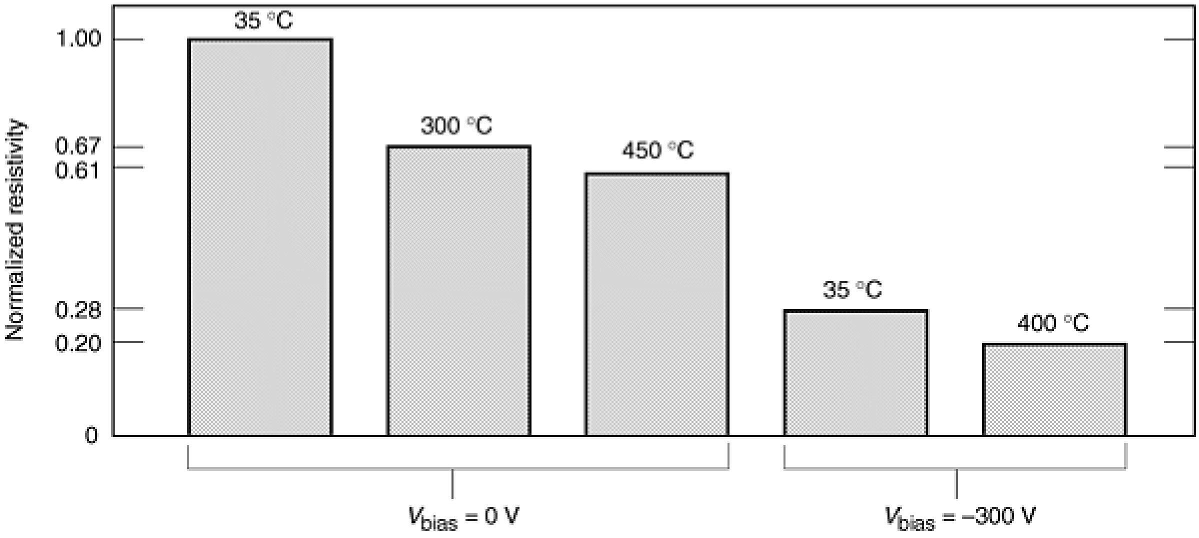

**Fig. 4 Relative effect of deposition temperature and bias on reactively sputter-deposited titanium nitride. A lower resistivity rating indicates that the titanium film is more dense (that is, hard) and stoichiometric. Source:**

**Ref 46**

In vacuum-based ion plating, the bombardment of the depositing film by energetic reactive gas ions enhances the chemical reaction (Ref 48, 49). In reactive deposition, the extent of the reaction depends on the plasma conditions, bombardment conditions, and the availability of the reactive species. By limiting the availability, the composition of a deposit can be varied. For example, in the reactive ion plating of TiN, by reducing the availability of the nitrogen in the plasma at the beginning of the deposition, an initial layer of titanium is deposited. The composition can then be graded to TiN by increasing the availability of nitrogen in the plasma, thus forming a "graded" interface.

**Properties of Films Deposited by Ion Plating.** The properties of films formed by processes depend on a number of factors. Because the ion plating process has more deposition parameter variables than other PVD processes, the film properties can be varied over a wide range, depending on the process parameters.

***Film Adhesion.*** The adhesion of a deposited film to a surface depends on the deformation and fracture modes associated with the failure (Ref 19). Energetic particle bombardment prior to and during the initial stages of film formation can enhance adhesion by:

- Removing contaminant layers
- Changing the surface chemistry
- Generating a microscopically rough surface
- Increasing the nucleation density by forming nucleation sites (defects, implanted species, and recoil-implanted species)
- Increasing the surface mobility of adatoms
- Decreasing the formation of interfacial voids
- Introducing thermal energy and defects directly into the near-surface region, thereby promoting reaction and diffusion

Film adhesion can be degraded by the diffusion and precipitation of gaseous species to the interface. The adhesion can also be degraded by differences in the coefficient of thermal expansion of the film and substrate material in high-temperature processing, or the residual film growth stresses developed in low-temperature processing.

***Residual Film Stress.*** Invariably, atomistically deposited films have a residual stress that may be tensile or compressive in nature and may approach the yield or fracture strength of the materials involved. Generally, vacuum-deposited films and sputter-deposited films prepared at high pressures (>0.7 Pa, or 5 mtorr) have tensile stresses that can be anisotropic, with off-normal angle of incidence depositions. In low-pressure sputter deposition and ion plating, energetic particle bombardment can give rise to high compressive film stresses due to the recoil implantation of surface atoms (Ref 50, 51, 52, 53, 54). This effect is sometimes called *atomic peening* and generally requires 20 to 30 eV (3 to 5 aJ) per deposited atom of additional energy from bombardment. Studies of vacuum-evaporated films with concurrent bombardment have shown that the conversion of tensile stress to compressive stress is very dependent on the ratio of bombarding species to depositing species. The residual film stress anisotropy can be very sensitive to geometry and gas pressure (Ref 55, 56) during sputter deposition, due to bombardment of high-energy reflected neutrals and the effect of gas-phase and surface collisions at higher pressures. Figure 5 shows the effect of gas pressure on residual film stress in postcathode magnetron sputter deposition of molybdenum.

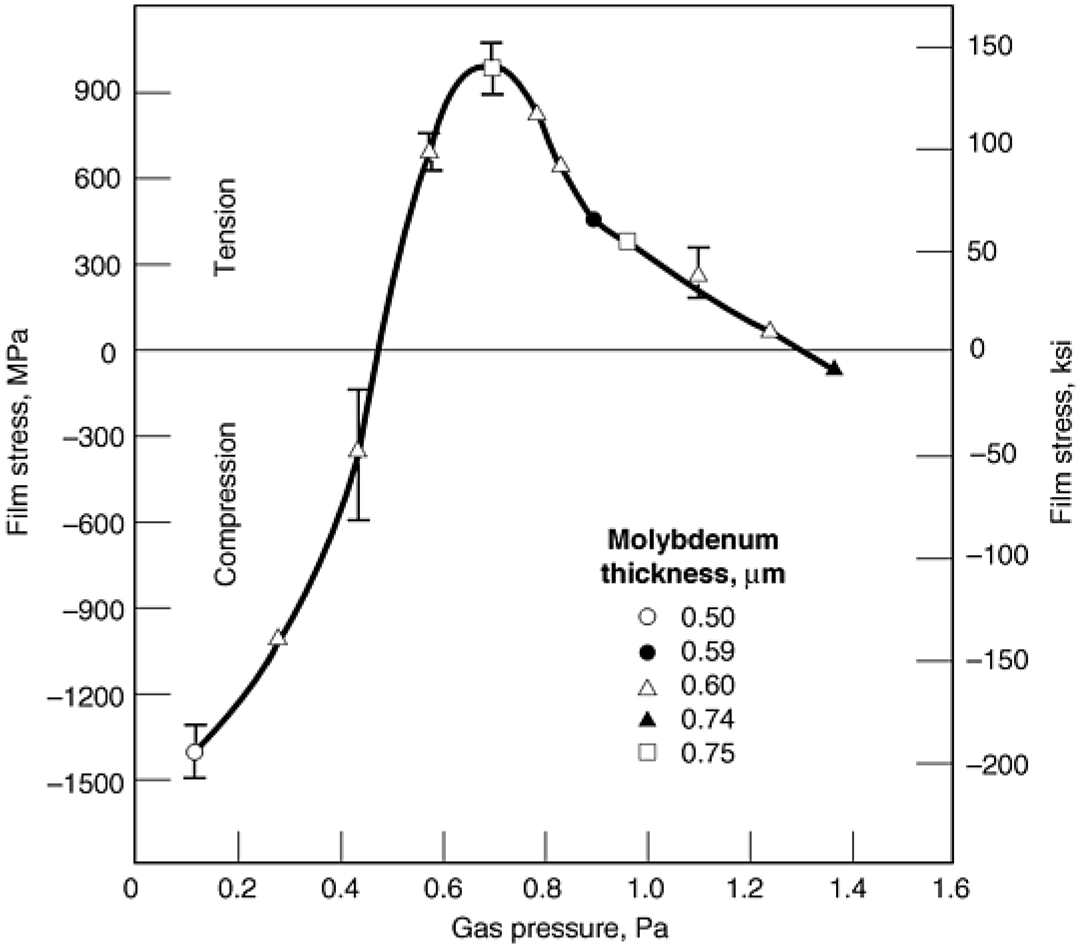

**Fig. 5 Effect of gas pressure on residual stress in molybdenum films formed by postcathode magnetron sputter deposition. High compressive stress at low pressures is a result of reflected high-energy neutral bombardment. The low stress at high pressures is a result of columnar growth in a low-density film. Bars on points indicate range of values. Source: Ref 56**

The lattice strain associated with the residual film stress represents stored energy, and this energy, together with a high concentration of lattice defects, can lead to:

- Lowering of the recrystallization temperature in crystalline materials
- A lowered strain point in glassy materials
- A high chemical etch rate
- Electromigration enhancement
- Room-temperature void growth in films
- Other such mass transport effects

***Film Density.*** Under nonbombardment conditions at low temperature, the morphology of the deposited material is determined by geometrical effects with the film density being a function of the angle of incidence of the depositing particles. Under ion plating conditions, forward sputtering, sputtering and redeposition, increased nucleation density, and increased surface mobilities of adatoms on the surface under bombardment conditions can be important in disrupting the columnar microstructure and thereby increasing the film density and modifying film properties (Ref 57, 58). The bombardment also improves the surface coverage and decreases the pinhole porosity in a deposited film. This increased density and better surface coverage is reflected in film properties such as (Ref 59, 60, 61):

- Better corrosion resistance

- Lower chemical etch rate
- Higher hardness
- Lowered electrical resistivity of metal films
- Lowered gaseous and water vapor permeation through the film
- Increased index of refraction of dielectric coatings

However, it has been found that if the bombarding species is too energetic and the substrate temperature is low, high gas incorporation, defect concentration, residual stress, and the formation of voids can lead to poor-quality films.

***Film Porosity.*** The porosity in atomistically deposited films results from:

- Incomplete surface coverage
- Deposition on particulate contamination that is subsequently dislodged
- Formation of a columnar film morphology
- Precipitation of voids at grain boundaries
- Precipitation of incorporated gases in the film

The increased surface-covering ability, densification of the film material, and disruption of the columnar morphology in ion plating decrease the film porosity unless bombardment gases are incorporated in the depositing film.

For more information about bombardment effects on film formation, see the article "Growth and Growth-Related Properties of Films Formed by Physical Vapor Deposition Processes" in this Volume.

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## Sources of Substrate Potential

The most common versions of ion plating use a potential on the substrate surface to accelerate ions to the surface. The potential on the surface can be applied by several methods.

**Applied Bias (dc).** A dc potential can be applied directly to an electrically conducting surface. Bombardment will be relatively uniform over flat surfaces where the equipotential field lines are conformal to the surface, but it will vary greatly if the field lines are curved, because ions are accelerated normal to the field lines. The dc discharge that is generated will fill the chamber volume if the pressure is sufficiently high. For pressures too low to establish a dc discharge, a magnetron configuration can be used to enhance the plasma over the surface of a web strip passing over the magnetron surface.

In the application of a dc potential, often the applied voltage and measured current (power expressed in watts/$cm^2$) to the surface is used as a process parameter and control variable. However, it must be realized that the bombarding ions generally have not been accelerated to the full applied potential due to the position of their formation, charge exchange collisions, and the physical collisions in the gas. The measured current consists of the incident ion flux (the ions may be multiply charged) and the loss of secondary electrons from the surface. The cathode power is a useful process parameter to maintain reproducibility only if parameters such as gas composition, gas pressure, system geometry, and so on are kept constant.

**Applied Bias (rf).** An rf potential (e.g., 13.56 MHz) must be applied to a surface if the surface is an insulator. Otherwise, charge buildup on the surface will result in arcing over the surface or through the insulating layer if it is thin (Ref 62). When applying an rf potential, the potential of the surface in contact with the plasma will vary continuously, although it will always be negative with respect to the plasma. The dc component of the bias will depend on the presence of blocking capacitance in the circuit and whether a dc bias supply is present. The energy of the ions that bombard the surface will depend on the frequency of the rf source and the gas pressure. Maximum bombardment energy will be attained at low frequencies and low gas pressures. When using rf sputtering as a vapor source, a different rf frequency and power may be used on the substrate (Ref 63).

The rf bias has the advantage that it can establish a discharge in the space between the electrodes at a pressure lower than that required in a dc bias. It has the limitation that the rf electrode is like a radio antenna, and the plasma density formed over the surface depends on the shape of the substrate/fixture system. In some cases, the substrate/fixture should be surrounded by a "cage" to smooth out the electric field and give a more uniform plasma density. In all cases, ground shields should be kept well away from the rf electrode, and in the case of an insulator, the insulator should completely cover the rf electrode.

**Applied Bias--dc plus rf.** A dc potential and an rf potential can be applied at the same time if an rf choke is used in the dc circuit to prevent the rf from entering the dc power supply. By applying a dc bias, the insulating surface is exposed to bombardment for a longer period of time during the rf cycle.

**Self-Bias.** A negative self-bias is induced on an insulating or floating surface due to the higher mobility of the electrons compared to that of the ions. The higher the electron energy, the higher the negative self-bias generated. Figure 6 shows a technique for inducing a high self-bias by accelerating electrons away from a source and magnetically confining them so that they must bombard a substrate surface. It is possible to generate a positive self-bias if the electrons are prevented from bombarding the surface by using a magnetic field, because ions can reach the surface by scattering and diffusion. For example, substrates in a postcathode magnetron sputtering system can have a positive self-bias.

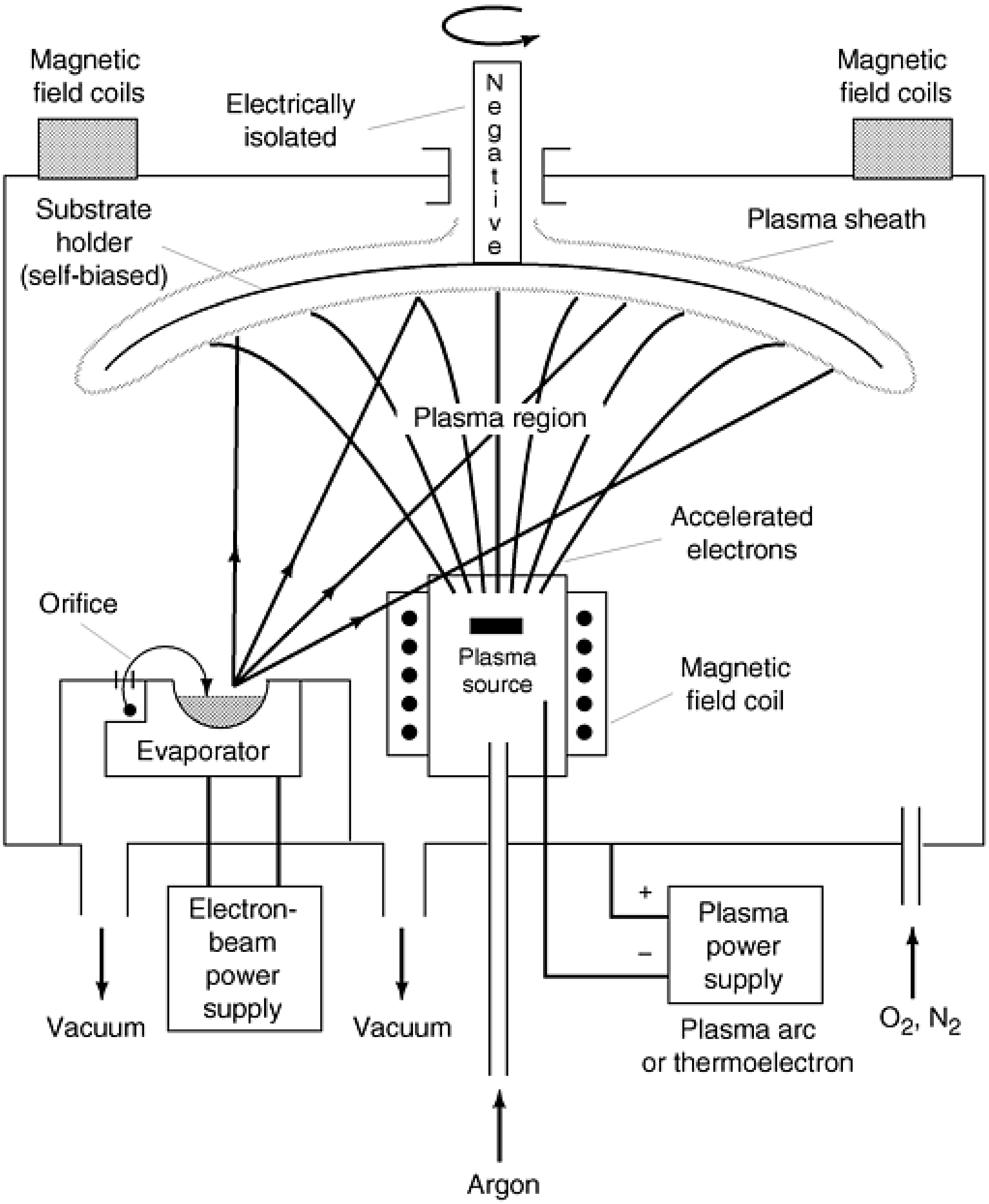

**Fig. 6 Generation of a high self-bias and a plasma using accelerated electrons, an electrically isolated substrate holder, and a confining magnetic field. The vaporization source is a differentially pumped e-beam evaporator.**

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### Sources of Bombarding Species

The energetic species used to bombard the growing film can be either ions or neutrals, although acceleration of charged ions is the most common way to obtain a controlled bombardment.

**Plasmas.** A common source of energetic bombarding species is ions accelerated from an inert or reactive gas plasma. The plasma can be formed using a number of configurations. The most common configuration is the dc diode with an electrically conductive substrate serving as the cathode. When the substrate or depositing film is an electrical insulator, the plasma can be formed by making the substrate an rf electrode in an rf plasma system.

Bombardment can be enhanced by having a superimposed rf and dc potential on the substrate. In some cases, the plasma can be formed by the electrons used to vaporize the source material (Ref 64, 65, 66, 67, 68).

In some cases, auxiliary plasmas are used to provide the ions. Often these auxiliary plasmas are formed using a hot electron-emitting filament (Ref 69), a hollow cathode (Ref 70, 71), or a plasma arc source. The electrons can be confined with a magnetic field, as shown in Fig. 7.

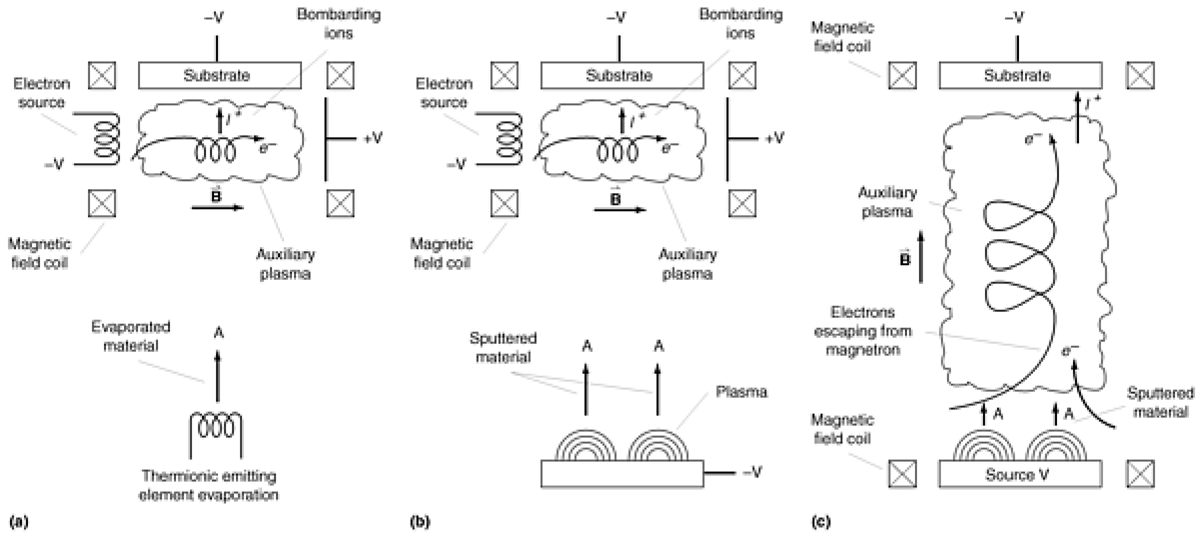

**Fig. 7 Schematic showing selected methods used to provide a plasma near the substrate. (a) Hot cathode configuration. (b) Magnetically confined plasma configuration. (c) Unbalanced magnetron configuration**

**Gas Ions and Film Ions Generated by Arc Sources.** Low-voltage, high-current arcs are a source of ions. If the arc is in a vacuum, then the vaporized electrode material is highly ionized and is often multiply charged (Ref 72, 73). In a vacuum, a positive space charge in the plasma between the electrodes accelerates the ions away from the electrodes. If the gas pressure is low, the ion can bombard a surface with appreciable energy. An arc can also be established with a gas present to generate a *plasma arc*. In a plasma arc, both the vaporized material (film ions) and gaseous species are ionized and can be accelerated to bombard the growing film. The ions from the arc can be used to sputter clean the surface at a high particle energy. If the accelerating voltage is high enough, the ion bombardment can prevent any net deposition on the substrate (Ref 65, 74).

**High Energy Neutrals.** In sputter deposition, ions bombarding a sputtering cathode can be neutralized and be reflected with an appreciable portion of their incident energy. If the gas pressure is low (~< 0.4 Pa, or 3 mtorr, as shown in Fig. 1), the high-energy reflected neutrals can bombard the growing film and affect the film properties (Ref 75, 76).

High-energy neutrals are also formed by charge exchange processes in the higher-pressure dc diode plasma configurations where the substrate is the cathode (Ref 77, 78, 79, 80).

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## Sources of Depositing Species

**Thermal Vaporization.** The various thermal vaporization sources can be used in ion plating. For plasma-based ion plating, the resistively heated sources are most often used. Low-energy electron-beam heating from hollow cathode sources and thermionic sources can be used, often with a magnetic confining field. This allows the electrons to heat the material to be vaporized and also to create the plasma. High-energy electron-beam heating can be used, but this requires isolating the electron-emitting filament from the plasma by the use of a conductance baffle with a hole to allow the electron beam to enter the plasma/crucible region (differentially pumped e-beam) (Ref 1, 81).

At high vaporization rates, gas phase nucleation generates ultrafine particles in the plasma (Ref 1). These particles become negatively charged, are suspended in the plasma, and do not deposit on the substrate. However, when the plasma is extinguished, the ultrafine particles will deposit on surfaces in the system.

**Physical sputtering** is often used as a source of depositing material. However, when using dc magnetron sputtering configurations, the plasma is confined in a region near the target and is not available as a supply of ions for substrate bombardment. In this case, the plasma used to supply these ions can be from an unbalanced magnetron configuration, the use of rf in conjunction with the dc magnetron, or the use of an auxiliary plasma source. A hot filament auxiliary plasma source and an unbalanced magnetron plasma source configurations are shown in Fig. 7(a) and 7(c), respectively.

**Arc Vaporization.** An arc can also be established with a gas present, giving a plasma arc. In a plasma arc, both the vaporized material and gaseous species are ionized (Ref 82, 83, 84). Either a solid cathodic arc surface or a molten anodic arc surface (Ref 85, 86) can be used. Ion species are then accelerated to the substrate under an applied bias. A problem with the cathodic arc vaporization source is that the arc causes the emission of molten globules (that is, macroparticles or macros) that deposit on the film surface. Various techniques are used to eliminate the globules from the plasma. Arc vaporization sources are widely used in tool coating, even though they present a source of globules. The arc source and a sputtering source can be combined into one design (Ref 87). It has been found that by using the arc discharge for sputter cleaning, the cleaning and heating can be performed much faster than by using a dc diode discharge, due to the high ionization and the multiply charged heavy metal ions in the arc discharge (Ref 88). In addition, the surface smoothness is increased during arc-sputter cleaning (Ref 74). Figure 8 shows some arc-source ion plating configurations.

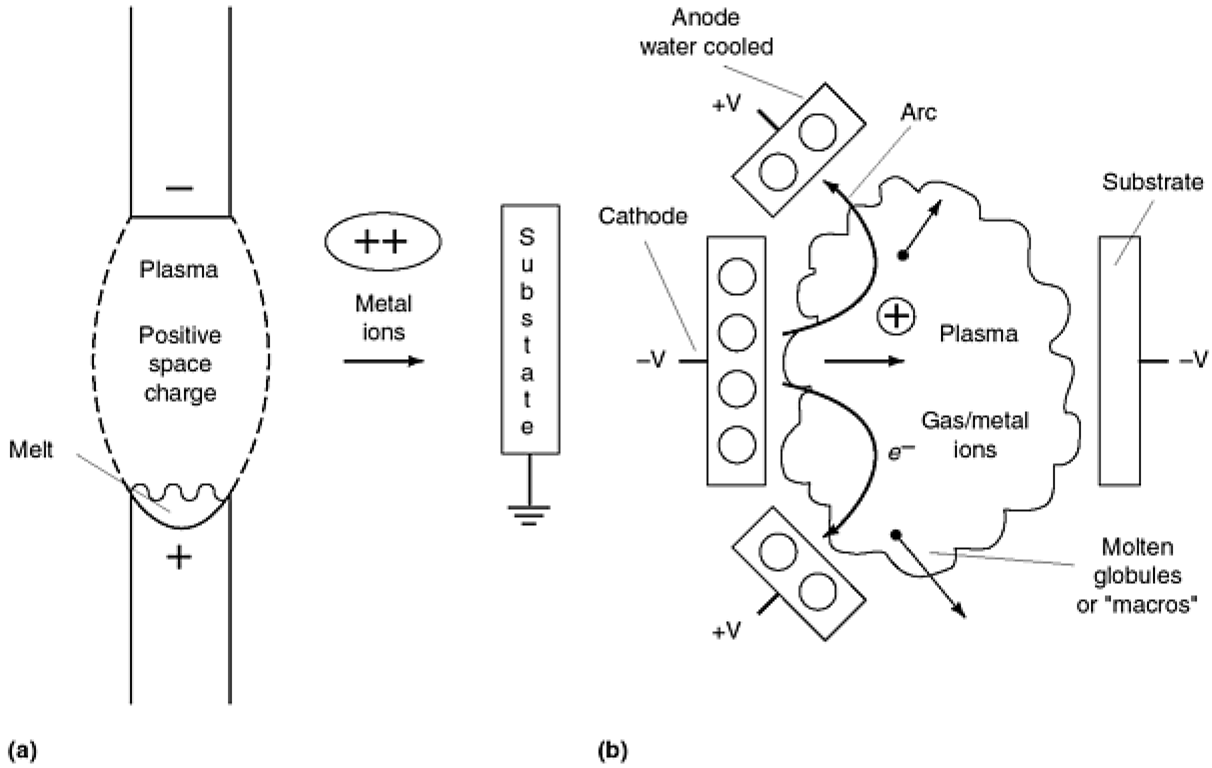

**Fig. 8 Typical arc sources used in ion plating. (a) Vacuum arc/molten anode source. In the vacuum, the ions are accelerated away from the positive space charge in the plasma. (b) Cathodic arc vaporization source. In the plasma, the film ions are thermalized in the plasma, but both the film ions and the gas ions are accelerated to the substrate under an applied bias.**

**Chemical Vapor Precursor Gas.** Gaseous chemical vapor precursor species containing the material to be deposited can be used as a deposition source. Using a chemical vapor precursor species in a plasma is very similar to plasma enhanced chemical vapor deposition (PECVD), in which the plasma is used to decompose the chemical species and to bias PECVD where ions from the plasma are accelerated to the substrate surface (Ref 43). Typical chemical vapor precursor gases are $TiCl_4$ for titanium, $SiH_4$ for silicon, and $C_2H_4$ for carbon, diamond-like carbon (DLC), and diamond.

The chemical vapor precursor may not be completely dissociated, so that it will deposit a compound material or material that has some of the original compound-forming material in it. For example, $SiH_4$ can be used to deposit amorphous silicon containing hydrogen. The chemical vapor precursor can be injected into the plasma (Ref 1, 89) in plasma-based ion plating or into a confined plasma ion source in vacuum-based ion plating (Ref 90, 91, 92).

**Laser vaporization** with concurrent ion bombardment has been used to deposit high-quality high-temperature superconductor films at relatively low substrate temperatures (Ref 93). Laser vaporization creates a large number of ions in the vapor "plume," and these can be accelerated to the substrate surface. This technique has been used to deposit hydrogen-free DLC films (Ref 94).

For more information about sources of depositing species, see the other articles in this Section.

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## Ion Plating Bombardment Parameters

A variety of ion plating configurations can be used (Fig. 9). Each configuration will have somewhat different parameters that need to be controlled. Ideally, the ion plating parameters that should be controlled are:

- Ion species and ionization state
- Particle energy
- Flux ratio
- Gas composition and mass flow
- Bombardment uniformity
- Substrate temperature
- Gas incorporation
- Fixturing

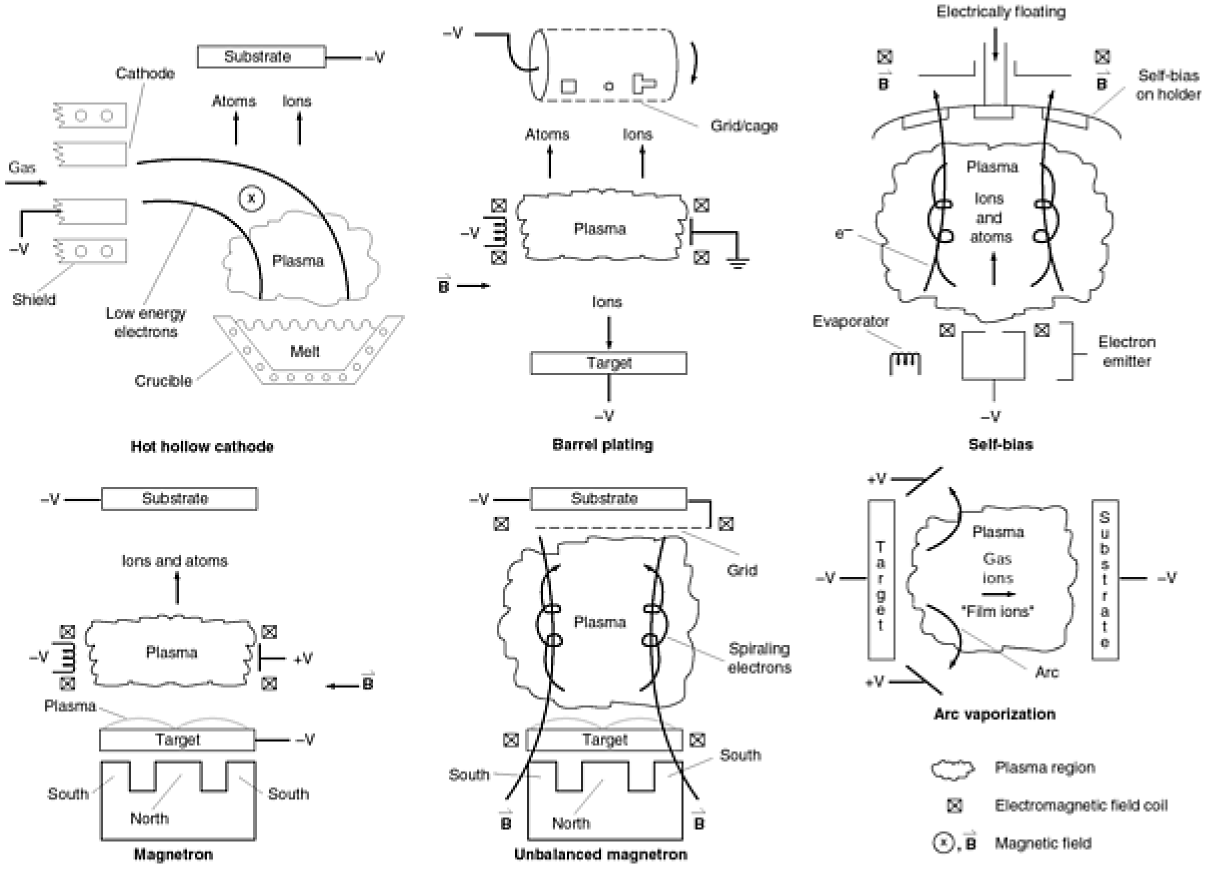

**Fig. 9 Typical configurations used in ion plating**

**Ion Species.** The mass of the bombarding species is important to the energy and momentum transferred during the collision. From the laws of conservation of energy and the conservation of momentum, the energy, $E$, transferred by the physical collision between hard spheres is given by:

$$E_t/E_i = 4M_tM_i \cos^2 j \; /(M_i + M_t)^2 \qquad \textbf{(Eq 1)}$$

where $E$ = energy, $M$ = mass, i = incident particle, t = target particle, and $j$ = the angle of incidence as measured from a line joining their centers of masses. The maximum energy transfer occurs when $M_i = M_t$ and the motion is along a path joining the centers ($j = 0°$). In some cases, bombardment by self-ions (that is, ions of the target material) can result in self-sputtering. This occurs when atoms of the sputtered material become ionized and bombard the target.

The most common inert gas species used for plasma formation and ion bombardment is argon, because it is the least expensive of the inert gases. Krypton is sometimes used, and historically mercury was used. Common reactive gases used in plasmas are nitrogen and oxygen. A mixture of inert gas and reactive gas is often used to increase the momentum transfer efficiency in reactive deposition. Helium is sometimes mixed with other gases to increase the thermal conductivity of the gas mixture to aid in substrate cooling.

**Particle Energy.** The energetic particle energy and energy distribution are important parameters. The energy should be high enough to give appreciable energy transfer on collision, but it should not be high enough to be physically implanted and trapped in the depositing film where it can precipitate and form voids. Neither should it be high enough to cause excessive sputtering. For low-temperature deposition, the ion energy should not exceed about 300 eV (48 aJ). If the substrate is heated to 400 °C (750 °F) or greater, the energy can be increased, because the implanted ions are continually being rapidly desorbed. For low-pressure sputter deposition, the presence of high-energy reflected neutrals from the sputtering target can be an important parameter.

**Flux Ratio.** The ratio of depositing atoms to bombarding species is important to the film properties. Typically, to complete the disruption of the columnar morphology of the growing film and to obtain the maximum density and least microporosity, the energy deposited by the bombarding species should be about 20 eV (3 aJ) per depositing atom or about 20 to 40% resputtering (Ref 95, 96, 97).

**Gas Composition and Mass Flow.** Gas composition is an important processing variable in ion plating. In reactive deposition, the gas mass flow can be an important variable that is sensitive to the fixture/system geometry. The gas used for an inert plasma should be free of contaminants (for example, water vapor and oxygen) that will become activated in the plasma. Inert gases can be purified using heated reactive surfaces (for example, titanium or uranium chip beds). Reactive plasmas should be free of contaminants. For example, in reactive gases or gas mixtures, water vapor can be removed by cold traps using zeolite adsorbers.

Mixtures of gases can be used to deposit films having differing compositions and properties such as color. For example, titanium deposited in a nitrogen plasma to form titanium nitride is a gold color, but with a mixture of nitrogen and methane the color can be made bronze, rose, violet, or black as the $TiC_xN_y$ varies in composition.

The gas distribution into the deposition system is an important factor in obtaining uniform bombardments over a surface and uniform activation of a reactive gas.

**Bombardment Reproducibility.** In vacuum-based ion plating, the ion and atom fluxes can be measured directly by using a Faraday cup ion collector and a mass deposition meter (for example, a quartz crystal deposition monitor). The presence of high-energy reflected neutrals from the sputtering target in the vacuum environment is difficult to measure and can be an unknown processing parameter when a sputtering source is used. In plasma-based ion plating, the ion flux and flux energy distribution are difficult to measure directly. In both vacuum-based and plasma-based ion plating bombardment and deposition, consistency, uniformity, and reproducibility are controlled by having a consistent vaporization source, system geometry, fixture motion, gas composition, gas flow, and substrate power (that is, voltage and current).

Fixturing is often the key to bombardment and deposition uniformity. Fixtures can be in the form of holders that move the substrates or move the deposition sources (Ref 98). Often a three-dimensional object is rotated in front of the deposition source to randomize the deposition angle of incidence, increase uniformity of bombardment, and give a more uniform morphology to the deposit (see the article "Growth and Growth-Related Properties of Films Formed by Physical Vapor Deposition" in this Volume). In some cases, especially when using an rf bias, irregularly shaped objects are surrounded by a grid that is electrically tied to the object, thus giving a smooth equipotential surface around the object. Figure 10 shows the use of a rotating "cage" to hold loose parts to be coated (Ref 99).

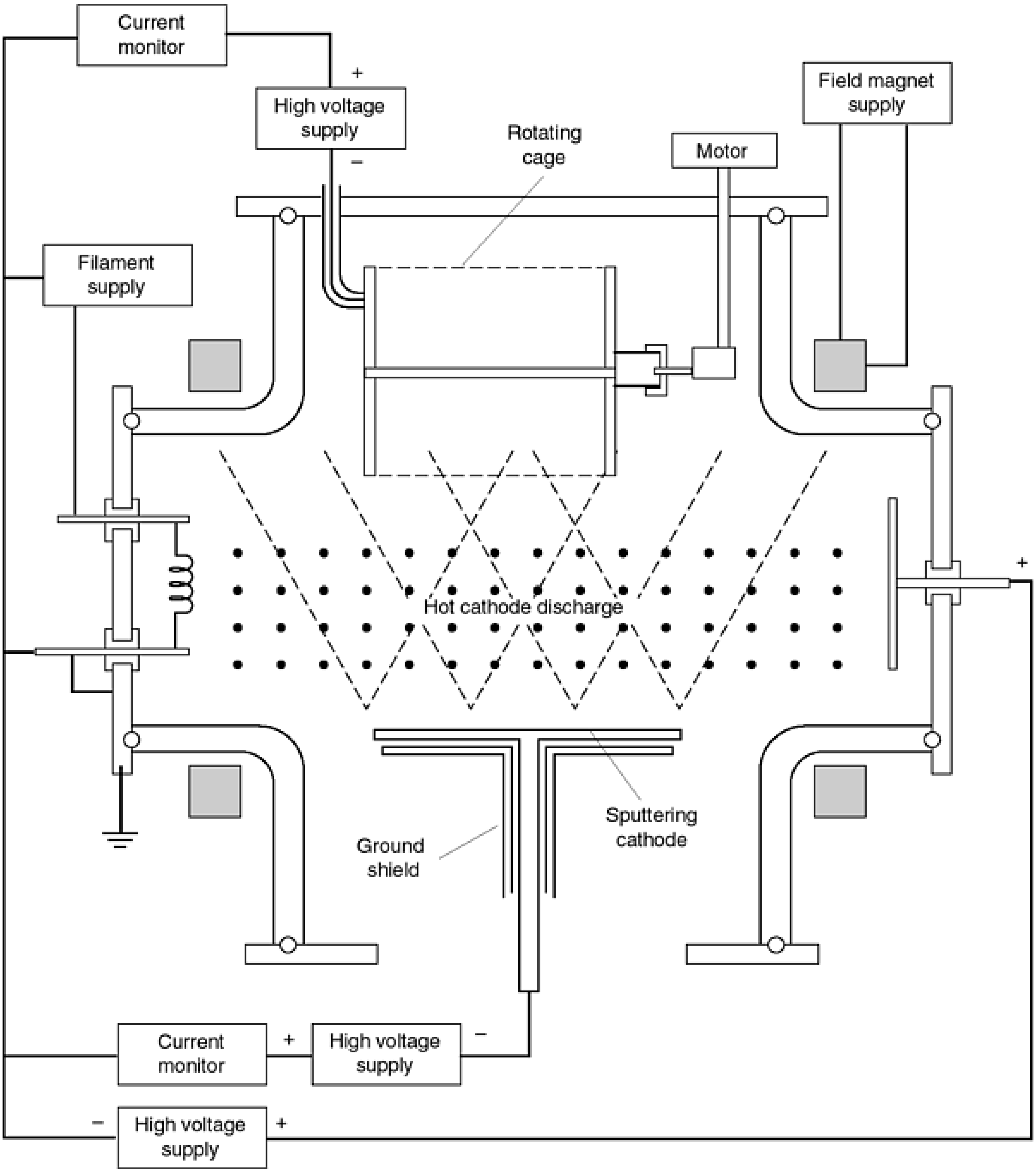

**Fig. 10 Schematic showing key components of a barrel-plating configuration used in ion plating. The grid allows the acceleration of ions through the grid-holes to bombard the small parts enclosed within the rotating barrel (cage). Source: Ref 99**

**Substrate Temperature.** In some cases, ion plated films are deposited without deliberate heating of the substrate. This is particularly advantageous when the substrate is thermally sensitive (for example, a plastic). In the extreme, the deposition can be periodic to allow cooling of the substrate between depositions. For example, the substrates can be mounted on a drum and alternately rotated in front of a deposition source and allowed to cool between depositions (Ref 100, 101, 102).

For the highest-density deposit and the most complete reaction, an elevated temperature is generally desirable (Ref 103). Substrate heating can be done by ion bombardment prior to and during deposition (Ref 74), but often a more controllable technique is to have an auxiliary heating source, such as a radiant heater or electron-bombardment heating. In tool coating, for example, the tool is often heated to just below the tempering temperature.

**Gas Incorporation.** At low substrate temperatures, bombarding gas can be incorporated into the growing film, particularly if the bombarding energy is high. To minimize gas incorporation, the bombarding energy should be kept low (that is, less than 300 eV, or 50 aJ), or a heavy bombarding particle (for example, krypton or mercury) can be used, or the substrate temperature can be kept high (that is, greater than 300 °C, or 570 °F). Low-temperature bombardment can be used to deliberately incorporate gas into the surface of a depositing film. In sputter-ion vacuum pumps, for example, trapping is used to pump inert gases and to incorporate insoluble light and heavy gases in depositing films (Ref 104, 105).

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## Process Monitoring and Control

The equipment used for ion plating is very similar to that used in sputter deposition (see the article "Sputter Deposition" in this Volume). The exception is that in ion plating, the substrate is a sputtering target and often has a complex configuration that requires fixturing in order to obtain uniformity of bombardment, reactive gas availability, and film deposition. The plasma-based ion plating process is generally made reproducible by duplicating the geometry and process parameters used. The effects of the bombardment are generally determined by the property changes measured after deposition.

The amount of bombardment is often quoted as the amount of resputtering or the amount of energy per deposited atom that is added by the bombardment. Typically, for the maximum densification about 20 eV (3 aJ) per deposited atom must be added by bombardment. To avoid gas incorporation at low substrate temperatures, the bombardment energy should be less than 300 eV (50 aJ), which means that there must be about one high-energy particle to ten depositing atoms. Another measure of the bombardment is the resputtering rate of the film. Typically a resputtering rate of 20 to 30% is needed for full densification (Ref 96).

When using the IBAD configuration, the ion plating variables can often be measured directly. For example, in a grid-extraction ion gun, the ion energy is determined by the extraction grid voltages and the ion flux can be measured using a

Faraday cup. In the vacuum environment, the deposition rate can be easily monitored using a quartz crystal deposition monitor.

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## Advantages and Limitations of Plasma-Based Ion Plating

Plasma-based ion plating is the most commonly used ion plating configuration.

**Advantages** of plasma-based ion plating (Ref 1, 2, 106) include:

- Excellent surface-covering ability ("throwing power") under the proper conditions
- Ability to have in situ cleaning of the substrate surface
- Ability to introduce heat and defects into the first few monolayers of the surface to enhance nucleation, reaction, and diffusion
- Ability to obtain good adhesion in many otherwise difficult-to-deposit systems
- Enhancement of reactive deposition process (activation of reactive gases, bombardment-enhanced chemical reaction, and adsorption of reactive species)
- Flexibility in tailoring film properties by controlling bombardment conditions (for example, morphology, density, and residual stress)
- Equipment requirements are equivalent to those of sputter deposition
- Source of depositing material can be from thermal vaporization, sputtering, or chemical vapor precursor gases

**Limitations** of plasma-based ion plating include:

- Many processing parameters must be controlled
- Contamination can be released from surfaces and "activated" in the plasma to become an important process variable
- To bombard growing films of electrically insulating materials, the surfaces must either attain a self-bias or must be biased with an rf potential
- Processing and "position equivalency" can be very dependent on substrate geometry and fixturing (that is, obtaining uniform bombardment and reactive species availability over a complex surface may be difficult)
- Bombarding gas species can be incorporated in the substrate surface and deposited film if too high a bombarding energy is used
- Substrate heating can be excessive
- High residual compressive growth stresses can be introduced into the film layer

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## Applications of Ion Plating

Typical applications of the ion plating process include:

- Good adhesion between a film and substrate (for example, silver on steel for mirrors, silver on beryllium for diffusion bonding) (Ref 65)
- Electrical conductive layers (aluminum, silver, and gold) on plastics and semiconductors
- Low-shear solid film lubricants (for example, silver and gold) (Ref 107)
- Wear and abrasion-resistant coatings [for example, TiN, $TiC_xN_y$, $(Ti\text{-}Al)C_xN_y$, $Ti_{0.5}Al_{0.5}N$] on cutting tools (Ref 74), dies, molds, and jewelry
- Decorative coatings (TiN yields gold-colored deposit, $TiC_xN_y$ yields rose-colored deposit, TiC yields black deposit, ZrN yields brass-colored deposit) applied to hardware, jewelry, guns (Ref 108), and cutlery
- Corrosion protection [aluminum on uranium (Ref 109); mild steel (Ref 110, 111) and titanium; carbon and tantalum on biological implants]
- Deposition of electrically conductive diffusion barriers (for example, HfN and TiN on semiconductor devices)
- Deposition of insulating films (for example, $SiO_2$ and $ZrO_2$)
- Deposition of optically clear, electrically conducting layers (indium-tin-oxide) (Ref 112)
- Deposition of permeation barriers on webs (Ref 113, 114, 115)

Ion plating has also been used to coat very large structural parts with aluminum for corrosion protection (replacing cadmium) (Ref 104).

Ion plating provides a means of modifying film properties that does not exist in other PVD techniques. This gives it a place in the range of PVD deposition techniques available for "surface engineering." Often the applications of ion plating are very substrate-specific, so that fixturing is a very important consideration in coating uniformity, unit cost, and cost-of-ownership for a specific application. The ability to devise an optimal fixture design is often the key to a successful process.

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# Ion-Beam-Assisted Deposition

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## Introduction

ION-BEAM-ASSISTED DEPOSITION (IBAD) refers to the process wherein evaporated atoms produced by physical vapor deposition (PVD) are simultaneously struck by an independently generated flux of ions. The extra energy imparted to the deposited atoms causes atomic displacements at the surface and in the bulk, as well as enhanced migration of atoms along the surface. These resulting atomic motions are responsible for improved film properties, including better adhesion and cohesion of the film, modified residual stress, and higher density, when compared with similar films prepared by PVD without ion bombardment. When the ion beam or the evaporant is a reactive species, compounds such as refractory silicon nitride ($Si_3 N_4$) can be synthesized at very low temperatures. Furthermore, adjustment of the ratio of reactive ions to atoms arriving at the substrate surface allows adjustment of the stoichiometry of solid solutions. Detailed reviews of the IBAD process can be found in Ref 1, 2, and 3.

**Process Utilization.** The feature that distinguishes IBAD from the other PVD processes discussed in this Section of the Volume is that the source of vapor and the source of energetic ions are separated into two distinct hardware items, as opposed to plasma-based techniques, such as direct current (DC), radio frequency (RF), and magnetron sputtering; plasma-enhanced chemical vapor deposition; and certain forms of ion plating in which both the evaporant flux and ion flux are derived by extraction from a plasma. Therefore, there is more control over the deposition parameters in the IBAD process, because the ion flux and the evaporant flux can be varied independently. The other major difference between the plasma techniques and IBAD is the higher pressure (0.13 to 13 Pa, or $10^{-3}$ to $10^{-1}$ torr) required by the operation of the plasma-based methods in order to sustain a plasma. Because IBAD techniques typically operate in the collision-free pressure regime, the evaporant and beam atoms follow straight-line paths to the substrate. This also limits IBAD to line-of-sight applications.

The two most common geometries used in IBAD processing are shown in Fig. 1. Details of the methods are described elsewhere (Ref 4, 5, 6). Normally, a broad beam from an ion source, such as a Kaufman-type ion gun, impinges on a substrate simultaneously with the deposited atoms. The PVD source is usually an electron-beam source, but it could also be a thermal source or a sputter target, in the case of dual-ion-beam sputtering. The simplest geometry for the generation of uniform films and the treatment of complex geometries is a small angle (<30°) between the vapor and ion sources.

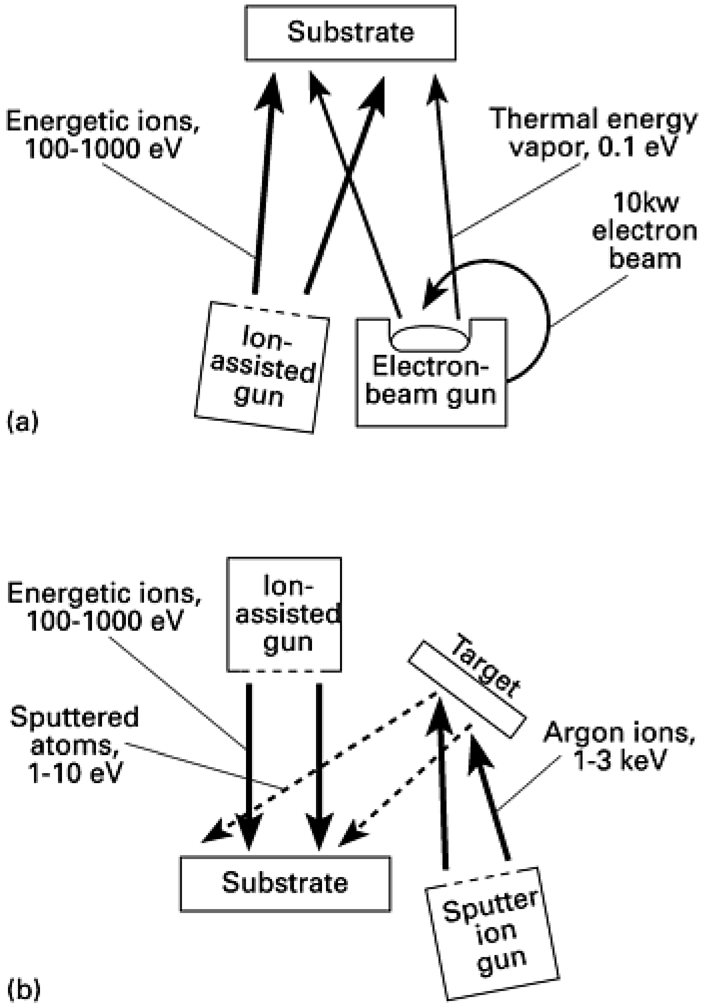

**Fig. 1 Two common processing techniques. (a) Ion-beam-assisted deposition (IBAD). (b) Dual-ion-beam sputtering (DIBS)**

Typical levels of ion-beam energy are between approximately 50 and 1000 eV for Kaufman-type ion guns. The ion beam has a uniform flux over a large area, depending on the diameter of the ion extraction apertures (typically, 30 to 80 mm, or 1.2 to 3.1 in.). The energy levels for beams from an ion implanter are 20 to 100 keV. Large areas are obtained by rastering the beam over the exposed surfaces. Research indicates that while the adhesion of IBAD films at low energies (500 eV to 3 keV) is excellent (Ref 7, 8, 9), an additional improvement in adhesion can sometimes be gained at higher energies (20 to 40 keV) if the film and substrate are not normally miscible. On the other hand, other properties, such as the absorption in optical films, increase as the energy increases because of greater displacement damage (Ref 10, 11, 12). Minimal absorption is obtained at energies below 500 eV. Therefore, for films intended for environmental protection, wear resistance, decorative coatings, and similar applications, a slight advantage might be derived from utilizing higher beam energies, although it would not normally be enough to warrant the greater expense of high-energy ion sources and beam-handling optics. However, for films intended for optical and microelectronics applications, lower energies are preferred in order to minimize beam damage resulting in optical absorption and the formation of electrically active defects.

For the low-energy range (50 to 1000 eV), inelastic collisions of the incident ions with the surface atoms deposit the energy into the surface according to the expression:

$$E \text{ (per film atom)} = R(E_b)$$

where $R$ is the ratio of beam atoms to evaporant atoms arriving at the surface and $E_b$ is the energy per atom in the ion beam. For the arrival of four beam atoms for every ten evaporant atoms ($R$ = 0.4) and a beam energy of 200 eV, the average energy deposited in the surface for every film atom is 80 eV. This should be contrasted to the thermal energy of evaporated film atoms without ion bombardment, which is $E$ = 0.15 eV/atom. This parameter can be tightly controlled and independently varied over a wide range by changing the beam output of the ion source and the energy of the ion beam. In plasma-based techniques, there is a larger spread of energies of the energetic flux components, with unknown ratios of the ion to thermal atom flux. The independent control of these parameters is more limited.

**Physical and Chemical Aspects.** The physical processes that occur at the surface during the film formation of IBAD are shown in Fig. 2. The lower right portion of Fig. 2 shows a very dilute neutral plasma consisting of background gas ("g") at a thermal energy of 0.03 eV, which is present throughout the chamber, as well as vapor atoms ("v") with an energy of either 0.15 eV (produced by the electron-beam evaporator shown in Fig. 1a) or 1 to 10 eV (produced by the sputter source shown in Fig. 1b). The vapor atoms have a velocity vector directed toward the substrate and are confined to the region between the vapor source and the substrate. The gas and the vapor impinge on the film surface at individual rates that are determined by the chamber pressure and the evaporation rate, respectively. The lower left portion of Fig. 2 shows a 200 eV $N^+$ beam directed toward the substrate. Some of this charged plasma is charge-exchange neutralized in near collisions with the ambient gas atoms, resulting in an energetic 200 eV neutral $N^0$, which continues in the direction of the substrate, and a 0.03 eV $N^+$ charged atom that gets expelled from the positive column of charge represented by the ion beam. As a result of charge exchange, the neutralized (high-velocity) atoms will not be counted by the charge-collection system.

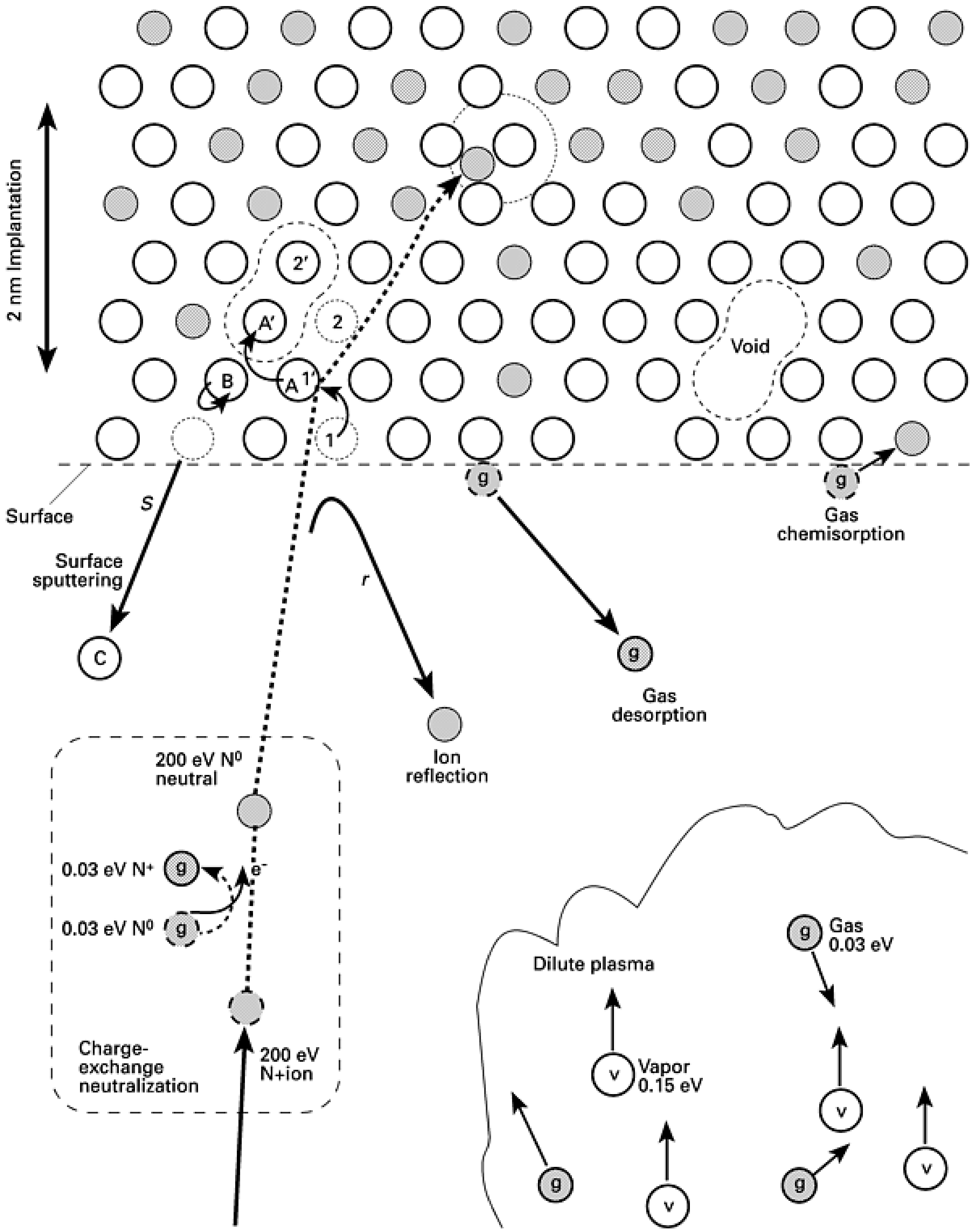

**Fig. 2 Physical and chemical processes at the film-vacuum interface during ion-beam-assisted deposition and dual-ion-beam sputtering**

In the central portion of Fig. 2, the ions, which consist of $N^+$ in this example, are either implanted into the first few atomic layers or reflected from the surface with a reflection coefficient, *r.* As a result of ion bombardment, some of the deposited and/or implanted atoms are sputtered from the surface with a sputtering coefficient, *S.* The sputtering process is shown as resulting from a three-step process, in which energy is transferred in a collision sequence, or cascade, from the ion to atom A, and then to atom B, which causes atom C to be sputtered. Additional surface processes shown are:

- The ion-stimulated thermal desorption of a physisorbed gas atom (binding energy ~0.05 eV) caused by a

thermal spike event in the vicinity of the ion impact
- The ion-stimulated chemisorption of the gas impurity to form chemical bonds with the deposited atoms (binding energy ~2 eV per bond)

The upper portion of Fig. 2 shows the processes that occur within the film. For this example, imagine that the vapor atoms are titanium and the ions are nitrogen. The large, open circles are titanium atoms condensed out of the vapor phase that form the film. They are more numerous near the surface because the nitrogen ions represented by the small, shaded circles have a finite range in the lattice of five atomic layers. In the deepest three layers shown, there are equal numbers of titanium and nitrogen atoms, giving stoichiometric titanium nitride. This also means that the rate of arrival of titanium atoms has been adjusted to be nearly equal to the rate of arrival of the nitrogen ions. Also shown in the near-surface region is a void that is formed in most metallic depositions at thermal energies. The random nature of the positions along the surface, where the vapor atoms land, coupled with the low mobility of the atoms after impact, leads to void formation.

The upper left portion of Fig. 2 represents the process of film densification. As the ion enters the lattice, it slows down upon inelastic collisions with other atoms in the lattice. The dashed line enclosing atoms A' and 2' indicates a void, identical to the one shown on the right, which was present prior to the arrival of the ion. In this schematic, the unprimed symbols are the atom positions before the ion collision, the primed symbols are their positions after the ion collision, and the faint dashed circles represent missing atoms after the collision is over. Upon entering the lattice, the ion strikes atom A, knocking it into one of the void positions (A'), but on the way, atom A also strikes atom B, whereupon its motion causes atom C to be sputtered, as already noted. Next, the ion knocks atom 2 into void position 2', leaving position 2 empty, and the thermal excitation of the ion impact causes atom 1 to jump into position 1', the position formerly held by atom A. Thus, before the collision, there were two atoms missing in the bulk, whereas after the collision, only one atom is missing, and the film has a net increase in density. Finally, the N ion comes to rest in an interstitial position, which represents a defect in the crystalline structure. This defect can be eliminated by a subsequent collision or it can remain in the film.

The atomic displacement mechanisms in the bulk of the film depicted in Fig. 2 are generic to any energetic deposition process. The plasma and surface processes depicted in that figure are conceptually simple, compared with the physical description of processes that occur in plasma-based deposition systems. For that reason, the production of reproducible films and graded composition films by IBAD is straightforward.

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## Processing Equipment

**Laboratory.** Most of the IBAD systems that exist in government, industry, and university laboratories are designed for sample sizes with diameters less than 30 mm (1.2 in.). These facilities are able to perform depositions on a small scale for limited batch sizes.

One common means of fabricating an IBAD system is to utilize commercially available electron-beam-source "box coaters" that are capable of large-area, high-volume coating applications and then modify them to accept commercially available low-energy, high-current ion guns of various designs. Deposition rates are determined by the electron-beam-source evaporation rate and the required arrival ratio of ions to atoms for a particular coating. When the required arrival ratios are between 0.1 and 1.0, the maximum current of a Kaufman-type ion gun (~1 mA/cm$^2$) translates into deposition rates of about 40 to 4 µm/h (100 Å/s to 10 Å/s), respectively, for a system based on an electron beam source.

**Production.** Many applications require large areas to be coated. Linear ion guns are made with lengths up to 1000 mm (40 in.) and widths of 20 mm (0.8 in.), whereas circular-aperture ion guns have diameters ranging from 10 to 380 mm (0.4 to 15 in.). Systems that can handle workpieces with a 1 m (40 in.) diameter have been built. In nonoptical applications, where film uniformity is not as strict a requirement, very large areas could be coated using existing equipment by the routine manipulation of the workpieces.

Even larger surface areas can be handled by using continuous coating schemes. The primary obstacle to scale-up is the requirement of line-of-sight processing, especially for odd-shape parts. Cylinders can easily be coated, but it is not yet clear whether complex shapes, like gear teeth, can be uniformly and reliably coated. Figure 3(a) shows a scheme developed for the large-area, high-volume deposition of optical films, which could be adapted easily for sheet-metal applications (Ref 13). Figure 3(b) depicts a prototype large-area, high-volume system used for sheet steel (Ref 14), which will be discussed later.

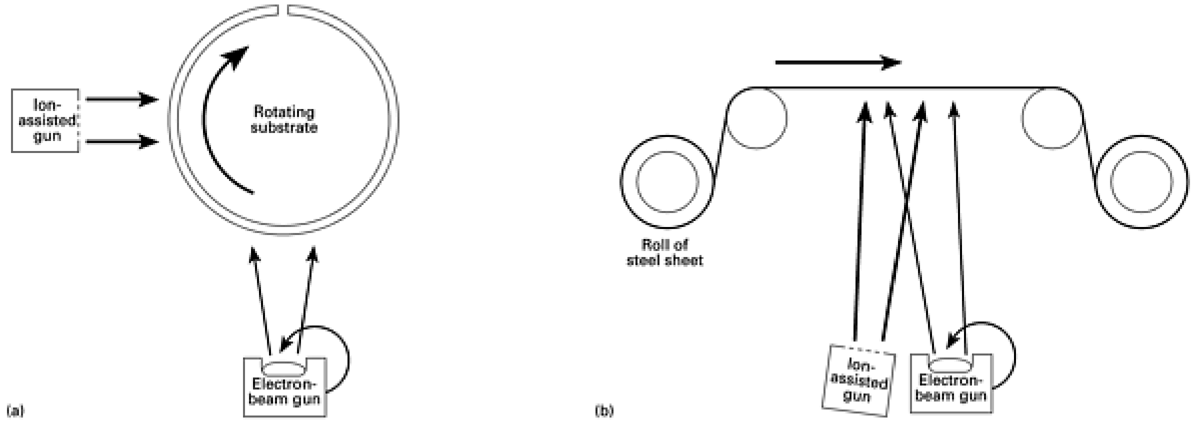

**Fig. 3 Two methods used for large-area, high-volume implementation of ion-beam-assisted-deposition. (a) For optical films. (b) For steel sheet**

Dual-ion-beam-assisted deposition (DIBS) systems, which utilize ion-beam sputter deposition, are also commercially available for use on substrates that are up to 120 mm (4.7 in.) in diameter. Some of these units are used for semiconductor applications, as well as for nonelectronic applications, such as the deposition of molybdenum disulfide films for friction reduction. In the case of sputter deposition, maximum deposition rates depend on the material to be deposited and are considerably less than for systems based on an electron beam. Ion-beam-sputtering systems are particularly suited to highly controlled, thin-film, multilayer coating applications, where up to six different sputtering targets can be sequentially moved into the sputter target position. High-quality, multilayer x-ray mirrors; laser mirrors; metallic multilayers; and other products have been manufactured using this method.

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## Processing Variables and Parameters

In general, there are three modes of IBAD. Several examples of the material systems that are deposited using each of the modes are given in Table 1. Mode 1 of this table identifies a simple type of ion assist, in which inert heavy ions, such as argon, are used to improve the properties of an elemental film or a compound film that undergoes congruent evaporation. In this case, it is important to minimize the amount of argon incorporated into the film, which increases with the arrival ratio, *R*, and the beam energy. Therefore, the lowest *R* value possible, consistent with obtaining the desired film properties, should be used. This mode also includes materials such as cerium oxide, which is typically slightly substoichiometric when simply deposited by evaporation. An ion assist with argon ions can be used for densification only, or oxygen ions can be used for densification and to restore stoichiometry.

**Table 1 Three modes of film formation for ion-beam-assisted deposition (IBAD)**

| **Vapor** | **Ion or ion/gas** | **Film** |
|---|---|---|
| **Mode 1: IBAD** | | |
| Ge | Ar | Ge |
| Ag | Ar | Ag |
| $CeO_2$ | O | $CeO_2$ |
| $Ta_2O_3$ | O | $Ta_2O_5$ |
| **Mode 2: IBAD (Compound synthesis)** | | |
| Si | N | $Si_3N_4$ |
| B | N | BN |
| Si | $CH_4$ | SiC |
| Cu | O | $Cu_2O$ |
| **Mode 3: Reactive IBAD** | | |
| Ti | N/N | TiN |
| Ti | Ar/N | TiN |
| Nb | N/N | NbN |
| Al | O/O | $Al_2O_3$ |

Ge, germanium; Ar, argon; Si, silicon; N, nitrogen; $Si_3N_4$, silicon nitride; TiN, titanium nitride; Ag, silver; B, boron; $CeO_2$, cerium oxide; O, oxygen; $CH_4$, methane; SiC, silicon carbide; Nb, niobium; $Ta_2O_3$, tantalum oxide; $Ta_2O_5$, tantalum pentoxide; Cu, copper; $Cu_2O$, copper oxide; Al, aluminum; $Al_2O_3$, aluminum oxide

Mode 2 in Table 1 identifies an ion assist and compound synthesis group, in which there is little reaction probability of the ambient gas with the evaporant. All of the material that forms the compound in this deposition mode comes from the evaporation source, as well as directly from the ion beam.

Mode 3 in Table 1 covers compound synthesis that is possible only for very reactive materials. It can occur either with the gas associated with the ion beam (e.g., $N_2$ for titanium nitride) or when inert ions such as argon are used in conjunction with a secondary (background) gas supply of $N_2$. In the latter case, the purpose of the ions is to activate and control surface chemical reactions.

Table 2 is a selected compilation of materials that have been grown using IBAD processes. For application to metals, the oxides and pure metals are often used as corrosion-resistant coatings, whereas nitrides and some oxides are used as wear-resistant and corrosion-resistant coatings. The widespread application of these coatings for nonelectronic purposes is still new, but there is some evidence that the appropriate thickness for hard coatings for sliding wear resistance is 0.2 to 2 μm (8 to 80 μin.), and that for pin-hole-free corrosion-resistant coatings, a minimum thickness of 2 μm (80 μin.) is required. For abrasion-resistant coatings, very thick and hard coats can be deposited, although this has not been emphasized in the initial development of the technique. Optical coatings up to 15 μm (215 μin.) thick also have been deposited. Typical process parameters are shown in Table 3.

**Table 2 Deposition and synthesis of inorganic compounds by ion-beam-assisted deposition (IBAD)**

| Material | Method | Evaporant | Ion | Energy, eV | *R* | Gas | Temperature | | Comments | Ref |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | °C | °F | | |
| $ZrO_2$ | IBAD | $ZrO_2$ | $Ar^+$ | 600 | 0.82 | . . . | 20, 300 | 70, 570 | . . . | 15 |
| $ZrO_2$ | IBAD | $ZrO_2$ | $Ar^+/O_2^+$ | 600/1200 | 0.33 | $O_2$ | 20, 300 | 70, 570 | Best films w/ $O_2^+$ cubic and monoclinic | 16 |
| $ZrO_2$ | IBAD | $ZrO_2$ | $O_2^+/O^+$ | 600/1200 | 0-10 | . . . | 25 | 75 | . . . | 17 |
| $ZrO_2$ | Reactive IBAD | $ZrO_2$ | $O_2^+$ | 1200 | . . . | $O_2$ | 275 | 525 | . . . | 18 |
| $TiO_2$ | Reactive IBAD | TiO, $TiO_2$ | $O_2^+$ | 0-100 | 0.3-0.6 | $O_2$ | 50-300 | 120-570 | . . . | 19, 20 |
| $TiO_2$ | Reactive IBAD | TiO | $O^-$ | . . . | . . . | $O_2$ | 25 | 75 | . . . | 21 |
| $TiO_2$ | Reactive IBAD | $Ti_2O_3$ | $O_2^+$ | . . . | . . . | . . . | . . . | . . . | Amorphous | 21 |
| $TiO_2$ | Reactive | TiO | $O^+$, $O_2^+$ | 30, 500 | 0-0.8 | $O_2$ | 50- | 120- | . . . | 22 |

| **Material** | **Method** | **Evaporant** | **Ion** | **Energy, eV** | ***R*** | **Gas** | **Temperature** | | **Comments** | **Ref** |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | **°C** | **°F** | | |
| | IBAD | | | | | | 100 | 210 | | |
| $TiO_2$ | Reactive IBAD | TiO, $TiO_2$ | $O_2^+$ | 30, 500 | 0-1.3 | $O_2$ | 50-100 | 120-210 | . . . | 23, 24 |
| $TiO_2$ | Reactive IBAD | TiO | $O_2^+$ | 600 | 0.3-0.9 | $O_2$ | 25 | 75 | . . . | 25 |
| $TiO_2$ | Reactive IBAD | $TiO_2$ | $O_2^+$ | 300 | 0.1-0.4 | $O_2$ | 175 | 345 | Optimum $R = 0.2$ | 26 |
| $SiO_2$ | Reactive IBAD | SiO | $O^-$ | . . . | . . . | $O_2$ | 290 | 555 | . . . | 21 |
| $SiO_2$ | Reactive IBAD | SiO | $Ar^+$ | 600 | 0.03 | $O_2$ | 25 | 75 | . . . | 25 |
| $SiO_2$ | Reactive IBAD | SiO | $O^+$, $O_2^+$ | 300, 500 | 0.25-1.7 | $O_2$ | 50-100, 275 | 120-210, 525 | Not sensitive to IBAD conditions | 18, 22 |
| $Al_2O_3$ | Reactive IBAD | $Al_2O_3$ | $O_2^+$ | 300-1000 | 0.08-0.8 | $O_2$ | 275 | 525 | Optimum $R = 0.2$ at 1000 eV | 18 |
| $Al_2O_3$ | Reactive IBAD | $Al_2O_3$ | $O_2^+$ | 300 | 1.33 | $O_2$ | 125 | 255 | . . . | 27 |
| $Al_2O_3$ | Reactive IBAD | $Al_2O_3$ | $O_2^+$ | 1200 | 0.6 | $O_2$ | 20, 300 | 70, 570 | . . . | 28 |
| $Al_2O_3$ | Reactive IBAD | Al | $O_2^+$ | 500 | 0.16 | $O_2$ | 25 | 75 | . . . | 29 |
| $CeO_2$ | Reactive IBAD | $CeO_2$ | $O_2^+$ | 300, 600, 1200 | 1.9 | $O_2$ | 20, 300 | 70, 570 | . . . | 30 |
| $CeO_2$ | Reactive IBAD | $CeO_2$ | $O_2^+$ | 1200 | 0.84 | $O_2$ | 20, 300 | 70, 570 | . . . | 31 |
| $HfO_2$ | Reactive IBAD | $HfO_2$ | $O_2^+$ | 300 | 0.25 | $O_2$ | 300 | 570 | . . . | 32 |
| $Ta_2O_5$ | Reactive | $Ta_2O_5$ | $O_2^+$ | 1200 | 2.6 | $O_2$ | 300 | 570 | . . . | 31 |

| **Material** | **Method** | **Evaporant** | **Ion** | **Energy, eV** | ***R*** | **Gas** | **Temperature** | | **Comments** | **Ref** |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | **°C** | **°F** | | |
| | IBAD | | | | | | | | | |
| $Ta_2O_5$ | Reactive IBAD | $Ta_2O_5$ | $O_2^+$ | 300-1000 | 0.08-1.4 | $O_2$ | 275 | 525 | Optimum $R = 0.6$ at 300 eV | 18 |
| $Ta_2O_5$ | Reactive IBAD | $Ta_2O_5$ | $O_2^+$ | 300 | 2.8 | $O_2$ | 125 | 255 | . . . | 27 |
| $VO_2$ | IBAD | V | $O_2^+$ | 600 | . . . | . . . | 800-600 | 175-1110 | . . . | 32 |
| $MgF_2$ | IBAD | $MgF_2$ | $Ar^+$ | 125-1000 | 0.04 | . . . | 25 | 75 | High *E*-preferential sputtering of F | 33 |
| $MgF_2$ | Reactive IBAD | $MgF_2$ | Freon ($C_2F_6$) | 80-1400 | 0.05-0.1 | $C_2F_6$ | 25 | 75 | Low *E* best | 34, 35 |
| $MgF_2$ | IBAD | $MgF_2$ | $O_2^+$ | 350-750 | 0.12-0.25 | $O_2$ | 20, 300 | 70, 570 | Crystalline | 36 |
| $MgF_2$ | IBAD | $MgF_2$ | $Ar^+$, $O_2^+$ | 300 | 0.3-0.34 | . . . | 25 | 75 | . . . | 37 |
| $LaF_3$ | IBAD | $LaF_3$ | $Ar^+$, $O_2^+$ | 300, 500 | 0.22-0.57 | . . . | 25 | 75 | $R = 0.05$, $O_2^+$ optimum | 37, 38 |
| Cryolite | IBAD | $Na_3AlF_6$ | $Ar^+$, $O_2^+$ | 200, 300 | 0.25-0.75 | . . . | 25 | 75 | $R = 0.75$ at 300 eV $O_2^+$ optimum | 37 |
| $ThF_4$ | IBAD | $ThF_4$ | $Ar^+$ | 300 | 0.05-0.35 | . . . | 25 | 75 | . . . | 39 |
| $Si_3N_4$ | Dual-ion-beam sputter | Si | $N^+$, $N_2^+$ | 680 | 2.05 | $N_2$ | <200 | <390 | Partially amorphous | 40, 41 |
| $Si_3N_4$ | Reactive IBAD | Si | $N_2^+$ | 60, 100 | 2.1 | $N_2$ | 25 | 75 | . . . | 42 |
| $Si_3N_4$ | IBAD | Si | $N_2^+$ | 500 | 0-1.33 | . . . | 25 | 75 | Corrosion protection, optical properties | 43, 44 |

| **Material** | **Method** | **Evaporant** | **Ion** | **Energy, eV** | ***R*** | **Gas** | **Temperature** | | **Comments** | **Ref** |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | **°C** | **°F** | | |
| $Si_3N_4$ | IBAD | Si | $N_2^+$ | 20,000-100,000 | 0-1 | . . . | <200 | <390 | Oxidation protection | 45 |
| $Si_3N_4$ | IBAD | Si | $N_2^+$ | 100 | 0-1.3 | . . . | <100 | <210 | Multilayer x-ray mirrors | 46 |
| $Si_3N_4$ | IBAD | Si | N | 500-1000 | 0-1.4 | $N_2$ | <100 | <210 | Process characterization | 4, 5 |
| $Si_{(1-x)}N_x$ | Reactive IBAD | Si | $N_2^+$ | 1000 | 0-1.3 | $N_2$ | <70 | <160 | Amorphous films | 47 |
| SiON | IBAD | Si | $O_2^+$, $N_2^+$ | 3000 | . . . | . . . | 300 | 570 | . . . | 41 |
| SiNH | IBAD | Si | $NH_3$ | 500 | 0-1.4 | $NH_3$ | <100 | <210 | Optical films | 48 |
| AlN | Dual-ion-beam sputter | Al | $N_2^+$ | 100-500 | 0-2.6 | $N_2$ | 25 | 75 | AlN at $R$ = 1 | 6 |
| AlN | IBAD | Al | $N_2^+$ | 200-1000 | 0.5 | N | 100 | 210 | Oriented films | 49 |
| AlN | Reactive IBAD | Al | $N_2^+$ | 250-1000 | 0.5-2.7 | $N_2$ | 100 | 210 | . . . | 50 |
| AlN | IBAD | Al | $N_2^+$ | 75, 500 | 1.05, 1.7, 3.4 | . . . | 25 | 75 | . . . | 29 |
| AlON | Reactive IBAD | Al | $N_2^+$ | 750 | 0.7-1.0 | $O_2$ | 100 | 210 | . . . | 51 |
| AlON | IBAD | AlN | $O_2^+$, $N_2^+$ | 300 | . . . | . . . | 300 | 570 | . . . | 41 |
| TiN | Reactive IBAD | Ti | $Ti^+$, $N^+$ | 30/40,000 | 0.001-0.6 | $N_2$ | 25-700 | 75-1290 | . . . | 52 |
| TiN | Reactive IBAD | Ti | N | 12,000 | . . . | $N_2$ | . . . | . . . | Structure | 53 |
| TiN | Reactive IBAD | Ti | $N_2^+$ | 5000 | 0-1 | $N_2$ | . . . | . . . | . . . | 54 |

| **Material** | **Method** | **Evaporant** | **Ion** | **Energy, eV** | ***R*** | **Gas** | **Temperature** | | **Comments** | **Ref** |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | **°C** | **°F** | | |
| TiN | Reactive IBAD | Ti | $N_2^+$ | 1000 | 0.01-0.03 | $N_2$ | . . . | . . . | . . . | 55 |
| TiN | Reactive IBAD | Ti | $N_2^+$ | 10-30,000 | 1.0 | $N_2$ | 300 | 570 | . . . | 56 |
| TiN | Reactive IBAD | Ti | $N^+$, $N_2^+$ | 20,000 | 1.0 | $N_2$ | 35 | 95 | . . . | 57 |
| TiN | Bias magnetron | Ti | $Ar^+$ + $N_2^+$ | 2-200 | 0.4-1.0 | $N_2$ | 300-600 | 570-1110 | . . . | 51 |
| TiN | Dual-ion-beam sputter | Ti | $N_2^+$ | 200 | 0.25 | $N_2$ | 400 | 750 | $Ti_3N_4$ forms with excess N | 58 |
| TiN | IBAD | Ti | $N_2^+$ | 30,000 | 0.12-0.77 | . . . | 100-300 | 210-570 | . . . | 59 |
| TiN | Reactive IBAD | Ti | $N_2^+$ | 500 | 0-1.1 | $N_2$ | 25 | 75 | Process parameters | 44 |
| TiN | Reactive IBAD | Ti | $Ar^+$ | 12,000 | 1 | $N_2$ | <250 | <480 | Comparison with other techniques | 60, 61 |
| TiN | Ion plating | Ti | $N^+$ + $N^+$ | 200 | . . . | $N_2$ | <100 | <210 | Batch processing of sheet metal | 14 |
| TiN | IBAD | Ti | $N^+$ | 20,000 | 0.37-1.1 | . . . | . . . | . . . | . . . | 62 |
| TiN | IBAD | Ti | $N^+$ + $N_2^+$ | 20,000 | 1.0 | . . . | 200-300 | 390-570 | Extensive data | 63 |
| TiN | Reactive IBAD | Ti | $N_2^+$ | 40,000 | 0-0.3 | $N_2$ | <100 | <210 | Oriented films | 64 |
| TiN | Reactive bias magnetron | Ti | $N_2^+$ | 300-500 | 4.1 | . . . | 550-850 | 1020-1560 | Single crystal, epitaxial | 65 |
| CrN | IBAD | Cr | $N_2^+$ | 20,000 | 0.5-2 | $N_2$ | . . . | . . . | Oriented films | 66 |

| **Material** | **Method** | **Evaporant** | **Ion** | **Energy, eV** | ***R*** | **Gas** | **Temperature** | | **Comments** | **Ref** |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | **°C** | **°F** | | |
| CrN | IBAD | Cr | $N_2^+$ | 12,000 | $10^{-4}$-0.1 | . . . | 25 | 75 | High hardness | 9 |
| BN | Reactive IBAD | B | $N_2^+$ | 25-40,000 | 0.7 | $N_2$ | 200 | 390 | Some cubic BN | 67 |
| BN | IBAD | B | $N_2^+$ | 120,000 | . . . | . . . | 300 | 570 | Ion-beam mixing | 68 |
| BN | IBAD | B | $N_2^+$ + $N^+$ | 200-1000 | 1.0 | . . . | . . . | . . . | . . . | 69 |
| BN | IBAD | B | $N_2^+$ | 80-500 | 1.0-2.0 | . . . | 280-300 | 535-570 | . . . | 70 |
| BN | IBAD | B | $N_2^+$ | 500 | 2.55 | . . . | 200 | 390 | . . . | 71 |
| BN | IBAD | B | $N_2^+$ | 200 | 1 | . . . | 300 | 570 | Cubic BN | 72 |
| BN | IBAD | B | $N_2^+$ | 250-2000 | 0-1.5 | . . . | 25 | 75 | Hardness, stress | 73 |
| BN | IBAD | B | $N_2^+$ | 2000-20,000 | . . . | $N_2$ | . . . | . . . | Cubic BN | 74 |
| TiC | IBAD | Ti, C | $Ar^+$ | 100,000 | 0.01 | . . . | 25 | 75 | *R*=Ar/Ti ratio | 75 |
| TiC | Ion plating | TiC | $Ar^+$ | 200 | . . . | . . . | <100 | <210 | Batch processing of sheet metal | 14 |
| ZrN | Dual-ion-beam sputter | Zr | $N_2^+$ | 200 | 0.25 | . . . | 400 | 750 | . . . | 58 |
| ZrN | Reactive IBAD | Zr | $N_2^+$ | 200-700 | . . . | $N_2$ | 25 | 75 | Coated shaver screens | 76 |
| ZrN | Reactive IBAD | Zr | $N_2^+$ | 30,000 | 1 | $N_2$ | <300 | <570 | Chemistry, microstructure | 77 |
| HfN | Dual-ion-beam sputter | Hf | $N_2^+$ | 200 | 0.25 | . . . | 400 | 750 | $Hf_3N_4$ also formed | 58 |

| **Material** | **Method** | **Evaporant** | **Ion** | **Energy, eV** | ***R*** | **Gas** | **Temperature** | | **Comments** | **Ref** |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | **°C** | **°F** | | |
| MoN | Reactive IBAD | Mo | $N^+$, $N_2^+$ | 40,000 | 1.0 | $N_2$ | 25-500 | 75-930 | B1 structure for 25 °C (77 °F) | 78 |
| MoN | IBAD | Mo | $N_2^+$ | 500-1000 | 0-1.2 | $N_2$ | <100 | <210 | Pure phases | 79 |
| $NbN_xC_y$ | Dual-ion-beam sputter | Nb | $N_2^+$ +$CH_4$ | 50-100 | . . . | $N_2$+$CH_4$ | <60 | <140 | . . . | 80 |
| InSnO | Reactive IBAD | $In_2O_3$-$9SnO_2$ | $O_2^+$ | 100 | 1.0 | $O_2$ | 25-400 | 75-750 | Amorphous <100 | 81 |
| InSnO | Reactive IBAD | InSnO | $O_2^+$ | 1200 | 0.7-1.0 | $O_2$ | 50-150 | 120-300 | . . . | 82 |
| $WSi_2$ | IBAD | W, Si | $Ar^+$ | 100-400 | 0.05-0.25 | . . . | 25-500 | 75-930 | Amorphous at room temperature | 83 |
| CuO | IBAD | Cu | $O_2^+$ | <200 | 0.01-0.1 | $O_2$ | 25 | 75 | Formed $Cu_2O$, CuO, $Cu_5O_4$ | 84 |
| YBaCuO | Reactive IBAD | $YBa_2Cu_4O_x$ | $Ar^+$ + $2O_2^+$ | 50 | . . . | $O_2$ | 560-640 | 1040-1180 | . . . | 85 |
| YBaCuO | IBAD | $BaF_2$, Cu, Y | $O^+$, $O_2^+$ | 50 | . . . | . . . | 600 | 1110 | Single-crystal epitaxial films | 86 |
| $MoS_2$ | Dual-ion-beam sputter | $MoS_2$ | $Ar^+$ | 1000 | 0.01-0.1 | . . . | 25 | 75 | Low friction | 87 |
| DLC | IBAD | C | $Ar^+$, $Ne^+$ | 200-1000 | 0.05-0.7 | . . . | <100 | <210 | . . . | 88 |
| DLC | Ion-beam sputter | C | Ar | 1200 | . . . | $H_2$ | 25 | 75 | Few diamond crystals in amorphous C | 89 |
| DLC | Ion-beam deposition | . . . | $C^+$ | 10-175 | . . . | . . . | <400 | <750 | . . . | 90, 91 |
| DLC | Ion-beam deposition | . . . | $CH_4$ | 100-1200 | . . . | $CH_4$ | 25 | 75 | Deposition rates microstructure | 92 |

| **Material** | **Method** | **Evaporant** | **Ion** | **Energy, eV** | ***R*** | **Gas** | **Temperature** | | **Comments** | **Ref** |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | **°C** | **°F** | | |
| DLC | Ion-beam deposition | . . . | $CH_4$ | 500-1000 | . . . | $CH_4$ | 25 | 75 | Composition, applications | 93 |
| B | IBAD | B | $Ar^+$ | 6000 | . . . | . . . | 25 | 75 | Low stress | 94 |
| B | IBAD | B | $Ar^+$ | 6000 | $10^{-4}$-0.1 | . . . | 25 | 75 | Corrosion protection, adhesion | 9 |
| B | IBAD | B | $Ar^+$ | 3000-15,000 | 0-0.1 | . . . | . . . | . . . | Stress control | 95 |
| C | Ion-beam deposition | . . . | $C^+$ | 5-200 | . . . | . . . | 25 | 75 | X-ray mirrors | 96 |
| C | IBAD | C | $Ar^+$ | . . . | . . . | . . . | . . . | . . . | Densification | 97 |
| Al | IBAD | Al | He, Ne, Ar, Kr, Xe | 200-20,000 | 0-0.3 | . . . | . . . | . . . | Thorough study | 98 |
| Al | IBAD | Al | $Ar^+$ | 50-2000 | 0.001-0.1 | . . . | 25 | 75 | Oriented films | 99 |
| Si | Ion-beam deposition | . . . | $Si^+$ | 5-200 | . . . | . . . | 25 | 75 | X-ray mirrors | 96 |
| Cr | IBAD | Cr | $Ar^+$ | 3000-15,000 | 0-0.1 | . . . | . . . | . . . | Stress control | 95 |
| Cr | IBAD | Cr | $N_2^+$ | 60,000 | 0.1 | . . . | . . . | . . . | Turbine blade coatings | 100 |
| Cr | IBAD | Cr | $Ar^+$ | 11,500 | . . . | . . . | 25 | 75 | Low stress | 8 |
| Cr | IBAD | Cr | $Ar^+$ | 6000 | . . . | . . . | 25 | 75 | Low stress | 94 |
| Cr | IBAD | Cr | $Ar^+$ | 60-800 | 0-1.5 | . . . | 25 | 75 | Stress, resistivity | 101, 102 |
| Fe | IBAD | Fe | $Ar^+$ | 60-800 | 0-1.5 | . . . | 25 | 75 | Stress, resistivity | 101, 102 |

| **Material** | **Method** | **Evaporant** | **Ion** | **Energy, eV** | ***R*** | **Gas** | **Temperature** | | **Comments** | **Ref** |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | **°C** | **°F** | | |
| Permalloy | IBAD | Fe-Ni | $Ar^+$ | 300 | . . . | . . . | . . . | . . . | Low stress | 103 |
| Co | IBAD | Co | $Ar^+$ | 60-800 | 0-1.5 | . . . | 25 | 75 | Stress, resistivity | 101, 102 |
| Ni | IBAD | Ni | $Ar^+$ | 60-800 | 0-1.5 | . . . | 25 | 75 | Stress, resistivity | 101, 102 |
| Ni | Ion-beam deposition | . . . | $Ni^+$ | 5-200 | . . . | . . . | 30 | 85 | X-ray mirrors | 96 |
| Cu | IBAD | Cu | $Ar^+$ | 60-800 | 0-1.5 | . . . | 25 | 75 | Stress, resistivity | 101, 102 |
| Cu | IBAD | Cu | $Ar^+$ | . . . | . . . | . . . | . . . | . . . | On polytetrafluoroethylene | 104 |
| Cu | IBAD | Cu | $Ar^+$ | . . . | . . . | . . . | . . . | . . . | . . . | 105 |
| Nb | IBAD | Nb | $Ar^+$ | 60-800 | 0-1.5 | . . . | 25 | 75 | Stress, resistivity | 101, 102 |
| Ag | IBAD | Ag | $Ar^+$ | . . . | . . . | . . . | . . . | . . . | On polytetrafluoroethylene | 104 |
| Ag | IBAD | Ag | $Ar^+$ | . . . | . . . | . . . | . . . | . . . | . . . | 106 |
| Ta | IBAD | Ta | $Ar^+$ | 60-800 | 0-1.5 | . . . | 25 | 75 | Stress, resistivity | 101, 102 |
| W | Ion-beam deposition | . . . | $W^+$ | 5-200 | . . . | . . . | 25 | 75 | X-ray mirrors | 96 |
| W | IBAD | W | $Ar^+$ | 60-800 | 0-1.5 | . . . | 25 | 75 | Stress, resistivity | 101, 102 |
| Au | IBAD | Au | $Ar^+$ | . . . | . . . | . . . | . . . | . . . | On polytetrafluoroethylene | 104 |
| Au | IBAD | Au | $Ar^+$ | . . . | . . . | . . . | . . . | . . . | On glass | 107 |

| Material | Method | Evaporant | Ion | Energy, eV | *R* | Gas | Temperature | | Comments | Ref |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | °C | °F | | |
| Au | IBAD | Au | Ar$^+$ | . . . | . . . | . . . | . . . | . . . | On glass | 94 |
| Au | IBAD | Au | Ar$^+$ | 300 | 0-1 | . . . | 25-250 | 77-480 | Good adhesion | 108 |

Source: Ref 1

**Table 3 Typical values of ion-beam-assisted deposition process variables**

| Variable | Value |
|---|---|
| Vapor deposition rate, μm/h (μin./h) | 1-40 (40-1600) |
| Chamber base pressure, Pa (torr) | 226 × 10$^{-7}$ (2 × 10$^{-7}$) |
| Operating pressure, Pa (torr) (with backfill gas), Pa (torr) | 0.003 to 0.03 (2 × 10$^{-5}$ to 2 × 10$^{-4}$)<br>0.007 to 0.03 (5 × 10$^{-5}$ to 2 × 10$^{-4}$) |
| Ion current, mA/cm$^2$ (mA/in.$^2$)<br>Fraction-exchange neutralized | 0.1-2 (0.6-13)<br>0.05-0.40 |
| Arrival ratio | 0.1-1.5 |
| Substrate temperature, °C (°F) | <100 (<210) |

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## Coating Properties

**Adhesion.** Because an ion gun is available in an IBAD system, substrates are normally sputter cleaned prior to deposition. This promotes improved bond formation between the substrate and the film. However, there are additional benefits from bombardment during deposition. One is that the surface is sputter cleaned of contaminants at the same time the substrate is exposed to the fluxes and is continuously cleaned during deposition. Another benefit is that there is atom movement across the interface caused by ballistic collisions such that film atoms are driven a few atomic layers into the substrate and substrate atoms are mixed into the film. This promotes the completion of interfacial bonding and also produces a robust, nonabrupt interface several atomic layers thick. The adhesive strength of these IBAD interfaces is typically 10 to 100 times higher than for the same films deposited at thermal energies with an electron beam or other PVD source without ion assistance. This bonding is enhanced for coating/substrate systems exhibiting high atomic miscibility.

Some of the systems that show adhesion improvement when deposited by IBAD are gold on copper (Ref 107), gold and silicon on glass (Ref 94), aluminum on iron (Ref 8), titanium nitride on steel (Ref 52), and copper, silver, and gold on polytetrafluoroethylene (Ref 104). Many more combinations have yet to be investigated. An excellent review (Ref 109) of the adhesion improvement of films by post-deposition bombardment gives further insight into the mechanisms of adhesion enhancement.

**Stress.** Most deposited thin films retain a residual compressive or tensile stress that limits the thickness that can be deposited. The accumulated stress either ruptures the interface bonds, causing delamination, or exceeds the cohesive forces of the material, causing film disintegration. Studies have shown that in most cases, a judicious combination of ion-bombardment parameters and substrate temperature can be chosen that will produce very small residual stresses in the coating. Therefore, conditions can normally be found where there are no thickness limitations to applications of IBAD coatings. This is a very important property for industrial applications.

Examples of low-stress films deposited by IBAD include chromium on glass by 11.5 keV argon bombardment (Ref 8), tungsten on silicon by 400 eV argon bombardment (Ref 101), boron and chromium on iron by 6 keV argon bombardment (Ref 94), and permalloy (iron-nickel) films on polypyromelitimide using 300 eV argon bombardment (Ref 103).

**Density.** An extremely important practical attribute of IBAD is the increase in film density, when compared with PVD films deposited without the aid of energetic ions. Such PVD films typically contain voids or columnar structures that produce a 10 to 20% density deficit relative to the bulk material. This is especially true for covalently bonded semiconductors and refractory metals. It is well established that the energetic ion beam applied to the film in the IBAD process can eliminate the voids and produce essentially bulk-density films. The mechanism for this densification is related to atomic displacements in the collision cascades, enhanced surface and bulk diffusion, recoil implantation, and ion mixing mechanisms (Ref 1, 2, 3).

Information on the densification of metal films is sparse and gives a mixed picture of whether or not IBAD causes densification. Gold films were found to be more dense (Ref 107), as were carbon films (Ref 97), but copper (Ref 105) and silver (Ref 106) films were found to be less dense. There is ample evidence for densification with semiconductors and oxides. The energy dependence for densification was studied for argon ions from 65 eV to 3 keV, and it was found that an arrival ratio of 0.1 at the low-energy level or 0.0003 at the high-energy level produced bulk-density germanium films (Ref 3, 110). For zirconium oxide films, IBAD using oxygen or argon ions produced nearly bulk-density films, when compared with evaporated films (Ref 16). In general, densification is found to occur in films deposited with an ion assist.

**Microstructure.** The effects of ion beams on the microstructure of films are numerous and complicated. For this reason, only some general observations are noted here. Most covalently bonded materials, such as semiconductors and silicon nitride or silicon carbide ceramics, are amorphous when deposited at room temperature. Silicon and germanium will be crystalline above the temperature of approximately 0.4 $T_m$, which is the melting temperature in degrees kelvin. Using IBAD, this characteristic temperature for achieving crystallinity can be lowered by approximately 200 K, because the atomic motion induced by the energetic atoms serves the same purpose as high substrate temperature (Ref 111).

Metals and ionic materials tend to be polycrystalline. In general, the ion beam decreases the grain size at low temperatures, but can increase it at higher temperatures, where annealing effects overcome the damage caused by the ion beam (Ref 102). The general observation that IBAD films are more ductile than bulk materials that usually contain larger grains has been attributed to this smaller grain size.

The orientation of films can be altered such that textured films are commonplace. The degree of texturing depends on beam angle, beam energy, beam flux, and substrate temperature (Ref 49). At high ion/atom ratios, the texture is such that the most loosely packed planes, which are favorable for ion channeling, are parallel to the ion-beam direction. At low ion/atom ratios, forward scattering of film atoms causes a close-packed fiber texture in the film plane for near-normal ion incidence (Ref 112). In some cases, epitaxial films can be induced to grow with an ion assist where they would not in the absence of ions. Examples include copper and aluminum on silicon (Ref 113, 114).

**Morphology.** In general, IBAD films are very smooth. If the substrate is initially atomically smooth, then processing conditions can be found for most coating materials that produce a remarkably small deterioration in smoothness. For very rough surfaces, the line-of-sight coverage means that there may be shadowing effects where part of the surface is not covered. This would render an anticorrosion coating useless, but it is not necessarily detrimental to antiwear coatings. For substrates of intermediate roughness, IBAD coatings tend to produce a smoother surface. In some rare cases and with specific processing parameters, the surface is roughened by an IBAD film, usually for low-melting-point metal films.

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## Advantages and Limitations

The IBAD process is a hybrid of PVD and ion implantation. It combines the advantages of both techniques, while eliminating most of the disadvantages of each. Table 4 lists the advantages and limitations of IBAD.

**Table 4 Advantages and limitations of ion-beam-assisted deposition**

| **Advantages, achievable benefits** |
|---|
| Low deposition temperature |
| High adhesion |

| |
|---|
| Control of stress level |
| Bulk density achievable |
| Control of microstructure (nanocrystalline; metastable crystalline or amorphous; textured; and epitaxial, for some materials) |
| Reproducible |
| Precise modulation of composition with depth |
| Highly versatile for metals, ceramics, semiconductors, dielectrics |
| **Limitations** |
| Moderately higher cost than physical vapor deposition |
| Line-of-sight processing |
| Technology in commercial infancy (limited vendors) |

Even polymers with low melting points can be coated, because the deposition temperature can be maintained between room temperature and nearly 100 °C (210 °F). The properties of adhesion, stress, and density are superior to those of PVD films, and there is a high degree of control over the microstructure. Depending on the deposition parameters, films can be deposited as:

- Nanocrystalline
- Amorphous
- Textured crystalline or epitaxial (for some materials)
- Metastable crystalline

Finally, the composition, or crystalline phases, can be precisely modulated as a function of thickness to produce functionally gradient materials with properties such as graded hardness, coefficient of thermal expansion, refractive index, density, tensile strength, and stress.

## Applications

In order to place IBAD processing in the proper context with respect to potential applications, examples of current and projected IBAD uses are described below. Applications are discussed in the areas of optical films, oxidation- and corrosion-protection coatings, and tribological coatings. Applications are quite extensive in the optical thin-film industry, where the primary advantage offered by IBAD is film densification. Refractive index stability and freedom from environmental degradation are thus direct benefits of using the IBAD process in these applications. Research in the area of wear- and corrosion-resistant coatings for metals and ceramics is in an early development stage.

Films deposited using dry, benign, energetic deposition techniques are also attractive for replacing wet electrochemical processes, such as chromium and cadmium plating, that can pollute the environment. As a result of research already conducted, corrosion and wear problems involving planar and cylindrical geometries of parts less than 1 m (40 in.) in size can already be addressed technically using these energetic-deposition techniques. The issue that needs further attention, then, is how each technique and the economics thereof relates to the scale-up of specific applications and associated geometries.

**Optical Films.** As already stated, the IBAD process was promoted earliest by those workers interested in optical thin films. This involved, in turn, two kinds of applications: those in which densification is the primary concern and those in which graded refractive index profiles are required.

For applications involving densification, low-energy argon or oxygen ions are typically used to bombard the optical thin films during deposition (Ref 16). As a result, the density is increased, sometimes up to that of the bulk material. The primary attraction is not necessarily that the refractive index is increased to near-bulk values, but that the index value is stable under humidity and temperature variations, because there are no voids or pores in the film that adsorb water vapor. This simplifies optical-coating design and promotes better control and reproducibility in the fabrication process. Another benefit of using low-energy ions is that adhesion to the substrate is improved, which also helps to increase production yields.

The IBAD process is just starting to be used to fabricate graded index coatings for antireflection coatings, reflection filters, and mirrors (Ref 115). Some of these devices can be tens of microns thick, which means that stress control becomes very important. In general, low energies are desired for the deposition of optical films to reduce absorption caused by radiation damage.

**Ion-Beam Deposition.** Several groups are depositing diamond-like carbon (DLC) by either direct ion-beam deposition or sputter deposition of carbon in the presence of ion bombardment (Ref 90). Using a Kaufman-type ion source, methane is introduced into the plasma and, at energies between 100 and 1000 eV, DLC is deposited at rates between 0.1 and 1 nm/s (1 and 10 Å/s). Applications include hard, protective coatings for optics and windscreens on vehicles. Although DLC absorbs strongly in the visible range, coatings that are between 20 and 200 nm (200 and 2000 Å) in thickness remain transparent enough to be used as protective transmission coatings. As of 1994, commercial sources are available to produce these coatings over reasonably large areas (200 mm, or 8 in., in diameter). The advantages of these coatings include low porosity, high scratch hardness, and high adhesion to most substrates.

**Aqueous Corrosion.** The first industrial application of IBAD for purposes of wear or corrosion resistance appears to be the coating of electric razor screens with titanium nitride (Ref 7). In this case, the choice of IBAD processing was dictated by both the superior adhesion of the films and a decreased number of pin holes, combined with low-temperature deposition on 316 stainless steel substrates. Because IBAD films are dense and have few pin holes, they are attractive for corrosion-protection applications.

Only a limited number of studies on the corrosion behavior of IBAD coatings have been made, but the early results look promising. Platinum, titanium carbide, titanium nitride, boron, diamond-like carbon, chromium nitride, boron nitride, chromium oxide, silicon nitride, and silicon coated on metals using the IBAD process provide excellent corrosion resistance (Ref 7, 8, 9, 43, 45, 116).

One company (Ref 13) has set up a processing line that coats steel sheet continuously with aluminum, titanium nitride, or aluminum oxide for decorative panel applications. Figure 3(b) depicts the apparatus. Part of the cost of the process is recovered by the use of inexpensive steel substrate and coating materials. The resulting films are adherent and more ductile than bulk materials, because of the microcrystalline or amorphous structures. Therefore, they can yield with the metal sheet so that some working of the metal should be possible after the coating is applied.

**High-Temperature Oxidation.** Work on achieving oxidation protection with IBAD coatings is also very new. Only a few results are in the literature describing the use of chromium nitride (Ref 100), titanium nitride (Ref 100), and silicon nitride (Ref 76) to protect titanium alloys. This seems to be a promising area for further research.

**Ion-Induced Chemical Vapor Deposition (CVD).** Several researchers have used reactive IBAD (mode 3 of Table 1) to produce unique hydrocarbon or ceramic films (Ref 117). In this process, a gas is introduced into the chamber, the substrate is cooled to induce condensation of the gas, and an ion beam strikes the surface. During the process, hydrocarbon bonds are broken, volatile species are released, and a coating is produced. For silicone oil vapor, the films can range from very low friction solid lubricants to very hard, corrosion-resistant silicon oxycarbide ($SiO_xC_y$) coatings, depending on the arrival ratio of ions to vapor-condensed atoms. This process is similar to CVD, in which the high temperature of the substrate provides the energy to initiate chemical reactions that are responsible for film formation. In the ion-beam case, the same or similar reactions can be beam-induced at room temperature, opening the possibility of depositing CVD-like films on polymers and other temperature-sensitive substrates.

**Friction and Wear.** The IBAD process is being used to deposit solid-lubricant coatings, such as molybdenum disulfide. Advantages are that the coatings adhere to the substrate and have a longer lifetime as a result of densification (better coherence) (Ref 87, 118).

Hard coatings, such as titanium nitride, are by far the most extensively studied (Ref 1). The hardness of these coatings can be varied over a large range by microstructure control (Ref 55). The ductility of these films, even for the highest hardness, is much larger than that for bulk material or CVD titanium nitride films. Boron nitride is also a coating that is readily deposited by IBAD and has good wear characteristics (Ref 119). The IBAD technique is the only one, as of 1994, that is capable of depositing cubic boron nitride that is theoretically as hard as diamond (Ref 72). Currently, molybdenum disulfide, titanium nitride, and ion-stimulated CVD of silicone are the most developed materials for tribological applications.

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## Future Trends

As a surface modification technique, IBAD is attractive because it retains the best features of PVD and ion implantation and eliminates the worst features. The application of IBAD films as wear- and corrosion-resistant coatings for metals and ceramics is just beginning. Because relatively thick coatings (i.e., many microns) of controlled composition and stress are achievable, it is expected that IBAD processing will be accepted into those application areas that currently use conventional PVD techniques without ion assistance.

## Health and Safety

There are no special health concerns associated with these techniques. The considerations are identical to those for conventional electron-beam evaporation sources and sputtering targets. The techniques involve very little solid waste of benign elemental materials.

# Arc Deposition

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## Introduction

THE VACUUM ARC is a form of electrical discharge that is sustained primarily on the electrons and ions that originate from the electrodes used to produce the arc. The value of using vacuum arc deposition to produce coatings stems from the copious quantity of ions of electrode material composition that are generated during the discharge. Because the output of the vacuum arc is highly ionized, it is possible to control both the trajectory of the coating material during its transit from source to part and the energy with which ions impinge on that part. This level of control can be contrasted to competing vacuum coating technologies, such as electron-beam evaporation and magnetron sputtering, where the atoms of coating material travel from the source to the part to be coated in an electrically neutral state.

Adjusting the deposition energy can produce coatings that have greater density, purity, and adhesion. Under favorable circumstances, the quenching of ions can produce coatings with structures that have unusual properties, such as the extremely hard and smooth amorphous diamond coatings that will be described in this article. Although the use of ion trajectory control to improve coating properties has not been extensively explored, it has been used to overcome the major drawback of the cold cathodic arc process: the production of micron-scale particles of electrode material, or macroparticles. Macroparticle formation and the approaches used for removal are described in Ref 1, 2, and 3.

Due to the ion charge state, vapor produced by vacuum arc techniques is typically more reactive than that produced using evaporative or sputter techniques. This increased reactivity can lead to compound coatings in which better stoichiometry is produced when deposition occurs in the presence of a reactive gas. For instance, when compared with electron-beam evaporation and magnetron sputtering, the cathodic arc can produce stoichiometric titanium nitride over a much wider range of nitrogen partial pressures (Ref 4). This can be particularly important when depositing compound coatings on complex shapes.

The most widely used type of vacuum arc is a cathodic arc with a cooled cathode. Because the source material remains solid, it can operate in any orientation. This avoids the difficulties associated with the reactivity of liquid metals. Once the arc is initiated, it self-focuses into a small spot at which the heat and the electron flux are sufficient to vaporize and ionize the cathode material and liberate enough electrons to sustain the discharge. The arc currents are typically 100 A, whereas the ion currents fraction is approximately 10% of that.

## Acknowledgements

This work was performed by Lawrence Livermore National Laboratory under the auspices of the U.S. Department of Energy, contract W-7405-Eng-48.

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## Process Utilization

Arc sources can be classified according to the duration of operation, the type of electrode that provides the metal vapor, and whether the arc comprises discrete spots or is distributed over a larger area of the electrode. There are pros and cons associated with using each type of arc. For example, in a pulsed cathodic arc source, the arc duration is typically short enough that direct cathode cooling is not needed, which simplifies the design and makes it easier to change target materials. In addition, the confinement of the arc spot to the cathode surface is not problematic, because the short arc duration typically means that there is not enough time for the arc spot to leave the cathode surface. Short arc durations also permit deposition of materials, such as silicon, that are vulnerable to cracking because of relatively poor thermal conductivity, coupled with a negative resistivity coefficient with respect to temperature, which slows arc spot motion. However, pulsed sources that have low duty cycles also have correspondingly low integrated coating rates.

Continuous cathodic arc sources are typically sustained by a low-voltage, high-current power supply, such as an arc welding supply. In this arc mode, the arc spots that appear to move rapidly on the negative electrode are actually separate arcing events that occur in rapid succession. The rate of apparent motion of the arc spot(s) is a strong function of:

- Cathode composition
- The presence and composition of any working gases
- The component of any magnetic fields parallel to the cathode surface

Continuous cathodic arc sources typically provide higher coating rates, but the cathode must be designed to dissipate the heat generated by the arc. Because the heat is concentrated in a small spot, direct water cooling is usually required. This leads to difficulty in changing cathodes and limits the use of some low thermal conductivity materials. In addition, arc confinement is essential, because damage to support components and contamination of the coating can occur if the arc spot leaves the cathode surface. More details on arc initiation, confinement, and other aspects of cathodic arc source design are provided in Ref 1, 2, and 3.

The cold cathodic arc source typically produces droplets of cathode material (macroparticles). These macroparticles result from the extreme localized heating of the cathode, which is due to the high current densities that are found in cold cathode arcs ($10^4$ to $10^8$ A/cm$^2$). Unless the macroparticles can be removed from the plasma stream, they become lodged in the coating and are usually considered to be defects.

**Macroparticle Filtering.** An extensive body of knowledge that describes the filtering of these macroparticles in cases where such defects are unacceptable is now available. Two useful sources are Ref 5 and 6. Although the design of macroparticle filters is also beyond the scope of this article, one example is shown in Fig. 1. Briefly, this approach uses magnetic fields in order to constrain arc-produced electrons to follow a curved path from cathode to workpiece. This sets up an electrostatic field that channels the ions through the filter. The macroparticles, however, follow straight-line trajectories into baffles and are stopped. Although there are numerous designs for such filters, they all lose at least half of the desired coating material during transit through the filter, which leads to a corresponding decrease in deposition rate.

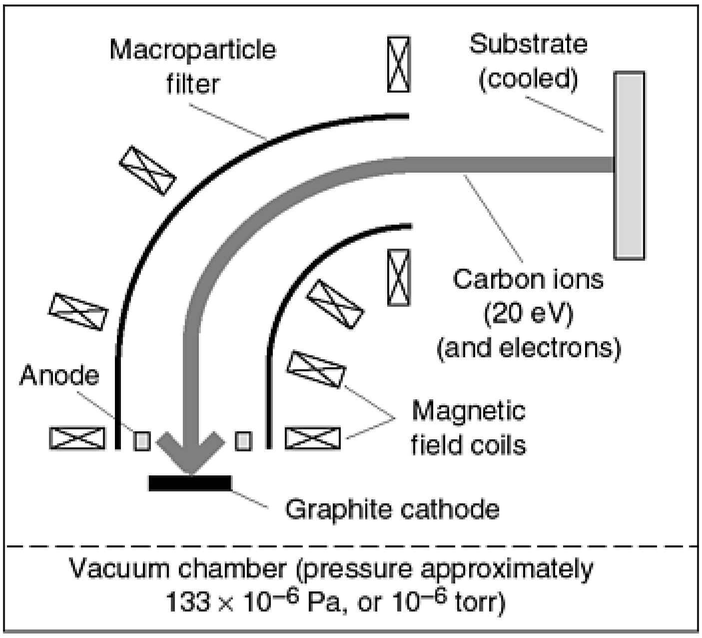

**Fig. 1 Generic filter for removing macroparticles from a cathodic arc**

A second general approach, which is appropriate in cases where a small number of macroparticles can be tolerated, is given by Coll (Ref 7). The cathode is placed behind a magnet structure that focuses the ion stream strongly at the coil location and then diverges outwardly toward the workpiece location. Arc confinement is provided by the magnetic field from the focusing coil (Fig. 2). The focusing action is thought to vaporize any macroparticles that pass through the plasma, reducing their number substantially. The source, however, requires a background gas pressure on the order of 1 Pa to operate, which can affect coating quality.

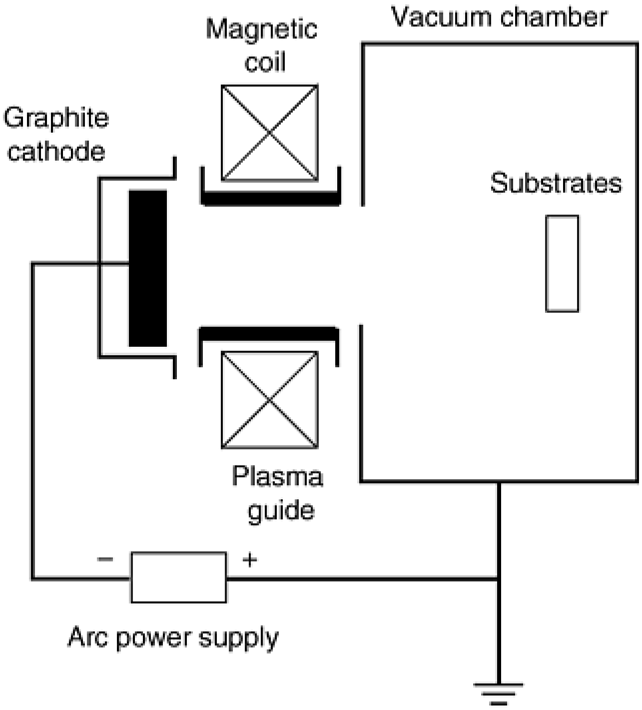

**Fig. 2 Approach for reducing number of macroparticles from a cathodic arc**

A third approach for avoiding macroparticles is to use an arc source that does not produce them. A broad class of such sources is based on a different type of arc, which is characterized by a much lower current density (~10 A/cm$^2$). This is about five orders of magnitude lower than that found in cold cathode arcs. The same arc currents are made possible because the arc is distributed over a much larger area of the electrode, which leads to the term ***distributed discharge arc*** (Ref 8). Although such distributed discharge arcs have been reported for both electrodes, most of the investigations to date have been on arcs that vaporize the positive electrode or anode.

**Arc Source Types.** Anodic arc sources can be classified according to the method by which ionization electrons are supplied (Ref 3). The sources can be hot filament (Ref 9), hollow cathode (Ref 10, 11, 12, 13), or cathodic arc (Ref 14, 15, 16). Typical configurations are shown in Fig. 3 and 4.

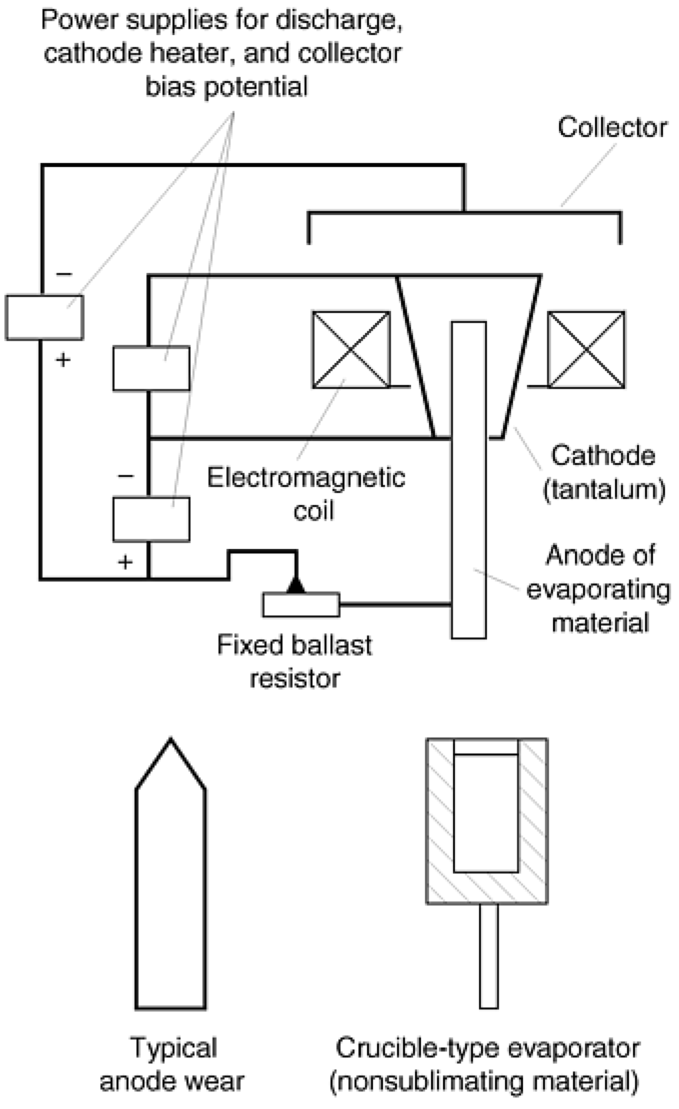

**Fig. 3 Anodic arc device. Source: Based on Ref 11**

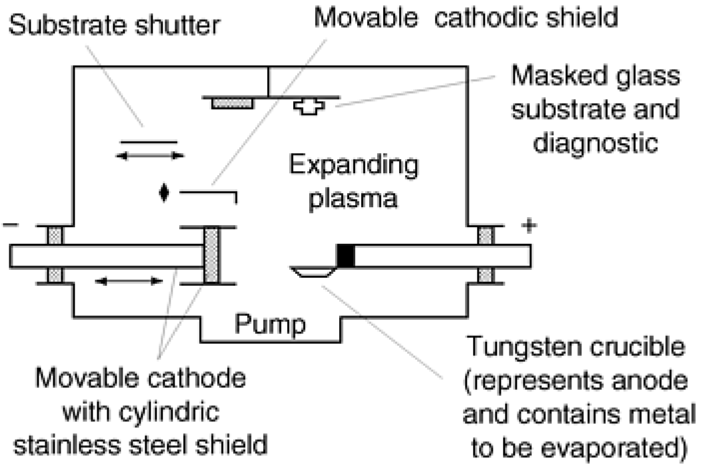

**Fig. 4 Arc discharge apparatus. Source: Based on Ref 18**

The hollow cathode arrangement described by Dorodnov (Ref 10, 11) operates as a self-sustaining arc (Fig. 3). The material to be evaporated, which forms the anode, is located within a hollow cathode. The anode material evaporates under a low-voltage (10-50 V), high-current (~100 A) electron beam, which, along with electrons trapped within the hollow cathode, ionizes the vapor (Ref 7). Because voltages are relatively low, sputtering of the cathode is minimized. Dorodnov reports using this source for chromium, carbon, magnesium, titanium, molybdenum, silicon, germanium, and copper (Ref 11). Saenko (Ref 13, 17) used this source to process substrates with diameters up to 150 mm (6 in.). Derkach and Saenko (Ref 12) incorporated a divergent plasma lens, which resulted in a 150 mm (6 in.) diameter copper vapor plasma with an ion-component beam uniformity of about 2%. The deposition rate was reported to be approximately 100 nm/s (4 μin./s).

The approach taken by Ehrich et al. (Ref 16) used a cathodic arc to supply ionization electrons to the vapor stream (Fig. 4). In this configuration, copper and zinc films were deposited at rates between 23 and 65 nm/s (0.9 and 2.6 μin./s) (below that reported by Dorodnov). The films were found to be homogeneous, with film purities up to 99.9% (Ref 14). The researchers determined an ion temperature of approximately 0.7 eV at plasma densities between $10^{15}$ and $10^{17}/m^3$ (Ref 18). These films were found to have densities that were lower than bulk material densities by 0 to 10%. Overall, this technique produced compact films with physical properties that were close to those of the bulk materials.

The use of shielding eliminated contamination of the deposited material that was due to cathodic bombardment (Fig. 4). This type of contamination, along with source contamination from the containment vessel, are issues that need to be addressed when designing this arc source. Dorodnov (Ref 11) suggests using a hearth made of the same material as that being evaporated. For vapors originating from sources that sublimate, such as carbon, actively cooled supports outside the heat-affected zone have been used. However, the relatively low evaporation rate (compared with the cathodic arc technique), short run times, and issues associated with filament lifetime have hindered the commercial development of the anodic arc source.

The utility of the anodic arc lies in its ability to generate a flow of predominant monocharged ions without macroparticles. This flow of single-charge-state ions facilitates deposition by allowing greater control of deposition energies. This can be contrasted with the cathodic arc, which produces multiple-charge-state ions. Deposition onto a biased substrate in the presence of multiple-charge-state ions may result in sputter damage to the substrate. Because the charge-state distribution in the anodic arc is nearly single valued, substrate sputtering can readily be controlled. Similarly, the monocharged nature of the anodic-arc-generated ions simplifies stream focusing and control. This facilitates usage in materials processing and as a plasma source in space research.

**The rate of deposition,** using arc technology in a laboratory environment can range from several angstroms/minute to 0.1 mm/s (4 mils/s) depending on the specific process chosen and the coating quality required. High-quality optical coatings of aluminum oxide and zirconium oxide have been produced using a cathodic arc with a macroparticle filter at rates of 35 μm/h and 20 μm/h, respectively (Ref 19).

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## Processing Parameters

Besides the typical processing variables that characterize other vacuum deposition processes, vacuum arc deposition offers additional control of the arrival energy of coating ions. In the case of conductive or semiconductive coatings, this bias can be controlled using a direct-current power supply. The level of bias is limited at the upper end by thermal considerations, because the part being coated is heated by condensing ions. Many of the trends that exist for other ion plating processes also apply to vacuum arc deposition. The main difference is ion composition. In the case of vacuum arc deposition, the ions are the particles that form the coating. With most other ion plating processes, the majority of ions involved are ionized gas molecules. This distinction can become important when coating parts that have complex shapes during a reactive process.

## Properties of Deposited Materials

Vacuum arc deposited coatings tend to have compressive stress that is due to the impact energy of ions on the part being coated. Titanium nitride can be deposited on cutting tools at relatively low temperatures and still maintain excellent adhesion and cutting characteristics.

The deposition of carbon films by the cathode arc presents a particularly interesting example. The carbon films produced by the deposition of ions of roughly 20 eV energy have a hardness of 40 to 100 GPa (6 to 15 × $10^6$ psi), a modulus of 300 to 500 GPa (45 to 75 × $10^6$ psi), and an optical transmission of 0.5 to 50 μm. The coating is amorphous, with primarily $sp^3$ bonding characteristic of crystalline diamond. It has a low coefficient of friction, 0.02 to 0.1, and a hydrogen content of less than 0.1%. This is an example of a material that can only be produced by the condensation of energetic ions.

## Process Advantages, Limitations, and Applications

One advantage of vacuum arc technology is the relative safety afforded by the low-voltage power supplies, compared with the high-voltage supplies necessary for sputtering and electron-beam evaporation. A second advantage is the relatively benign environmental impact of this technology, compared with competing means for depositing refractory metals, such as chemical vapor deposition.

All types of vacuum arc deposition processes share the same potential for making commercially valuable coatings. However, cold cathode sources produce macroparticles that may need to be removed in certain applications. Although hot sources avoid the macroparticle problem, they have other design constraints that must be evaluated, such as crucible reactions and heating and cooling cycle times.

As of 1994, the most important applications of coatings produced by the vacuum arc process involve the reactive deposition of nitrides for extending the useful life of cutting tools, reducing wear and friction in parts of machines, and providing a gold color in certain decorative applications. In particular, the cold cathode cathodic arc and one form of anodic arc have been used extensively in commercial environments for coating cutting tools with titanium nitride.

## Future Trends

As with any emerging technology, the vacuum arc will displace existing approaches only when a compelling advantage can be demonstrated. Situations in which extremely good adhesion is desired can represent opportunities for the vacuum arc process. Adhesion of copper to glass with bond strengths sufficient to fracture the glass during a pull test have been reported (Ref 20). Applications that require an efficient process for rapidly depositing refractory metal coatings can be opportune for the cathodic arc. This technology should be particularly attractive in situations where the presence of a small number of macroparticles does not present difficulties. It may also be attractive for producing hard, amorphous diamond coatings for various tribological applications. There are also numerous potential applications for corrosion-barrier coatings. Examples include coatings on fibers used in metal-matrix composites and protective coatings for turbine blades (Ref 1). Filtered arcs can produce very high-quality ceramic coatings at high deposition rates (Ref 21) because of the high reactivity of the ions.

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# Ion Implantation

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## Introduction

ION IMPLANTATION involves the bombardment of a solid material with medium-to-high-energy ionized atoms and offers the ability to alloy virtually any elemental species into the near-surface region of any substrate. This near-surface alloying can be performed irrespective of thermodynamic criteria such as solubility and diffusivity. These advantages, coupled with the additional possibility of low-temperature processing, have prompted explorations into applications in which the limitations of dimensional changes and possible delamination of conventional coatings are a concern. In almost all cases the modified region is within the outermost micrometer of the substrate, often only within the first few hundred angstroms (i.e., microinches) of the surface. Maximum. concentrations of several tens of atomic percent are usually achievable, although this depends on the ion-substrate combination.

During implantation, ions come to rest beneath the surface in less than $10^{-12}$ s. This rapid stopping time produces an ultrafast quench rate in the wake of the stopping ion. This allows many novel surface alloys or compounds unattainable by conventional (equilibrium) processing techniques to be produced at room temperature. These include substitutional solid solutions of normally immiscible or low-solubility elements. Such highly metastable and amorphous alloys often possess unique physical and chemical properties. Ion implantation has been used extensively in the semiconductor industry since the 1970s to introduce dopant atoms reproducibly into silicon wafers to modify electrical performance, and it is used routinely in several stages of integrated circuit production. It allows fabrication of electronic devices not producible by any other process, largely due to the highly reproducible control of dopant concentration levels over several orders of magnitude as compared to doping by thermal diffusion. Since the mid-1970s, the use of ion implantation and other closely related ion beam processes has expanded into a number of diverse application areas in the international research and development community. However, only relatively recently have applications in the industrial sector developed.

Research interests in metals have expanded from the initial friction and wear studies to include other areas, such as corrosion, oxidation, fatigue, and studies of basic metallurgical mechanisms (Ref 1, 2). In addition to metals, polymers and ceramics have been studied with the principal aims of increasing the conductivity of polymers (Ref 3) and improving the fracture toughness and tribological properties of ceramics (Ref 4).

On a commercial scale, the applications for ion implantation of metals continue to increase, at present mainly for antiwear treatment of high-value components. A large number of industrial trials have involved the implantation of nitrogen for improving the wear resistance of coated and uncoated tools and other precision components. Implantation appears to be an attractive technique for treating industrial components by stabilization of the microstructure (preventing a change in wear mode), by transformation to a wear-resistant mode, or by chemical passivation to prevent a corrosive wear mode (Ref 5).

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## Fundamentals of the Ion Implantation Process

Figure 1 shows a schematic view of the path of an individual ion as it loses energy in a material, thereby forming a shallow surface-modified region. As indicated in the figure, the ion does not travel in a straight path to its resting place, due to collisions with the target atoms. Target atoms are displaced from their lattice sites with sufficient energy that they can themselves displace additional target atoms, resulting in a collision cascade. These individual collisions with lattice atoms within a single collision cascade are shown in the insert at the bottom of Fig. 1.

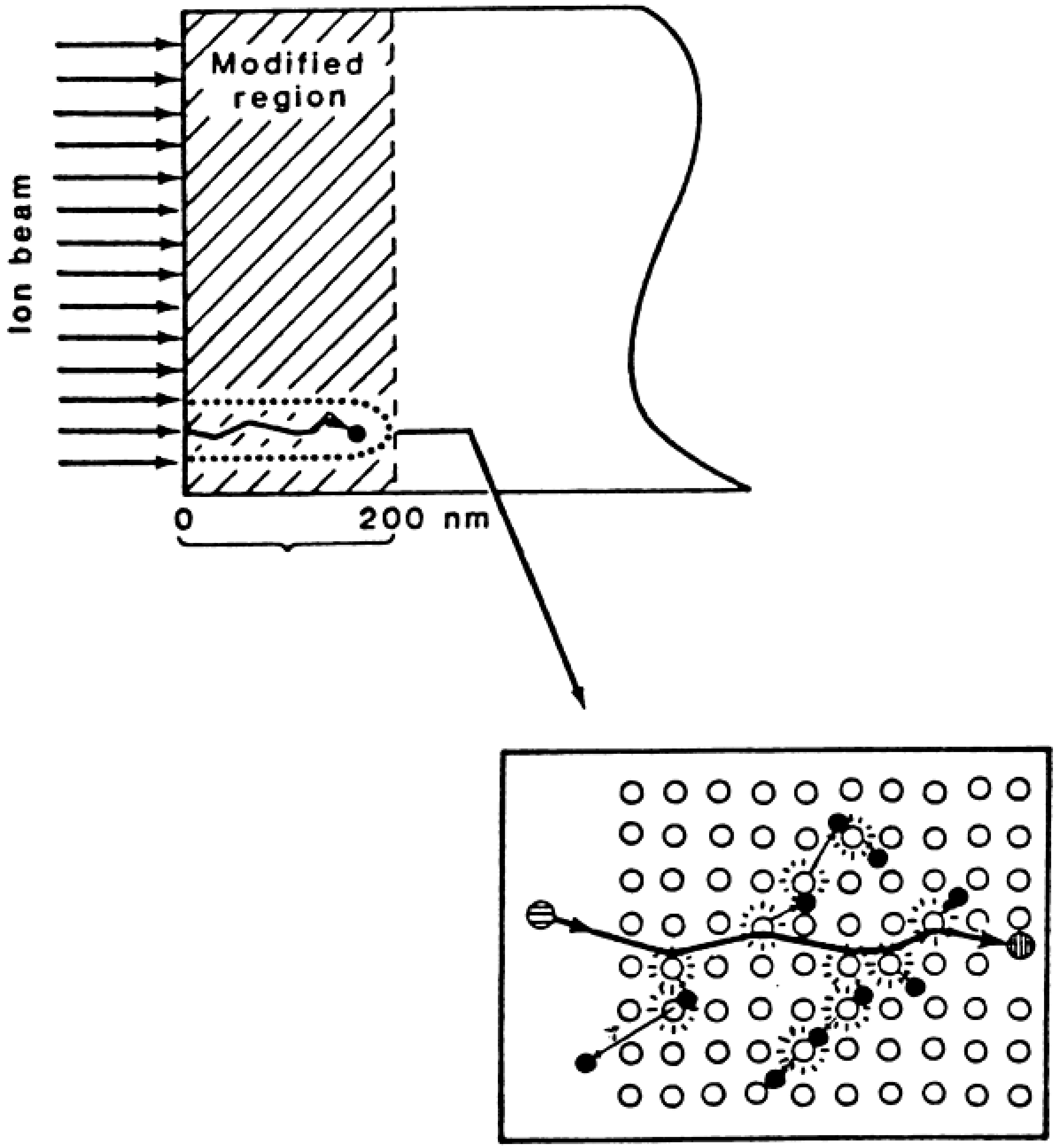

**Fig. 1 Schematic view of ion implantation process (top) and depiction of the interactions with substrate atoms in a single collision cascade (bottom). Source: Ref 6**

The actual integrated distance traveled by the ion is called the range, $R$. The net penetration of the ion into the material, measured as projected onto the original trajectory, is called the projected range. Ion implantation is a random process, normally producing a Gaussian-shaped impurity depth profile whose centroid is defined as the average projected range, $R_p$. The statistical nature of the scattering process gives rise to a distribution of ions around the projected range depth. The average fluctuation (standard deviation) in the projected range is called the range straggling, $\Delta R_p$.

The ion energy directly affects both the range and the distribution of the implanted ions in a given substrate. At higher energies a greater spread in the ion distribution (a greater $\Delta R_p$) is realized for a given dose, which is the number of implanted ions per unit area of the surface of the material (areal density), usually expressed as ions/cm$^2$. The areal dose (also called fluence) is a convenient unit of ion implantation because the actual volume concentration associated with an implantation is a function of ion species, ion energy, and substrate material. For metals, beneficial doses can span the range of $10^{15}$ to $10^{18}$ ions/cm$^2$, depending on the application (see the section "Applications" in this article). The determination of the implanted atomic concentration (atoms/cm$^3$) requires relating the areal density of implanted atoms to their spatial extent. At low ion doses, the implant profile can normally be approximated as a Gaussian distribution centered about the projected range. Accordingly, the width of the distribution can be expressed by the standard deviation of the Gaussian distribution, $\Delta R_p$. The expression for the peak concentration ($N_p$) of a Gaussian distribution is given in terms of the applied dose ($N_A$) and range straggling as:

$$N_p(atoms/cm^3) = \frac{N_A(atoms/cm^2)}{\sqrt{2}p\Delta R_p(cm)}$$

Figure 2 shows the projected range and range straggling for nitrogen ions implanted into iron versus the initial ion energy. The range distribution is shown as a Gaussian distribution with $R_p$ and $\Delta R_p$ characteristic of the ion energy. For a given energy, a lighter ion such as nitrogen will penetrate farther and will undergo more large-angle scattering (leading to a broader distribution) than would a heavier ion such as chromium. Each implanted ion can displace hundreds to thousands of lattice atoms as it travels into the substrate surface. This results in a net damage distribution that is also normally Gaussian-shaped but is situated closer to the surface than the range distribution, because each ion creates damage between the surface and its final resting place in the lattice. This lattice damage can render ionic or covalently bonded lattices amorphous during implantation, whereas a nondirectionally bonded (metal) substrate can either self-anneal, with no residual damage, or else can retain point defects or extended defects (e.g., dislocations) resembling those of a heavily work-hardened metal or alloy. Ion implantation of certain species (e.g., phosphorus in iron) can stabilize amorphous structures in metals in a manner analogous to bulk rapid quench techniques such as splat cooling.

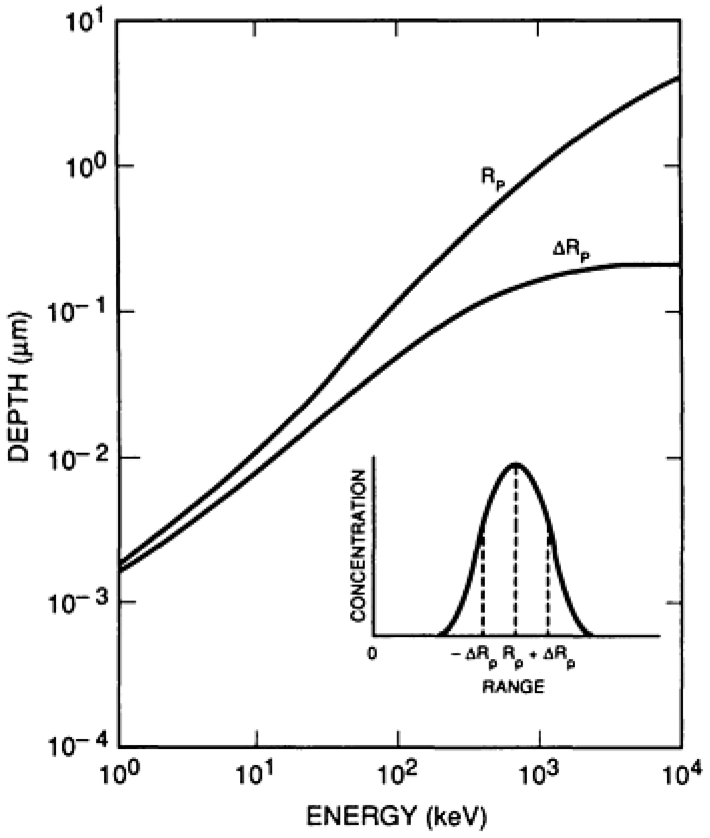

**Fig. 2 The projected range, $R_p$, and range straggling, $\Delta R_p$, of nitrogen ions implanted into iron vs. the initial ion energy. Source: Ref 6**

As an ion penetrates a material, there is a certain probability that a surface atom will be ejected from its lattice site, because there is some momentum directed back toward the surface in a collision cascade that allows an atom to receive sufficient energy to overcome its surface-binding energy. This phenomenon is called sputtering and is analogous to the erosion of materials by the impact of high-velocity particles. The ratio of the number of substrate atoms ejected per incident ion is commonly termed the sputtering coefficient, *S*. As a general rule, for a given substrate material, *S* will increase with increasing ion mass and will increase sharply at more oblique angles of incidence. For a given ion at normal incidence, *S* depends principally on the surface binding energy of the material, which can be related to its heat of sublimation. Therefore, for a given ion, *S* will decrease with increasing heat of sublimation for the substrate material. Values for *S* can range from less than 1 for the case of a light ion incident on a heavy substrate (e.g., nitrogen implanted into iron) to greater than 10 for very heavy ions in a lighter substrate (e.g., tantalum ions implanted into iron).

Figure 3(a) shows a schematic view of the evolution of the concentration depth profile of an implanted element for the case where *S* is greater than unity. In this particular example, the projected range of ions is shown as being 600 Å. This closely represents the implantation of 200 keV chromium ions into steel (or iron). At a low dose, the distribution is essentially Gaussian, as discussed earlier, and there is a low concentration of implanted atoms at the surface. However, as the dose increases and the surface is eroded, an increasing number of previously implanted atoms are exposed on the surface, and these near-surface atoms are subject to sputtering just as the target atoms are.

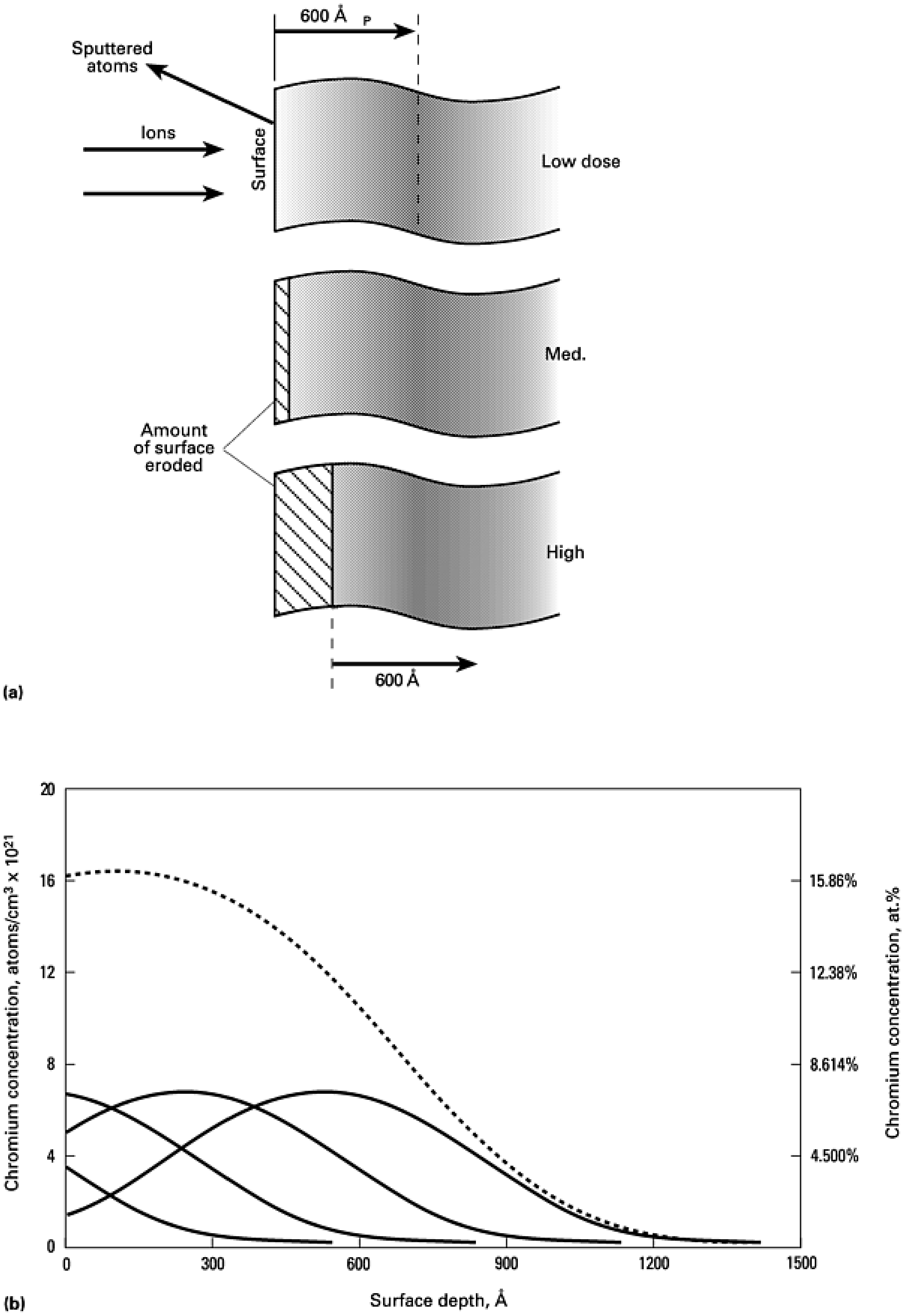

**Fig. 3 (a) Schematic view of the development of implanted impurity profiles from low to high doses. Source: Ref 6. (b) Computer simulation of four consecutive 5 × $10^{16}$ Cr/cm$^2$ implantations at 200 keV energy into iron, accounting for sputter erosion of the surface for each implantation. The sum of the four individual profiles (the curve of dark squares) yields a distribution with a maximum near the receded surface. Source: Ref 7**

At a particular dose level, called the saturation dose, a steady-state situation is established whereby the rate of removal of previously implanted atoms is equal to the arrival rate of energetic ions. The peak concentration of the implanted element distribution approaches the surface, as shown in Fig. 3(b), as the implanted dose increases and approaches the saturation dose. Generally, the maximum surface concentration of the surface element is equal to $1/(S + 1)$. For the example of 200 keV chromium ions in iron, $S$ has a value of about 5 atoms/ion, so the maximum surface concentration of chromium would be about Å or 16 at.%. In this case, the steady-state dose would be approximately $2 \times 10^{17}$ ions/cm$^2$. This behavior is quantitatively predicted by analytic models, as shown in Fig. 3(b), which illustrates the sputter removal of the surface and the surface enrichment of the implanted species resulting from successive (lower-dose) implantations.

For certain ion-substrate combinations and concentrations, chemical reactions with molecular species present in the vacuum chamber can be induced. An excellent example of this is titanium implantation into steel. At high titanium doses, highly reactive titanium atoms become exposed on the surface and react with the residual CO and $CO_2$ hydrocarbon molecules normally present in the vacuum chamber. When the partial pressure of carbon-containing molecules is $1 \times 10^{-6}$ torr or higher, the implantation results in the formation of an amorphous Fe-Ti-C surface layer that has been shown to reduce friction and wear greatly (see the section "Applications" in this article). When the background pressure in the chamber is less than $10^{-6}$ torr, there are insufficient carbon-containing molecules to produce the carburized surface layer. A consequence of these surface chemical reactions is a considerably reduced sputtering yield because of the increase in the surface binding energy due to compound formation. This phenomenon has been exploited by deliberately introducing gases into the vacuum chamber during implantation. For example, for tantalum implantation into steel, where normally $S$ is approximately 10, the introduction of oxygen into the chamber to $1 \times 10^{-5}$ torr (partial pressure) reduces the sputtering by more than a factor of three, due to the formation of an almost pure $Ta_2O_5$ layer at the surface for a tantalum dose of $2 \times 10^{17}$ ions/cm$^2$.

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## Advantages and Limitations of the Ion Implantation Process

Table 1 gives the advantages and limitations of the implantation process for surface modification.

**Table 1**

| **Advantages** | **Limitations** |
|---|---|
| Produces surface alloys independent of thermodynamic criteria | Limited thickness of treated material |
| No delamination concerns | High-vacuum process |
| No significant dimensional changes | Line-of-sight process |
| Ambient-temperature processing possible | Alloy concentrations dependent on sputtering |
| Enhance surface properties while retaining bulk properties | Relatively costly process; intensive training required compared to other surface treatment processes |
| High degree of control and reproducibility | Limited commercial treatment facilities available |

The ability to use ion implantation to inject alloying species forcibly into the near-surface region of virtually any material, independent of thermodynamic criteria such as solid solubility and diffusivity, is an important feature for applying the process to basic metallurgical studies. For example, one can prepare supersaturated or metastable systems and study their return to equilibrium by suitable thermal annealing and observation of their microstructure. This application of ion implantation technology has been exploited to measure low-temperature diffusion, solid solubility, and trapping phenomena in alloys (Ref 8).

Because implanted near-surface layers are an integral part of the substrate, without an interface, they can sustain very high stresses without the occurrence of the delamination that plagues certain types of coatings, especially those deposited at low temperatures.

Strictly speaking, ion-implanted surfaces do experience a dimensional change, albeit on a microscopic level (typically less than 0.1 μm, or 4 μin.), due to erosion caused by sputtering. In addition, at doses greater than $10^{17}$ ions/$cm^2$ some degree of surface roughening may occur due to sputtering effects. The accumulation of insoluble implanted gaseous species may also cause surface blistering. However, from a practical engineering perspective it is normally accurate to portray implantation as a process that does not significantly affect substrate dimensions or topography.

Implantation processing can be carried out at near-ambient temperatures, but this depends on the thermal mass of the substrate, the relative ion beam power ($W/cm^2$) being delivered to the substrate, and, critically, the ability to conduct heat away from the substrate, because radiative cooling is negligible at desired processing temperatures. The latter factor depends on the thermal conductivity between the substrate and the fixturing to which it is attached in the vacuum chamber.

The limited thickness of the implanted layer (typically less than a micrometer) is an intrinsic limitation of the ion implantation process and is dictated by the physics of the energy loss processes. For applications requiring thicker surface-modified regions, it may be desirable to employ hybrid ion beam/coating processes. See the article "Ion-Beam-Assisted Deposition" in this Volume.

Ion implantation is intrinsically a vacuum process requiring background pressures of $10^{-5}$ torr or less. Manipulation of components, through the use of vacuum-compatible fixtures, and thermal heat sinking are often required to ensure both uniform dosage and adequate cooling to dissipate the imposed heat load on the component due to the energetic ion beam. This requirement poses some limitations on the types of substrates that can be implanted.

Directed beam ion implantation is a line-of-sight process. It lacks the so-called throwing power of certain other plasma-based coating processes, which can better treat irregular surface features due to multiple scattering of atoms (ions) within the higher-pressure plasma.

As discussed previously, implanted atoms are always in an intimate mixture with atoms of the original substrate, thus forming a surface alloy. However, because of sputtering, desired alloy concentrations may be unattainable for many ion-substrate combinations.

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## Equipment and Processing Times

As of 1994, ion implantation processing technology is still a relatively specialized process compared to many conventional surface treatment techniques. Most implanters in use today for metals applications require highly trained operators because they were originally built for processing silicon wafers, which required very rigorous process control, Such implanters have been subsequently modified for more general use. Typically, the cost of processing components in these types of systems is higher per unit area than for conventional coatings or surface modification techniques.

Figure 4 is a schematic of a typical medium-current semiconductor implanter adapted for metals implantation. This implanter uses a versatile ion source capable of producing heavy metal ion beams of most elements by introducing metal vapor or a volatile compound of the element into the plasma discharge of the ion source. After the positive ions are extracted from the ion source, they are mass analyzed by being passed through a 90° sector magnet. They are subsequently accelerated to their ultimate energy (typically 30 to 200 keV), then directed and scanned over the target.

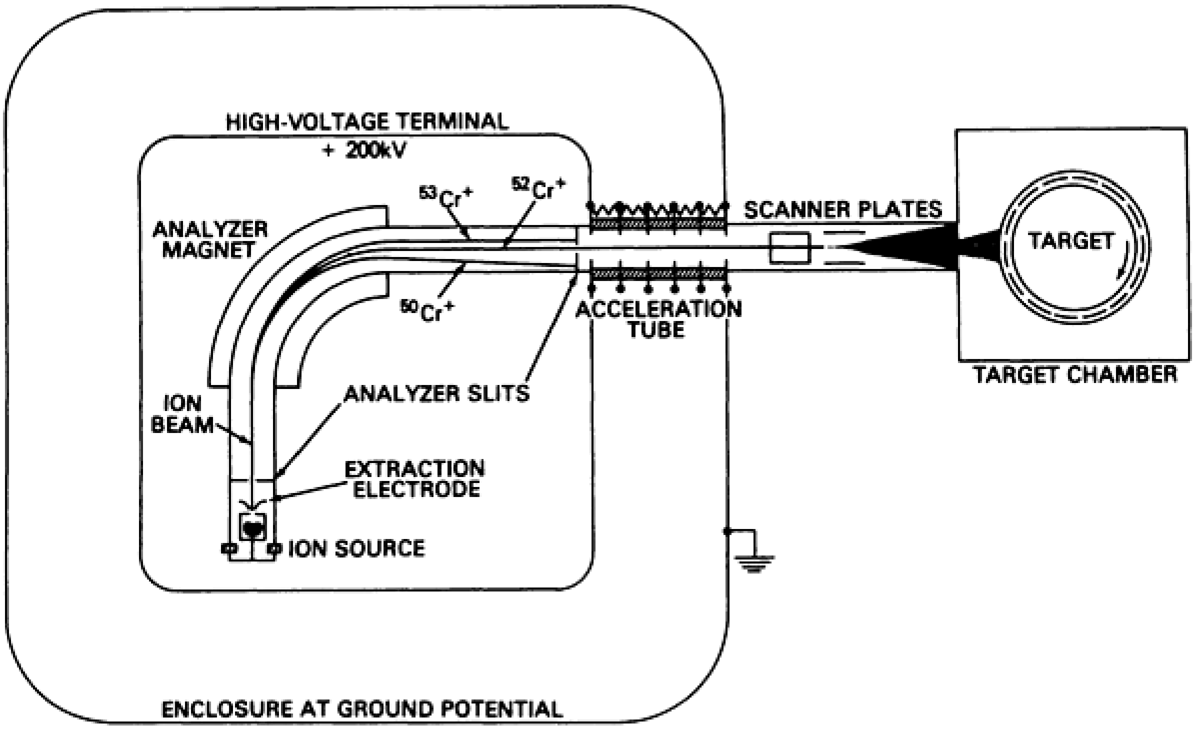

**Fig. 4 Schematic of Naval Research Laboratory implantation facility for surface alloying. Mass analyzed $^{52}Cr^+$ beam being transported for the implantation of bearing components to improve their corrosion resistance. The footprint of this machine is about 2.5 × 4 m. Source: Ref 9**

An implanter of this design can produce from 1 to 10 mA (6 to 60 × $10^{15}$ ions/s) of positive ion beam, depending on the size and design of the ion source. At an energy of 100 keV, this beam current corresponds to energy densities of 100 to 1000 W in the envelope of the beam. It is therefore imperative to either spread this beam energy over a large area or to ensure good thermal conductivity of the substrates to a heat sink in order to limit beam heating. Both of these approaches are used in practice. The actual processing times can be determined by knowing the area to be treated, the ion current intensity, and the geometrical factors involving manipulation of the substrates through the beam to ensure uniform surface coverage. For a stationary substrate, an average beam current of 1 mA will deliver $10^{17}$ ions in about 15 s, a typical ion dose required for each square centimeter of the substrate. The actual implantation time will therefore depend on the area over which the beam is scanned to ensure both dose uniformity and adequate cooling. Larger batch sizes help reduce beam heating and improve the economics of processing.

Several approaches have been taken to simplify and reduce the cost of implantation treatments, such as using alternative ion source designs when using mass analysis (Ref 10). Large-scale dedicated systems have also been built without mass analysis to implant nitrogen into fairly massive components. One such unit in the United Kingdom has a processing chamber that is more than 2 m in diameter and 2 m in length and has been used to implant components such as automobile camshafts, dies, and plastic molds weighing more than 500 kg. A similar system has been constructed in the United States (Ref 11). Another large-scale non-mass-analyzed unit, which has a target platen 2 ft in diameter, has been built and installed in a U.S. Army Aviation Depot for high-current (25 mA) nitrogen implantation of metal cutting tools (Ref 12).

A second approach, called plasma immersion ion implantation (PIII) or plasma source ion implantation (PSII) (Ref 13, 14), involves immersing the object to be implanted in a plasma and pulsing it to a high negative voltage (50 to 100 kV), thereby extracting the ions from the plasma. Because the plasma completely surrounds the component(s), the line-of-sight restriction of conventional ion implantation is greatly alleviated, with the result that more complex geometries can be implanted and/or less complicated fixturing can be used. A current restriction to this technique, however, is that it is limited to readily ionized plasma species (mainly gaseous elements such as nitrogen) and conducting substrates.

A third approach is to produce heavy ion beams from solids by using a metal vapor vacuum arc (MEVVA) discharge in a pulsed mode (Ref 15), yielding non-mass-analyzed ion beams extracted from a broad beam source (up to 50 cm in diameter). These sources have been demonstrated to produce up to 100 mA currents of metals. The commercial development of this source has been projected to yield low unit costs and high production throughput (Ref 16).

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## Applications

Table 2 outlines some of the research and development applications that have been pursued using directed beam ion implantation technology. Of the properties listed, the tribological aspects of ion implantation have received the most attention (Ref 17). In spite of the relatively shallow penetration of implanted ions (typically nitrogen), implanted surfaces have often demonstrated a high degree of resistance to wear under mild abrasive or lubricated sliding conditions. This wear resistance is especially noteworthy in alloy surfaces that contain elements forming stable nitrides. Titanium and Co-Cr alloy orthopedic prostheses for hips and knees are among the most successful commercial applications of ion implantation components for wear resistance. In use, these components, shown in Fig. 5, articulate against an ultrahigh-molecular-weight polyethylene mating surface. Tests at several laboratories have indicated that wear reductions of 10× to 100× may be realized by the implantation of nitrogen ions into the alloy. To date tens of thousands of such components have been ion implanted prior to surgical implantation.

**Table 2**

| **Surface properties modified** | **Substrates studied** | **Ions species used** | **Comments, references** |
|---|---|---|---|
| Wear | Steels, WC, Ti, Co/Cr alloys, TiN coatings, electroplated Cr | N, C<br>10-20 at.%<br>$\geq 10^{17}$ ions/cm$^2$ | Ti, Co/Cr alloys largest use commercially in orthopedic devices (Ref 5, 9, 17) |
| Friction | Steels | Ti plus C implants<br>$\geq 10^{17}$ ions/cm$^2$ | Dual implants give amorphous surface layer (Ref 18) |
| Fatigue | Ti alloys, steels | N, C<br>$\geq 10^{17}$ ions/cm$^2$ | Implantation effective for surface initiated fatigue (Ref 5) |
| Fracture toughness | Ceramics: $Al_2O_3$, TiN | Ar<br>$10^{15}$-$10^{17}$ | Radiation damage critical, ion induced compressive stress helpful (Ref 4, 19) |

| | | | |
|---|---|---|---|
| | | ions/cm$^2$ | |
| Aqueous corrosion catalysis | Steels, Ti alloys, Pt | Cr, Ta, Cr plus P<br>$\geq 10^{17}$ ions/cm$^2$ | Ion implant can mimic "normal" alloys; amorphous and unique surface alloys possible (Ref 20) |
| Oxidation | Superalloys | Y, Ce<br>$\geq 10^{15}$ ions/cm$^2$ | Low effective doses; implanted species stay at metal-oxide interface (Ref 21, 22) |
| Electrical conductivity | Polymers | Ar, F<br>$10^{12}$-$10^{17}$ ions/cm$^2$ | Permits chain scissoning, doping; conductivity approaches disordered metal levels (Ref 3, 23) |
| Optical: Refractive index | Glasses, electrooptics | Li, Ar<br>$10^{15}$-$10^{17}$ ions/cm$^2$ | Chemical doping and lattice disorder both important (Ref 24, 25) |

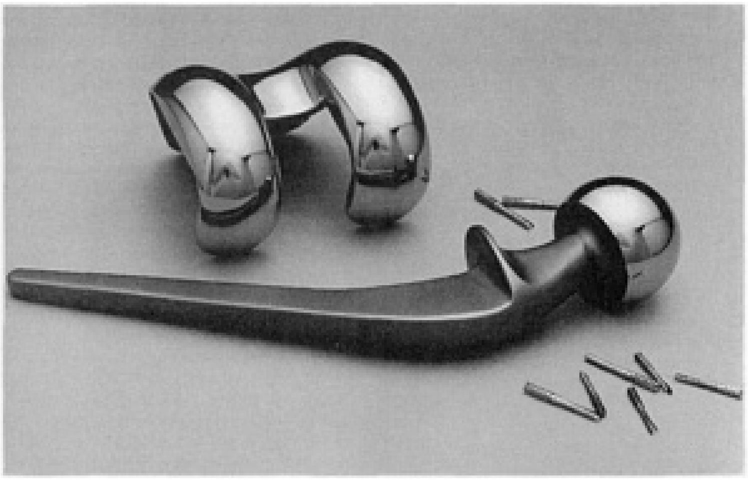

**Fig. 5 Surgical prostheses of Ti-6Al-4V alloy of types being commercially ion implanted for wear benefits**

Ion implantation is also being investigated as a means of improving the performance of certain types of coatings. Two examples are the implantation of nitrogen ions into (a) physical vapor deposited TiN coatings, such as on cutting inserts to increase their lifetimes, and (b) electroplated chromium to produce a CrN surface layer that inhibits the formation of microcracks, thus increasing the useful life of the electroplate. The latter use is of particular interest because of steadily increasing environmental concerns.

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## Health and Safety

Ion implantation of gaseous elements, whether using conventional ion implantation or the PSII process, does not involve the use of any toxic or hazardous material and produces no effluent that requires special precautions. Semiconductor applications typically do use toxic gases for production of ion beams, and chlorine gas is sometimes used for producing heavy metal ion beams. However, implanters using a MEVVA, high-temperature, or sputtering heavy ion source do not require the use of toxic gases. The use of high voltages for ion acceleration and ion beam handling requires adequate training of personnel and proper design of equipment for shock protection and reduction of x-ray levels to within acceptable limits.

## Future Trends

Commercial ion implantation processing is presently a service business directed toward high-value components whose lifetime extension warrants the processing costs. The largest markets are presently orthopedic devices and specialized tooling. However, a growing body of research and develoment workers are exploring the PIII process because of the attractive scaleup possibilities for large objects with complicated shapes. The ongoing development of high-current, heavy ion sources is also expected to open up new process applications. These include both high-temperature, versatile heavy ion sources (Ref 10) and MEVVA sources (Ref 15, 16) for applications not requiring mass analysis. The potential for scaleup must continue to be guided by the intrinsic depth limitations of this technique, which will proscribe applications subject to severe abrasion or erosion.

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## Introduction

DIFFUSION COATINGS are deposited either by heating the components to be treated in contact with the powder coating material in an inert atmosphere (solid-state diffusion) or by heating them in an atmosphere of a volatile compound of the coating material (out-of-contact gas-phase deposition, or chemical vapor deposition). Solid-state diffusion methods include pack cementation, which is the most widely employed diffusion coating method and the process described in most detail in this article, and various slurry or powder-paint methods of coating metal parts and assemblies. The most widely used coatings are those based on aluminum (aluminizing), chromium (chromizing), and silicon (siliconizing). Substrate materials include nickel- and cobalt-base superalloys, steels (including carbon, alloy, and stainless steels), and refractory metals and alloys.

This article is divided into two major Sections. The first Section describes the widespread use of diffusion coatings for elevated-temperature protection of turbine components for aircraft engines or ground- or marine-based gas turbines. The second Section reviews diffusion-coated ferrous alloys.

High-temperature oxidation-resistant diffusion coatings for molybdenum, niobium, tantalum, and tungsten substrates are described in the article "Surface Engineering of Refractory Metals and Alloys" in this Volume. In addition, information on the use of diffusion coatings for wear resistance, for example, coatings based on boron (boronizing) via pack cementation or complex carbides (vanadium carbide, chromium carbide, and niobium carbide) deposited from salt baths, can be found in *Heat Treating,* Volume 4 of the *ASM Handbook;* see the articles "Boriding (Boronizing)" and "Thermoreactive Deposition/Diffusion Process," respectively.

## Diffusion Coatings for Gas Turbine Engine Hot Section Parts

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Blades and vanes made from nickel- and cobalt-base superalloys that are used in the hot sections of all gas turbine engines are coated to enhance resistance to hot corrosion. The most widely used coatings are those based on the intermetallic compounds NiAl and CoAl, which are formed by the diffusion interaction of aluminum with surfaces of the nickel and cobalt alloys, respectively. Diffusion chromium coatings are also used to protect against certain forms of molten salt hot corrosion. The majority of these diffusion coatings are manufactured by pack cementation and related "gas phase," or out-of-contact, processes.

The first public descriptions of pack cementation aluminizing were by Van Aller in a U.S. patent filed in 1911 (Ref 1) and in a technical paper by Allison and Hawkins in 1914 (Ref 2)--both from the General Electric Research Laboratories. The process consisted of embedding pieces to be coated in powder mixtures of aluminum, ammonium chloride, and graphite, and heating the assembly at 450 °C (840 °F) for two hours. A few years later, Gilson, of the same laboratory, patented the use of alumina, or aluminum oxide ($Al_2O_3$), as a substitute for graphite in the mix (Ref 3). The first known use of pack cementation aluminizing of gas turbine parts was for stationary cobalt superalloy vanes in about 1957 (Ref 4). Rotating nickel superalloy turbine blades may have been first aluminized by hot dipping in molten aluminum (Ref 5). Kelley (Ref 6) described his invention of pack cementation chromizing of steels in 1923. Comprehensive reviews of chromide coatings on steels were published in 1951 and 52 (Ref 7, 8). Aluminide coating of chromized steels to further improve high-temperature oxidation resistance was patented in 1953 (Ref 9). The time of first widespread use of chromide coatings on gas turbine parts is obscure but probably occurred in Europe in the early 1960s (Ref 10, 11).

Pack cementation siliconizing of iron and steels with powder mixtures of ferrosilicon, ammonium chloride, and alumina was described in 1954 (Ref 12). Siliconizing of nickel and cobalt superalloys does not produce practically useful coatings because of the formation of low-melting, brittle silicide phases (Ref 13). Minor additions of silicon to aluminide coatings on superalloys do enhance hot corrosion resistance.

Major developments in diffusion coatings for superalloys (and steels) over the last two decades include modifications of aluminide diffusion coatings with chromium (Ref 14), platinum (Ref 15), and to a lesser extent, silicon. The theory of codeposition of combinations of aluminum, chromium, silicon, and the so-called reactive metals (yttrium, rare earths, hafnium, etc.) has been refined and straightforward processes have been developed (Ref 16). Out-of-contact gas-phase coating (chemical vapor deposition, or CVD) has gained in use, not only for coating complex air-cooling passages, but as an overall versatile, environmentally friendly, cost-effective technology (Ref 17, 18, 19). It is estimated that more than 90% of all coated gas-turbine hot-section blades and vanes are coated by pack cementation and related processes.

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## Principles of Pack Diffusion Coating

**Aluminizing.** Pack diffusion coating may be considered as a CVD process carried out with the aid of a powder mixture (pack), in or near which the part to be coated (substrate) is immersed or suspended, containing the element or elements to be deposited (source), a halide salt (activator), and an inert diluent such as alumina (filler). When the mixture is heated, the activator reacts to produce an atmosphere of source element(s) halides which diffuse in the pack and transfer the source element(s) to the substrate on which the coating is formed.

Figure 1 presents schematic diagrams of the diffusion zones in a series of packs used for the production of aluminide coatings on nickel- and cobalt-based superalloys, in which the source is aluminum or an aluminum alloy and the activator an ammonium or sodium halide. Upon heating, the activator reacts with aluminum to form $H_2$(g) or Na(g) and a series of volatile aluminum halides. The nature and partial pressures of the major constituents in the gas phase in equilibrium with aluminum at high activity in the pack, and at lower activity at the surface of the coating, can be calculated when the free energies of formation of the halides and the activity versus composition relationship for aluminum in the source alloy and coating are known. In the presence of a high aluminum activity, no significant amounts of the halides of other metals in the source or superalloy appear in the gas phase, and these metals are, therefore, not transported in packs of this type. Alloying is used simply to control the activity of aluminum in the source in order to obtain a desired concentration of aluminum at the surface of the coating.

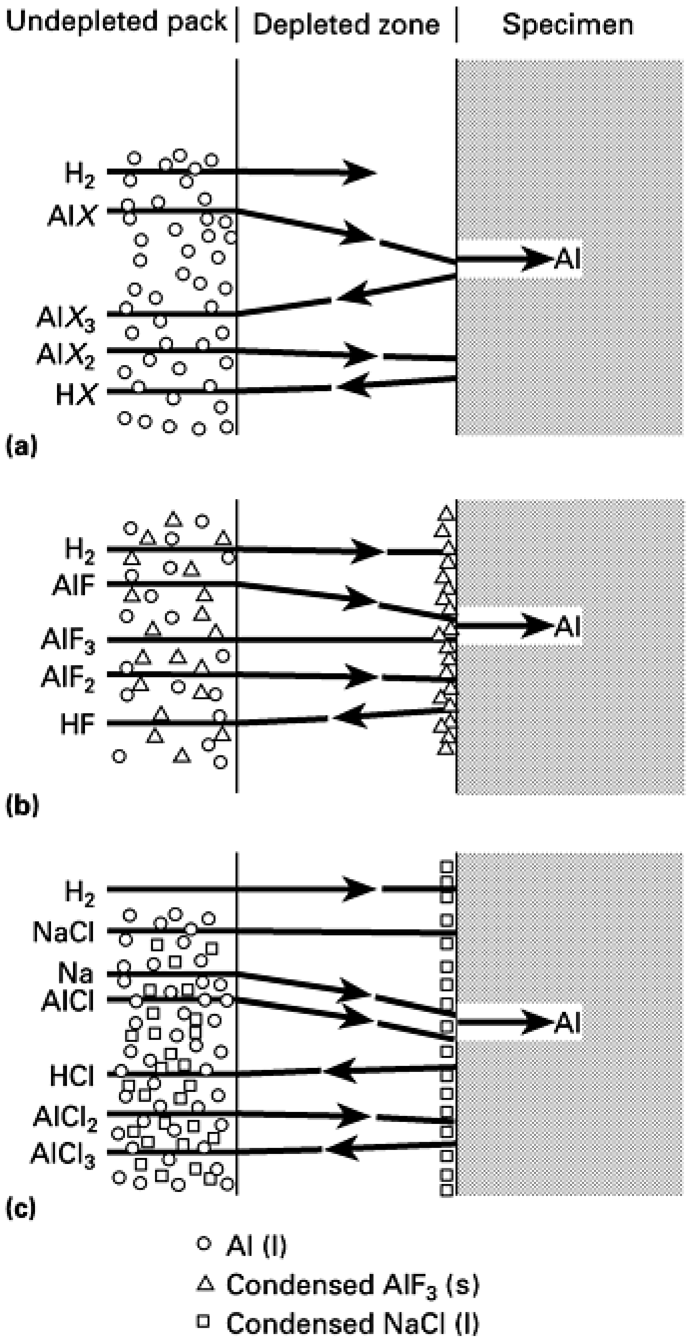

**Fig. 1 Schematic diagrams of the fluxes of the major diffusing gaseous species in aluminizing packs activated with (a) $NH_4X$ ($X$ = Cl, Br, or I), (b) $NH_4F$, and (c) NaCl. Source: Ref 20, 21**

Diffusion of the gaseous halides takes place across an aluminum-depleted zone which forms as a result of transport of aluminum into the coating under the action of the partial pressure gradients which exist between the pack and the coating surface (Ref 20, 21). The rate of diffusion of constituent $i$ is proportional to:

$$D_i(P_i-P_i') = D_i\Delta P_i$$

where $D_i$ is the interdiffusion coefficient of $i$ with the residual gas in the system, and $P_i$ and $P_i'$ the partial pressures of $i$ in the bulk pack and at the surface of the coating, respectively. The instantaneous rate of transport of aluminum from the pack to the coating, obtained by summing the contributions from each of the diffusing aluminum halides, can be expressed as:

$$J_{\mathrm{Al}} = (\varepsilon/dRT) \sum \alpha_i N_i D_i \Delta P_i$$

where $J_{\mathrm{Al}}$ is the rate of transport of aluminum in moles/cm$^2$ · s; $d$ is the effective diffusion distance in cm; ε is a constant to correct for the porosity of the pack; $\alpha_i$ is a factor to correct for the possible condensation of activator (to be discussed later); $N_i$ is the number of gram atoms of aluminum in the $i$th species; $D_i$ is diffusion coefficient of constituent $i$ in cm$^2$/s; $P_i$ is the partial pressure of constituent $i$ in atm; $R$ is the gas constant in cm$^3$ · atm/mole· deg; and $T$ is temperature in degrees Kelvin, K. For the case of aluminization in a static pack with a high aluminum source, after a short period of time the aluminum concentration at the surface of the coating reaches a constant value, different from that in the source. Under this condition the weight of aluminum $W_g$ (g/cm$^2$· s) transported to the substrate in $t$ (s) is given by a parabolic expression (Ref 22):

$$W_g^2 = K_g t$$

where

$$K_g = (2\rho\varepsilon M/RT) \sum \alpha_i N_i D_i \Delta P_i$$

in which ρ is the pack aluminum concentration in g/cm$^3$, and $M$ is the gram-atomic weight of aluminum. The diffusion of aluminum into the coating is also governed by a parabolic expression:

$$W_s^2 = K_s t$$

where $K_s$ is the rate constant for diffusion in the solid, which can be evaluated if diffusion coefficients are known for the phases in the coating. Both $K_g$ and $K_s$ are functions of the surface composition of the coating, and this unknown composition can be determined from the condition that at steady state $K_g = K_s$.

Figure 1(a) shows, in order of increasing partial pressure, the principal diffusing species in a pack activated with $NH_4X$ ($X$ = Cl, Br, or I), and the direction of diffusion of each species. The thermodynamic calculations indicate that $\Delta P_i$ is greater for Al$X$(g) and Al$X_3$(g) than for the other halides (Table 1). Since, furthermore, the diffusion coefficients of the halides decrease with increasing molecular weight, it can be deduced that in packs activated with ammonium chloride, iodide, or bromide, aluminum is transported mainly by the diffusion of Al$X$(g) to the coating surface where the reaction:

$$3\mathrm{Al}X(g) = 2\mathrm{Al}(s) + \mathrm{Al}X_3(g)$$

occurs. The Al(s) diffuses to form the coating while Al$X_3$(g) diffuses back and reacts with Al(l) in the pack to regenerate Al$X$(g). Moreover, since the value of $\Delta P_i$ for AlCl is greater than those for AlBr and AlI, it is expected that ammonium chloride should be a better activator than the bromide or iodide.

**Table 1 Values of $\Delta P_i$ for the major diffusing gaseous species in variously activated aluminizing packs at 1093 °C (2000 °F)**

| **Activator** | **$\Delta P$ at 1093 °C (2000 °F), atm** | | | | | | |
|---|---|---|---|---|---|---|---|
| | **Al$X$** | **Al$X_2$** | **Al$X_3$** | **Na$X$** | **Na** | **H$X$** | **$H_2$** |
| $NH_4Cl$ | $1.27 \times 10^{-1}$ | $1.59 \times 10^{-2}$ | $-0.93 \times 10^{-1}$ | . . . | . . . | $-5.35 \times 10^{-3}$ | $4.41 \times 10^{-2}$ |
| $NH_4Br$ | $7.66 \times 10^{-3}$ | . . . | $-3.70 \times 10^{-3}$ | . . . | . . . | $-1.93 \times 10^{-5}$ | $1.52 \times 10^{-5}$ |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $NH_4I$ | $1.38 \times 10^{-3}$ | . . . | $-3.01 \times 10^{-4}$ | . . . | . . . | $-3.21 \times 10^{-4}$ | $2.21 \times 10^{-5}$ |
| $NH_4F$ | $1.96 \times 10^{-1}$ | $1.40 \times 10^{-2}$ | 0 | . . . | . . . | $-3.38 \times 10^{-4}$ | 0.2108 |
| NaF | $7.85 \times 10^{-2}$ | $1.94 \times 10^{-3}$ | $-3.15 \times 10^{-3}$ | 0 | $8.22 \times 10^{-2}$ | $-1.81 \times 10^{-4,}$ | . . . |
| NaCl | $4.34 \times 10^{-3}$ | $2.21 \times 10^{-5}$ | $-0.69 \times 10^{-6}$ | 0 | $3.74 \times 10^{-3}$ | $-1.51 \times 10^{-4}$ | . . . |
| NaBr | $1.71 \times 10^{-3}$ | . . . | $6.79 \times 10^{-6}$ | 0 | $9.95 \times 10^{-4}$ | . . . | . . . |
| NaI | $4.52 \times 10^{-3}$ | . . . | $4.9 \times 10^{-9}$ | 0 | $3.53 \times 10^{-3}$ | $-5.12 \times 10^{-5}$ | . . . |

Note: $a_{Al}$ in the pack = 1; $a_{Al}$ at the coating surface = 0.01. Values for $NH_4Br$, $NH_4I$, and NaBr activated packs taken from Ref 20.

In packs activated with $NH_4F$ (or $AlF_3$) (Fig. 1b), $AlF_3$ appears as a solid at the operating temperature, and its vapor pressure is uniform throughout the pack. This constituent, therefore, does not diffuse in the gas phase. As indicated by Fig. 1(b) and the $\Delta P_i$ values in Table 1, aluminum is transported primarily by the diffusion of AlF(g) to the coating surface where deposition takes place by the reaction:

$$3AlF(g) = 2Al(s) + AlF_3(s)$$

The $AlF_3(s)$ which is formed deposits as crystalline solid at the surface, some of which may adhere to the coating. The supply of AlF(g) is maintained by the reverse reaction in the pack.

In packs activated with a sodium halide such as NaCl (Fig. 1c), $NaX(l)$ appears as a condensed phase in the pack. Aluminum deposition occurs mainly by the diffusion of Na(g) and $AlX(g)$ to the coating surface where a reaction of the type:

$$AlX(g) + Na(g) = Al(s) + NaX(l)$$

occurs with the deposition of $NaX(l)$ at the surface. The flux of $AlX(g)$ is maintained by the reverse reaction in the pack. Due to the presence of solid or liquid activator, the operating characteristics of packs containing a condensed halide phase differ from those of packs activated with ammonium chloride, bromide, or iodide in the following ways:

- The condensed activator phase serves as a reservoir whose evaporation compensates for leakage of halide vapors out of "semisealed" coating chambers, resulting in more stable pack behavior over time
- The halide partial pressures and, therefore, the rate of aluminum deposition, increase much more rapidly with temperature, since they vary with the vapor pressure of the condensed phase, which increases rapidly with increasing temperature
- Activator as well as aluminum is transported to the coating surface

The expression given for $K_g$ indicates that the instantaneous flux of gaseous halides will increase with an increase in the density (g/cm$^3$) of aluminum in the pack. The increase would not be directly proportional to $\rho$, however, since increasing the flux of aluminum would increase the aluminum concentration at the surface of the coating and, therefore, have a complex effect on the aluminum transfer rate as a whole.

**Codeposition of Aluminum and Other Elements.** For successful codeposition, the thermodynamic equilibrium between the source elements in the pack and halides in the gas phase must permit the attainment of sufficiently high partial pressures for the halides of all elements desired to be transferred (Ref 16). The partial pressures are functions of the free energies of formation of the halides and activities of the elements in the source alloy. As illustrated by the curves in Fig. 2, the partial pressures of chromium and silicon halides in a pack in which aluminum, chromium, and silicon are present at equal activity are orders of magnitude below those of the aluminum halides, and too low to support the codeposition of an appreciable amount of these metals. An estimate of the general conditions under which codeposition is possible can be obtained by considering the equilibrium constant K for the simple reaction involving a source alloy of two metals A and B and the volatile halides A$X$ and B$X$:

$$\mathrm{A}X(\mathrm{g}) + \mathrm{B}(\mathrm{s}) = \mathrm{B}X(\mathrm{g}) + \mathrm{A}(\mathrm{s})$$

where

$$\mathrm{K} = (P_{\mathrm{B}X}/P_{\mathrm{A}X})(a_\mathrm{A}/a_\mathrm{B})$$

or

$$\mathrm{K} = \exp(-\Delta G^0/RT)$$

and

$$\Delta G^0 = \Delta G_{\mathrm{f,B}X} - \Delta G_{\mathrm{f,A}X}$$

The activity ratio at which $P_{\mathrm{A}X} = P_{\mathrm{B}X}$ is given by:

$$a_\mathrm{A}/a_\mathrm{B} = \exp\,(-\Delta G^0/RT)$$

If A$X$ is more stable than B$X$, the sign of $\Delta G^0$ will be positive and $a_\mathrm{A}/a_\mathrm{B} < 1$. The activity ratio varies rapidly with $\Delta G^0$. For example, at $T = 1300$ K, when $\Delta G^0 = 50{,}000$ J/mole, $a_\mathrm{A}/a_\mathrm{B} = 9.8 \times 10^{-3}$, and when $\Delta G^0 = 100{,}000$ J/mole $a_\mathrm{A}/a_\mathrm{B} = 9.6 \times 10^{-5}$. Conversion of the activity ratio to a composition ratio requires a knowledge of the thermodyamic properties of the source alloy. If this behaves as an ideal solution, the calculations suggest that codeposition is unlikely to occur if the free energies of formation of the source alloy halides (per gram-atom of Cl) differ by more than 50,000 J/mole. The codeposition of chromium with aluminum has been achieved by using chromium-rich source alloys containing 5-10 wt% aluminum (Ref 16, 24, 25). In this case the large negative deviation from ideality of the chromium-aluminum alloys (Ref 26) helps to compensate for the large formation free energy difference between the aluminum and chromium halides.

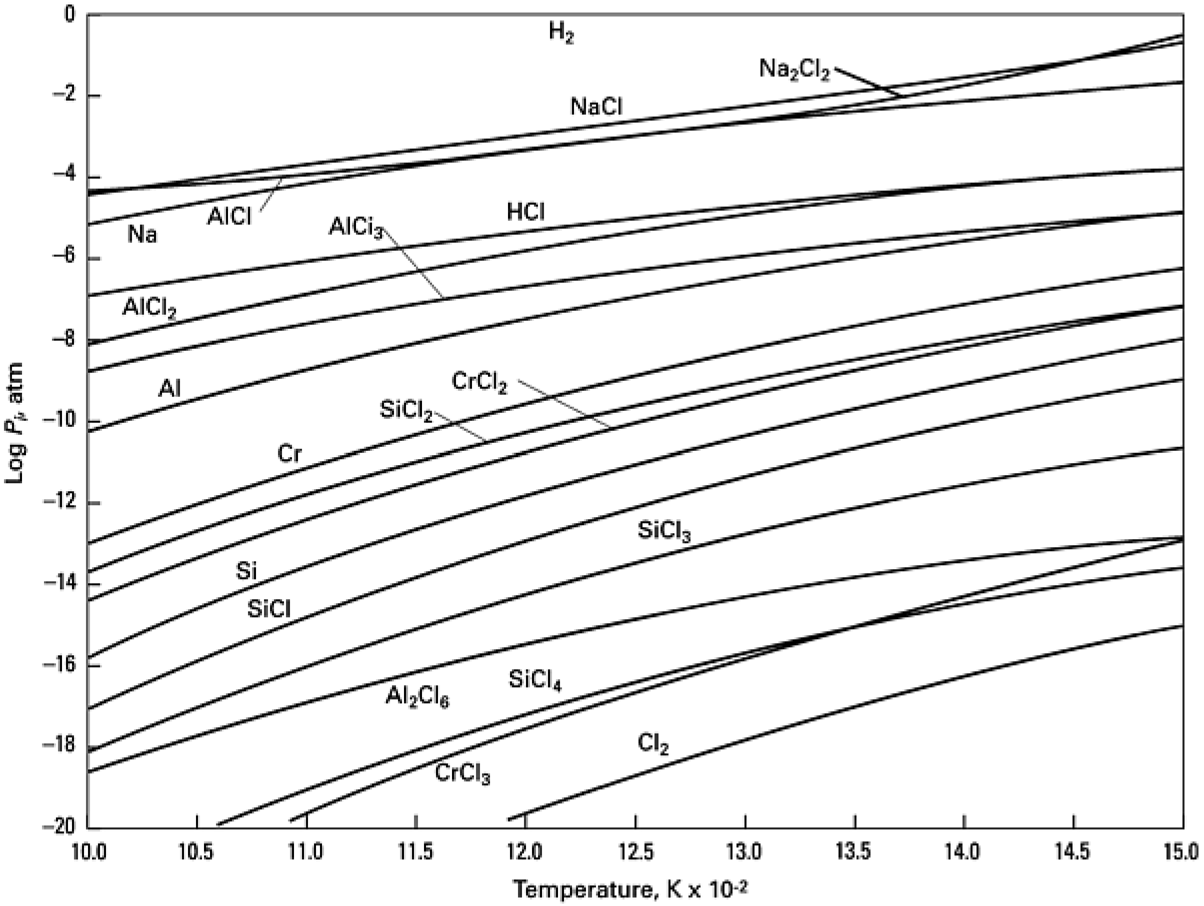

**Fig. 2 Equilibrium partial pressures of gaseous species in a NaCl-activated pack containing pure aluminum, chromium, and silicon and a residual atmosphere of $H_2$. Source: Ref 23, 24**

**Chromizing.** Although many of the same principles apply to chromizing as to aluminizing packs, the fact that chromium halides are less stable than aluminum halides introduces several new factors (Ref 27, 28). In ammonium halide activated chromizing packs, $CrX_2(l)$ appears as a condensed phase. The major constituents in the gas phase in equilibrium with chromium in the pack are $CrX_2(g)$, $CrX_3(g)$, $HX(g)$, and $H_2(g)$. The partial pressure of $HX(g)$ is high enough so that hydrogen reduction according to the reaction:

$$CrX_2(g) + H_2(g) = Cr(s) + 2\ HX(g)$$

at the coating surface is an important mechanism for the deposition of chromium. Since the free energies of formation of $FeX_2$ and $CrX_2$ are comparable, if the substrate is an iron-base alloy the exchange reaction

$$CrX_2(g) + Fe(s) = Cr(s) + FeX_2(g)$$

also occurs. The $FeX_2(g)$ diffuses back into the pack where the reverse reaction leads to the deposition of Fe(s) on the particles of the source alloy, thus changing its composition, while the Cr(s) diffuses into the coating. In this case, the weight of the substrate does not change significantly since it loses one atom of iron for every atom of chromium gained. The exchange reaction does not occur to an appreciable extent when nickel- or cobalt-base alloys are chromized, since the halides of these elements are sufficiently less stable than those of chromium so that significant concentrations of these halides do not appear in the gas phase. The replacement of hydrogen with argon as a protective atmosphere, such as would be possible if $CrX_2(s)$ were used as an activator, would significantly change the deposition rate because of elimination of the hydrogen reduction reaction.

**Siliconizing.** In packs activated with $NH_4Cl$, the principle constituents in the gas phase in equilibrium with pure Si(s) below 1500 K are $SiHCl_3(g)$, $SiCl_4(g)$, $SiCl_3(g)$, HCl(g), and $H_2(g)$ (Ref 28). Free energy considerations indicate that concentrations of the halides of nickel, cobalt, molybdenum, and tungsten in the gas phase would be very small, and these elements would therefore be immobile in such a pack. Hydrogen reduction of $SiHCl_3(g)$ and $SiCl_4(g)$ are predicted to be the most probable silicon deposition reactions at the coating surface when the substrate is a nickel- or cobalt-base superalloy, or pure tungsten or molybdenum:

$$SiHCl_3(g) + H_2(g) = Si(s) + 3HCl(g)$$

$$SiCl_4(g) + 2H_2(g) = Si(s) + 4HCl(g)$$

In a pack for the coating of these metals activated with $SiCl_4(l)$, in which $SiHCl_3$, HCl, as well as $H_2$ would be absent, silicon deposition would presumably occur mainly via the disproportionation reaction:

$$2SiCl_2(g) = Si(s) + SiCl_4(g)$$

and, to a smaller extent, by:

$$4SiCl_3(g) = Si(s) + 3SiCl_3(g)$$

Formation free energy values indicate that various amounts of iron, chromium, and titanium chlorides will appear in the gas phase, and these substrate elements will exhibit varying degrees of mobility in a chloride activated siliconizing pack. In this case, exchange reactions such as:

$$SiCl_4(g) + 2M(s) = 2MCl_2(g) + Si(s)$$

and

$$SiCl_2(g) + M(s) = MCl_2(g) + Si(s)$$

may play a significant role in the deposition process. Finally, since for the reaction:

$$3/2SiCl_4(g) + Al_2O_3(s) = 3/2SiO_2(s) + 2AlCl_3(g)$$

where $\Delta G^0$ = -15,400 cal at 1300 K, alumina is evidently not inert in a siliconizing pack, and the use of a different filler such as silica, or silicon dioxide ($SiO_2$) is advisable.

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## Properties of Diffusion Coatings on Superalloys

**Coating Formation Mechanisms.** Diffusion aluminide coatings on superalloys are classified by microstructure as being of the "inward diffusion" or "outward diffusion" type according to the seminal work of Goward and Boone (Ref 29). The classification was derived from studies of aluminide coating formation on a typical nickel superalloy, Udimet 700, which has a nominal composition of Ni-15Cr-17Co-5Mo-4Al-3.5Ti. It was observed that for pack mixes containing pure aluminum (unit or "high" activity), coatings formed by predominant inward diffusion of aluminum through $Ni_2Al_3$, and deeper in the coating, through aluminum-rich NiAl (for pure nickel, by inward diffusion through $Ni_2Al_3$ only). The diffusion rates are abnormally high--practical coating thicknesses can be achieved in a few hours at 760 °C (1400 °F). A typical as-coated microstructure is shown in Fig. 3(a). Upon further heat treatment at, for example, 1080 °C (1975 °F) for four hours, the microstructure shown in Fig. 3(b) is formed--the coating matrix is now NiAl. The single-phase region in the center of the coating is nickel-rich NiAl grown by predominant outward diffusion of nickel from the substrate alloy to react with aluminum from the top layer. The inner layer, or so-called interdiffusion zone, consists of refractory metal (tungsten, molybdenum, tantalum, etc.) carbides and/or complex intermetallic phases in a NiAl and/or $Ni_3Al$ matrix, formed by the removal of nickel from the underlying alloy, thereby converting its Ni-$Ni_3Al$ structure to those phases. Conversely, if the activity of aluminum in the source is reduced by alloying with, for example, nickel or chromium, to a level where nickel-rich NiAl is formed at the surface, the coating, shown in Fig. 3(c), grows by predominant outward diffusion of nickel from the substrate to form NiAl by reaction with aluminum from the source. The lower layer of this coating is formed as previously described. Diffusion rates are relatively low so the coating process must be carried out at higher temperatures--usually greater than 1000 °C (1830 °F). These mechanisms are consistent with those observed by Janssen and Rieck (Ref 30) and later by Shankar and Seigle (Ref 31) during studies of diffusion in the simple nickel-aluminum system. Figure 4 shows the ratios of diffusion rates of nickel and aluminum across the range of stoichiometry of NiAl (Ref 31). At the high aluminum limit of NiAl, diffusion is by predominant motion of aluminum, confirming the earlier postulate of Goward and Boone (Ref 29). A coating with a matrix of NiAl formed by this diffusion mechanism is shown in Fig. 3(d). Upon further heat treatment, this coating will stabilize with a structure similar to that shown in Fig. 3(b).

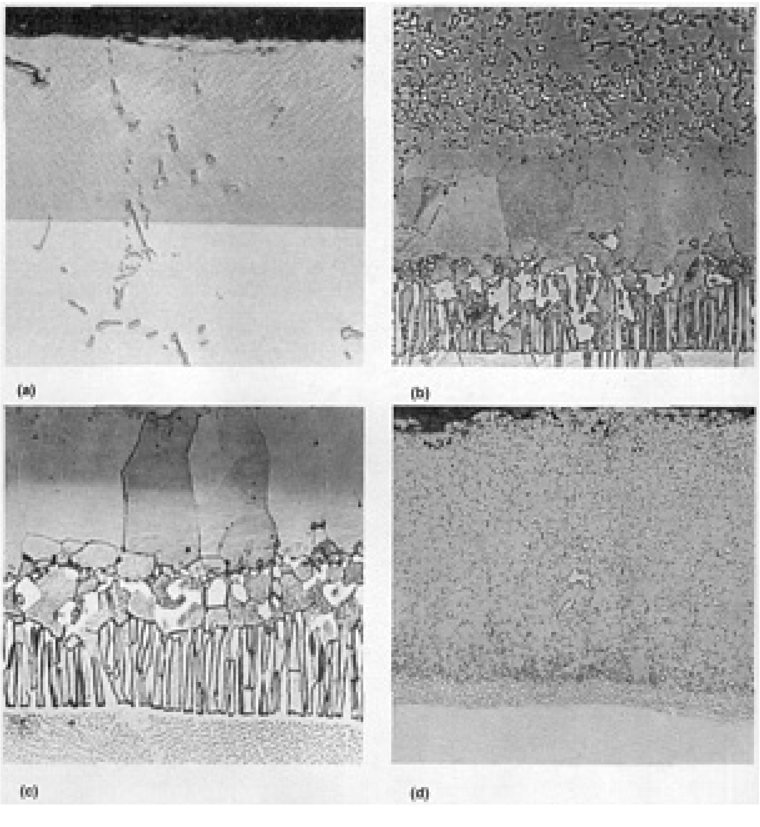

**Fig. 3 Archetypical microstructures of aluminide coatings on a nickel superalloy. (a) Inward diffusion based on**

**$Ni_2Al_3$ (and aluminum-rich NiAl). (b) Same as (a) but heat treated at 1080 °C (1975 °F). (c) Outward diffusion of nickel in nickel-rich NiAl. (d) Inward diffusion of aluminum in aluminum-rich NiAl. Source: Ref 29**

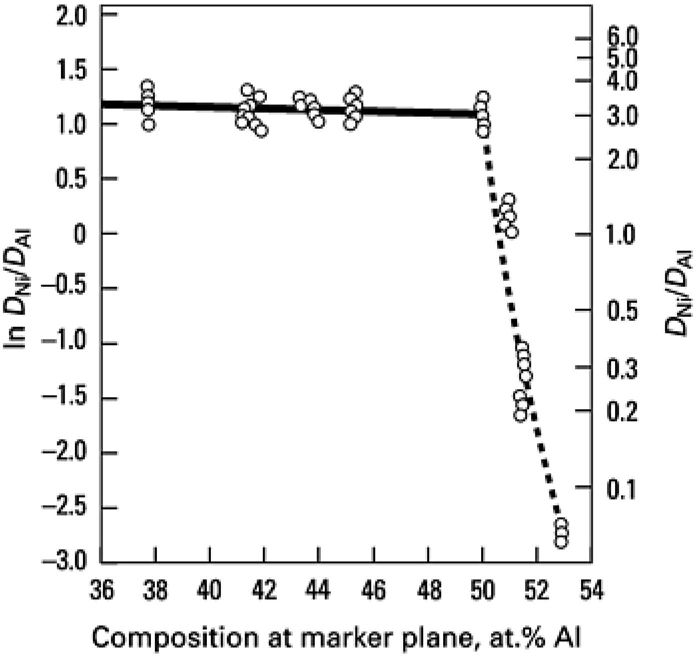

**Fig. 4 Ratio of diffusion coefficients of nickel and aluminum as a function of aluminum in NiAl. Source: Ref 31**

The above mechanisms apply equally to those coatings formed by out-of-contact or CVD processes, from slurry "slip packs" (Ref 32), and from aluminum alloy powders deposited on superalloys by slurry spraying or by slurry electrophoresis (Ref 33). Coatings applied by spraying (Ref 34, 35) or electrophoretically depositing (Ref 33) pure aluminum or low-melting aluminum alloys, for example, Al-10Si, and then heat treating, form by dissolution of the superalloy into the melt until the melt solidifies, followed by diffusion of aluminum similar to that described above.

All known aluminide-based coatings on nickel superalloys, including those modified by chromium, platinum, and silicon, have one of the archetypical microstructures described above. For pure nickel and nickel alloys containing no aluminum, (or <0.2% Al), the interdiffusion zone does not form. For pure nickel, Kirkendall voids and alumina, from oxygen in the nickel, form at the coating/substrate interface (Ref 29). For nickel alloys containing no aluminum, voids, refractory metal layers, and alumina form at the interface (Ref 29). The adherence of the resulting coatings is compromised and they may not be practically useful. It is anticipated that similar mechanisms apply to the coating of cobalt superalloys. Again, the absence of aluminum in many of these alloys precludes the formation of the interdiffusion zone common to most nickel superalloys. Rather, a refractory metal (tungsten, chromium) carbide forms at the juncture to the base alloy (Ref 40). As described for similar nickel-base alloys, this refractory metal carbide and alumina formed from oxygen in the aluminum-free alloys, can also compromise the adherence of these coatings. Special processing conditions, involving slow coating growth at high temperatures (up to 1095 °C, or 2000 °F) from relatively low aluminum activity sources, can sometimes be used to achieve satisfactory coating adherence. Minor additions of aluminum (1 to 2%) to cobalt superalloys completely obviate these problems--stable interdiffusion zones then form analogous to those on most nickel superalloys (Ref 36).

Diffusion chromide coatings formed on a nickel superalloy by pack cementation and out-of-contact processes are illustrated in Fig. 5. The coating deposited by pack cementation is overlaid with a thin layer of alpha-chromium as shown in Fig. 5(a). Users generally require that this phase be absent. It must then be removed chemically, or alternatively the coating applied by an out-of-contact process to produce the structure shown in Fig. 5(b). These coatings usually then contain chromium to the extent of 20 to 25% at the outer surface. Coating formation, from chromium-alumina-activator (usually ammonium chloride) packs or from out-of-contact sources (powders or chromium granules as described in Ref 18) involves approximately equal rates of interdiffusion of chromium and nickel. Significant depletion of titanium and aluminum from the alloy surface occurs because the sources do not contain these elements. The desired coatings are thus solid solutions of chromium in the remaining nickel-base alloy. Internal oxides of aluminum and titanium can form because the oxygen potential of the sources is normally sufficient to cause internal oxidation. This can be avoided by adding aluminum to the sources in amounts just below that which would cause aluminizing rather than chromizing (Ref 38).

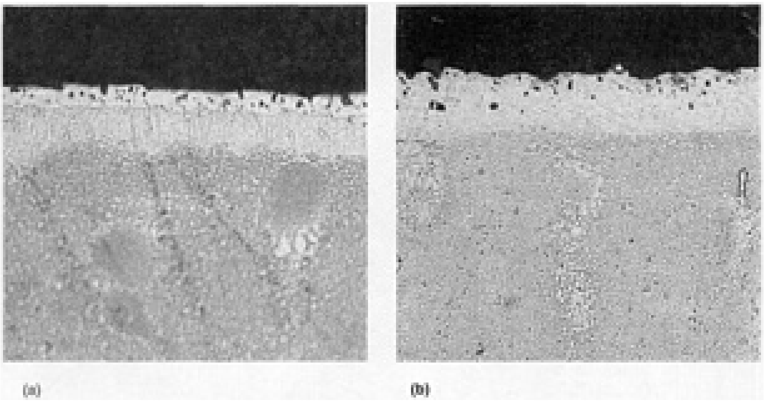

**Fig. 5 Chromium diffusion coatings on a nickel superalloy by (a) pack cementation and (b) out-of-contact gas-phase processing. Both at 500×. Source: Ref 37**

Rapp and co-workers (Ref 16) have refined the theory of codeposition of aluminum, chromium, silicon, and reactive elements (yttrium and hafnium) by pack cementation and related processes and have demonstrated the benefits derived therefrom. These processes and coatings should find practical applications in the near future.

**Coating Protection and Degradation.** Simple aluminide coatings resist high-temperature oxidation by the formation of protective layers of alumina and can be used up to about 1150 °C (2100 °F). The coatings degrade by loss of aluminum due to spalling of oxides under thermal cycling conditions. Incorporation of reactive elements, such as yttrium and hafnium, by codeposition during aluminizing (Ref 16) can significantly improve adherence of the protective alumina scales and therefore extend coating life. At temperatures above about 1000 °C (1830 °F) interdiffusion of the coatings with substrates contribute significantly to degradation (Ref 39). Practical coating service lives are limited to operating temperatures of 870 to 980 °C (1600 to 1800 °F) with only short excursions at the highest temperatures.

Chromium modifications, made by diffusion chromizing prior to aluminizing (Ref 14) or by codeposition of aluminum and chromium (Ref 16, 41, 42), have enhanced resistance to various forms of molten-salt hot corrosion. Electroplating with a thin layer of platinum (and possibly rhodium) followed by aluminizing (Ref 15) forms a coating with substantially improved resistance to both oxidation and high-temperature (Type I) molten-salt corrosion. Additions of up to about 5% Si improve both oxidation and hot corrosion resistance (Ref 13). Silicon can be codeposited with aluminum by pack cementation (Ref 16, 43) and related out-of-contact processes. So-called slurry processes wherein a liquid suspension of aluminum and silicon powders is applied to the alloy surface, then dried and fired at elevated temperatures, can also be used to incorporate silicon (Ref 35).

The oxidation and hot corrosion resistance of these coatings are more or less influenced by the composition of substrate alloys. Tantalum and hafnium improve cyclic oxidation and hot corrosion resistance, the latter element by improving the adherence of the protective layer of alumina (Ref 44). Molybdenum and tungsten compromise hot corrosion resistance.

Because of the brittle fracture behavior of NiAl up to temperatures of 650 to 775 °C (1200 to 1400 °F), all aluminide coatings exhibit such fracture below these temperatures while above these limits ductile behavior occurs (Ref 45). This behavior can either compromise or enhance thermal fatigue resistance of substrate alloys depending on such complex factors as the exact nature of the thermal cycle and the structure--equiaxed, directionally solidified, or single crystal--of the alloys (Ref 46). If these effects are limiting, designers may require use of more expensive overlay coatings of the MCrAlY (M = Co and/or Ni) and/or thermal barrier (zirconia) types.

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## Manufacturing Technology

A flow path for a typical production-scale pack cementation process is shown in Fig. 6. Practical manufacturing aspects of the various steps of the process are described below.

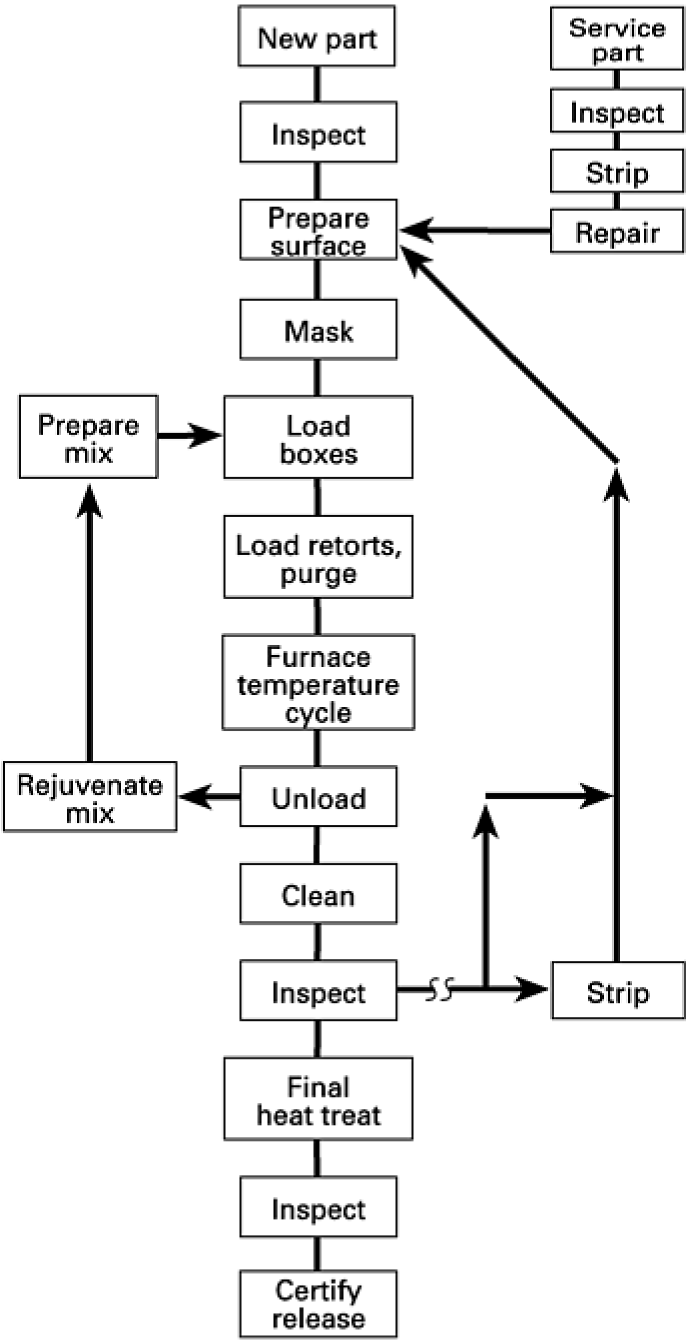

**Fig. 6 Flow diagram for typical pack cementation processes. Source: Ref 37**

**Inspection.** Visual and flow inspection of cooled airfoils before coating affords the last opportunity to determine if all surfaces are suitable for the intended use. Oxidized surfaces and the remains of investment casting core and shell materials can interfere with coating deposition and compromise useful service lives.

**Surface Preparation.** Surface preparation to remove superficial oxides is usually accomplished by grit blasting with intermediate sized alumina grit. Grit blasting with silicon carbide is avoided because any entrapped grit forms low-melting eutectic phases with superalloys. Vibratory finishing is used where a surface finish is specified to achieve aerodynamic design intent. Removal of oily residues from machining by vapor degreasing or low temperature burnout may be required.

**Masking** to prevent coating on critical mechanical contact surfaces, such as blade roots, may be required. This can be accomplished with mechanical, oxide barrier, or chemically reactive masks. Complete exclusion of coating by mechanical masks is difficult for processes with high throwing power, a property common to those run at higher temperatures, for example, >870 °C (1600 °F). Chemically reactive masks containing elemental or alloy powders which react with the coating species to prevent coating deposition on the surface are more effective at higher processing temperatures. Coating before machining, to obviate expensive masking requirements, is strongly recommended.

**Pack Mix (Source) Preparation.** Preparation of pack mixes requires the use of large-scale powder handling equipment designed for effective mixing, storage, and dispensing. Examples of mix (source) compositions are given in Table 2. Closed handling systems are now required for health and safety reasons. The possibility of explosive burning of metal powders must be excluded. In general, various chemical engineering technologies are applicable.

**Table 2 Examples of pack mixes/sources and processing parameters for various coatings on nickel and cobalt superalloys**

| Coating type | Source composition | Processing parameters |
|---|---|---|
| Pack aluminizing, inward diffusion in $Ni_2Al_3$ in nickel alloys(a) | 5-20% Al (Al-10Si), 0.5-3% $NH_4Cl$, balance $Al_2O_3$ powder | 1 to 4 h at 650 to 680 °C (1200 to 1255 °F) in air, argon, $H_2$; heat treat 4 to 6 h at 1095 °C (2000 °F) in argon |
| Pack aluminizing, inward diffusion in NiAl in nickel alloys(b) | 44% Al, 56% Cr $NH_4Cl$ balance $Al_2O_3$ powder | 5 to 10 h at 1040 °C (1900 °F) in vacuum (argon, $H_2$) |
| Pack aluminizing, outward diffusion in NiAl in nickel alloys(c) | 2-3% Al, 20% Cr, 0.25% $NH_4HF_2$, balance $Al_2O_3$ powder | 25 h at 1040 °C (1900 °F) in argon |
| Pack aluminizing of cobalt alloys(d) | 8% Al, 22% Cr 1% $NH_4F$, balance $Al_2O_3$ powder | 4 to 20 h at 980 to 1150 °C (1800 to 2100 °F) in argon |
| Gas-phase aluminizing, outward diffusion in NiAl in nickel alloys(e) | 10% $Co_2Al_5$, 2.5% NaCl, 2.5% $AlCl_3$, balance $Al_2O_3$ powder | 3 h at 1095 °C (2000 °F) in argon |
| Gas-phase aluminizing, outward diffusion in NiAl in nickel alloys(f) | 30% Al-70% Cr alloy granules, $NH_4F$ | 4 h at 1150 °C (2100 °F) in argon |
| Pack or gas-phase chromizing of nickel alloys(g) | 15% Cr, 4% Ni, 1% Al, 10.25% $NH_4Br$ or $NH_4Cl$, balance $Al_2O_3$ powder | 3 h at 1040 °C (1900 °F) in argon |

(a) U.S. Patent 3,544,348.

(b) U.S. Patent 3,625,750.

(c) U.S. Patent 3,716,398.

(d) U.S. Patent 3,257,230.

(e) U.S. Patent 4,132,816.

(f) Ref 18.

(g) U.S. Patent 3,801,353

**Loading Boxes and Retorts.** Loading of parts, which consists of embedding parts in coating powder mixtures in controlled positions in coating boxes ("boats"), is labor intensive and environmentally unfriendly. Automation with robotics is theoretically possible but no such systems are known to be in use.

**Furnace Temperature Cycle and Heat Treatments.** Furnaces with specified temperature capability and uniformity and associated inert gas delivery systems are the most costly components of coating plants. For most processes, coating boxes are loaded into retorts constructed of high-temperature alloys, for example, Inconel 600 or 601, and are capable of being sealed (sand, glass, or water-cooled seals) to exclude air. Retorts for gas-fired or electrically fired pit furnaces can be as large as 1.2 m (4.0 ft) in diameter and 2.4 m (8.0 ft) tall. A supply of inert gas, argon or hydrogen is required to purge retorts free of air and moisture, and to maintain an inert environment during the coating cycle.

A coating cycle includes bringing the retort and contents to temperature, holding at temperature for several hours, and then cooling to ambient temperature while maintaining the inert gas environment. Coating temperatures range from 650 °C (1200 °F) for low-temperature inward diffusion aluminizing to as high as 1150 °C (2100 °F) for outward-diffusion aluminizing of nickel superalloys. Processing times range from 4 to 24, h respectively. Some examples of time-temperature cycles are given in Table 2. Temperature uniformity within the retort load during the holding period is usually required to be within 14 °C (25 °F) of nominal. Off-gases from the process, carried by the inert gas flow, contain environmentally harmful chemicals such as aluminum chloride, hydrogen chloride, aluminum fluoride, hydrogen fluoride, and chromium chloride. These must be captured by scrubbing and filtering before the inert gas is vented to the atmosphere, and then disposed of in accord with applicable environmental regulations.

Unloading the retorts and boxes, separating the parts from powders and masking devices, and cleaning the parts, including thorough water washing, are currently labor intensive. Blades and vanes may require further heat treatment to cause proper development of the coating and/or to obtain optimum mechanical properties of the substrate alloy. Such treatments require inert or vacuum environments with the same rigid temperature controls as the coating thermal cycle.

**Source Rejuvenation.** It is common practice to rejuvenate powder mixes by additions of coating elements and alloys, and activators. Chemical analysis of the used mixes facilitates control of critical constituents. For simple systems historical data can sometimes be applied empirically for these purposes. Disposal of used mixes is quite costly under current environmental regulations. Recovery and recycling of expensive metals is being practiced with increasing frequency.

**Quality Control.** The most widely accepted quality control practice requires coating of representative samples with each processing cycle and destructively evaluating these to determine accordance with user specifications for thickness (in the range of 25 to 100 μm, or 1 to 4 mils for most applications), and microstructure. Quantitative analysis by x-ray fluorescense or electron microprobe for elemental composition, for example, aluminum, chromium, and platinum content, may also be required. Complete coating coverage can be confirmed by contact thermocouple measurement or by heat tinting aluminized nickel alloys in air at 621 °C (1150 °F) for one hour--coated areas exhibit a gold color and uncoated areas a dark blue color. Procedures for nondestructive coating thickness measurements are available (Ref 47), but are not widely used for control of new coating production. There is increasing interest in measuring coating thickness and aluminum content to judge the remaining life of coatings on used parts (Ref 48).

If inspection reveals faulty coatings, parts may be overcoated using appropriate time-temperature cycles. In extreme cases the coatings are stripped in acid solutions, for example, nitric or hydrochloric acid for aluminide coatings, and subjected to another full coating cycle. This is to be avoided because aluminide coatings are formed by consumption of the nickel component of the alloy and removal of the coating can result in significant reduction in critical part dimensions. Increasingly, statistical process control is being used to avoid these problems.

**Out-of-Contact Processes.** When aluminizing and/or chromizing are to be accomplished by out-of-contact CVD processes, all preparation steps are as described previously. For simple static aluminizing or chromizing, parts may be surrounded by suitable source material in the form of granules contained in baskets in a variety of coating box designs. A typical example is shown schematically in Fig. 7. Activator chemicals are simply sprinkled into the boxes which are then covered, placed in retorts, purged with inert gas and subjected to the usual time-temperature cycles. If coating of blade and vane cooling passages is required, a flow of the inert gas is used to carry the coating species through the passages (Ref 19). Alternatively, pressure can be lowered (Ref 49) or cycled (Ref 50) to accomplish internal passage coating. For so-called CVD processes, the coating species may be generated by passing reactive gases, based on hydrogen chloride or hydrogen fluoride in a carrier gas over the source material in a separate reactor with the gas stream directed into the main coating chamber to coat external or internal surfaces or both (Ref 17). In any case, all other items shown in Fig. 6 still apply. More detailed information on CVD processing can be found in the article "Chemical Vapor Deposition of Nonsemiconductor Materials" in this Volume.

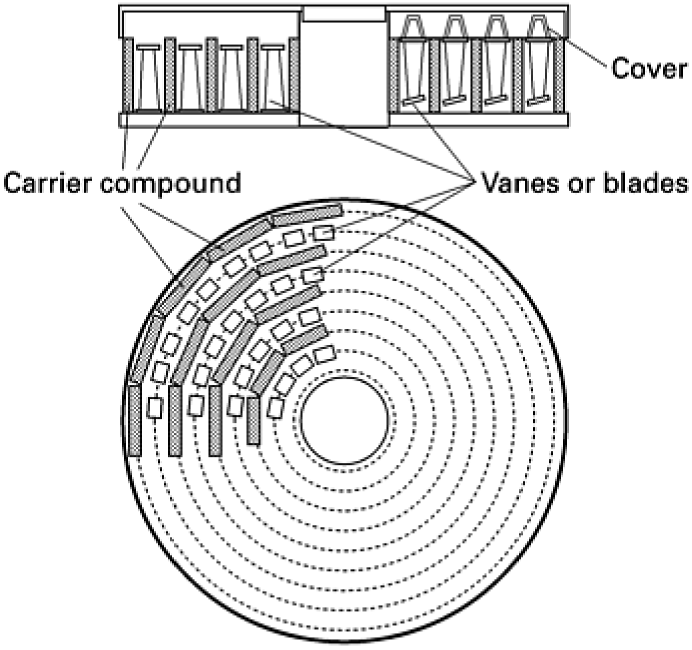

**Fig. 7 Schematic of a coating chamber for an out-of-contact aluminizing process. Source: Ref 18**

**Repair.** It is frequently possible to repair blades and vanes that have been in service for some time. To accomplish this, the first coating, now depleted during service, is removed by acid stripping. Parts are then repaired as appropriate, by welding, and/or brazing and re-machining (Ref 51). Suitable coatings are then re-applied as shown in Fig. 6.

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## Practical Applications

**For aircraft gas turbine blades** fabricated from moderately-corrosion resistant nickel alloys (those containing 12 to 15% Cr), simple aluminide coatings of the inward and outward diffusion types provide adequate protection for many contemporary engines. When alloys are more corrosion prone (those containing 7 to 10% Cr), current practice is to modify aluminide coatings by chromizing prior to aluminizing. Aluminizing should be by inward diffusion of aluminum to locate the higher chromium concentration in the outer layer of the coating (Ref 14). For more severe Type I hot corrosion resulting from exposure of engines to salt spray from marine environments, modification of aluminide coatings with silicon (or better, by platinum) can prove to be the more cost effective solution.

If more expensive structure modifications of nickel superalloys, such as single crystals, are used to full strength-temperature capabilities to enhance fuel efficiency, contemporary diffusion coatings may not meet design objectives for oxidation and/or thermal fatigue service lives of the turbine. For these conditions use of the more expensive MCrAlY overlay and/or ceramic (zirconia-based) thermal barrier coatings may be in order.

**Ground-Based and Marine Gas Turbines.** Achieving cost effective hot corrosion protection for ground- or marine-based gas turbines is a more complex problem because of wide variations in local environments with respect to air contaminants (salts, sulfur oxides, and other industrial pollutants) and fuel constituents (salts, sulfur, vanadium, etc.). Burgel (Ref 11) identified chromizing as one of the best solutions in ground-based engines subjected to severe Type II hot corrosion in the metal temperature range of 740 °C (1365 °F)--this in comparison to silicide, platinum-aluminide, and some MCrAlY type coatings. Chromide coatings are, however, not satisfactory above 800 °C (1470 °F). Platinum aluminides provide moderate protection at somewhat higher temperatures but may not be sufficiently resistant to lower temperature Type II hot corrosion. Similar considerations appear to apply for marine environments (Ref 52).

The trend for most ground-based gas turbines is toward the use of various modifications of MCrAlY type coatings, particularly those with higher chromium and perhaps silicon additions (Ref 53, 54). For the very latest machines operating at the higher temperatures for improved fuel efficiency, these coatings may be overaluminized (Ref 55, 56) and internal cooling passages simultaneously aluminized to resist increasingly severe oxidation conditions.

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## Future Development

Future development activity for pack cementation and related coatings, primarily for use in aircraft engines, will focus on more efficient automated and environmentally friendly manufacturing technology. In addition, means to incorporate additions of beneficial elements, such as hafnium and other oxygen-active elements, by codeposition with aluminum, should become practically available in the near future (Ref 16).

## Pack Cementation Aluminizing of Steels

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The pack cementation aluminizing process is used to improve the performance of steels in high-temperature corrosive environments. The complex aluminide intermetallic coatings formed during the process exhibit superior resistance to oxidation, carburization, and sulfidation (Ref 57). Table 3 provides a partial listing of commercial applications for the pack aluminizing process. Typical applications include carbon steel heat exchanger tubes used in sulfuric acid plants, low-alloy steel pipes and fittings used in petroleum refinery heaters, type 304 stainless steel vessels used in flue gas desulfurization systems, and HK or HP cast tubing for ethylene pyrolysis units.

**Table 3 Partial list of commercial applications of pack cementation aluminizing**

| Industry | Component | Typical materials aluminized |
|---|---|---|
| Hydrocarbon processing | Refinery heater tubes | $2\frac{1}{4}$% Cr-1% Mo steel |
| | Ethylene pyrolysis furnace tubes | Incoloy 802 |
| | Hydrodesulfurizer furnace tubes | $2\frac{1}{4}$% Cr-1% Mo steel |
| | Delayed coker furnace tubes | 9% Cr-1% Mo steel |
| | Catalyst reactor screens | 347 stainless steel |
| | Catalyst reactor grating | Carbon steel |
| Sulfuric acid | Gas-to-gas heat exchanger tubes | Carbon steel |
| Industrial furnace components | Aluminum plant furnace parts | Carbon steel |
| | Heat treating pots | Carbon steel |
| | Structural members | High-nickel alloy steel |
| | Thermowells | Carbon and stainless steels |
| Steam power and cogeneration | Waterwall tubes | $2\frac{1}{4}$% Cr-1% Mo steel |
| | Fluidized bed combustor tubes | $2\frac{1}{4}$% Cr-1% Mo steel |
| | Waste heat boiler tubes | Carbon steel |
| | Economizer and air preheater tubes | $2\frac{1}{4}$% Cr-1% Mo steel |

|  |  |  |
|---|---|---|
|  | Superheater tubes | $2\frac{1}{4}$% Cr-1% Mo steel |
| Aerospace[(a)] | Turbine blades | Nickel-base superalloy |
|  | Turbine vanes | Nickel-base superalloy |
| Flue gas scrubbers | $NO_x/SO_x$ removal units | 304 stainless steel |
| Chemical processing | Reactor vessels and tubing | 304/316 stainless steel |
| Cement | Cooler grates | Stainless steel, HP, HK |

(a) Aerospace applications are described in the Section "Diffusion Coatings for Gas Turbine Engine Hot Section Parts" of this article.

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## Generalized Reaction Agents and Products

As described in the previous Section of this article which dealt with diffusion coatings for turbine blades and vanes, the pack cementation aluminizing coating process is performed in a pack consisting of the following mixture:

- Aluminum--in the form of a pure metal powder or alloy powder
- Filler--a ceramic powder phase, to prevent sintering of the mix during high-temperature processing. Usually aluminum oxide is used
- Activator--a volatile halide, usually an ammonium or sodium halide, to act as a chemical transfer medium for the aluminum

The precleaned steel parts to be pack aluminized are placed in a retort, or reactor vessel, with the pack mixture. Using ammonium halide ($NH_4X; X$ = F,Cl,Br,I) as the activator, the following sequence of high-temperature reactions occurs when aluminum is deposited on the surfaces of an iron-base alloy:

- Decomposition of $NH_4X$

$$NH_4X(s) = NH_3(g) + HX(g)$$

- Formation of volatile aluminum halides

$$6HX(g) + 2Al(pack) = 2AlX_3(g) + 3H_2(g)$$

$$AlX_3(g) + 2Al(pack) = 3AlX(g)$$

- Deposition of aluminum onto steel (substrate) surface

$$2AlX(g) + 3Fe(substrate) = 2AlFe(alloy) + FeX_2(g) \text{ (displacement reaction)}$$

$$3FeX_2(g) + 5Al(pack) = 3AlFe(alloy) + 2AlX_3(g) \text{ (displacement reaction)}$$

$$3AlX(g) + 2Fe(substrate) = AlX_3(g) + 2AlFe(alloy) \text{ (disproportionation reaction)}$$

$$2AlX(g) + 2Fe(substrate) = 2AlFe(alloy) + X_2(g) \text{ (decomposition reaction)}$$

$$2AlX(g) + H_2(g) + 2Fe(substrate) = 2AlFe(alloy) + 2HX(g) \text{ (reduction reaction)}$$

-

It is probable that deposition occurs principally by the disproportionation reaction, with replacement of Al$X$ by the reaction $AlX_3(g) + 2Al(pack) = 3AlX(g)$. Rates of deposition are controlled by partial pressure gradients of reaction species between the source material and the coating surface.

Photomicrographs of the structure, including the diffusion zones, of pack aluminized low-carbon steel and type 304 stainless steel are shown in Fig. 8 (Ref 58). Comprehensive metallographic, x-ray, and electron microprobe analysis of the aluminum diffusion zone in stainless steels indicate an aluminum-rich surface (26-34 wt% Al) after undergoing this pack aluminizing process (Ref 59).

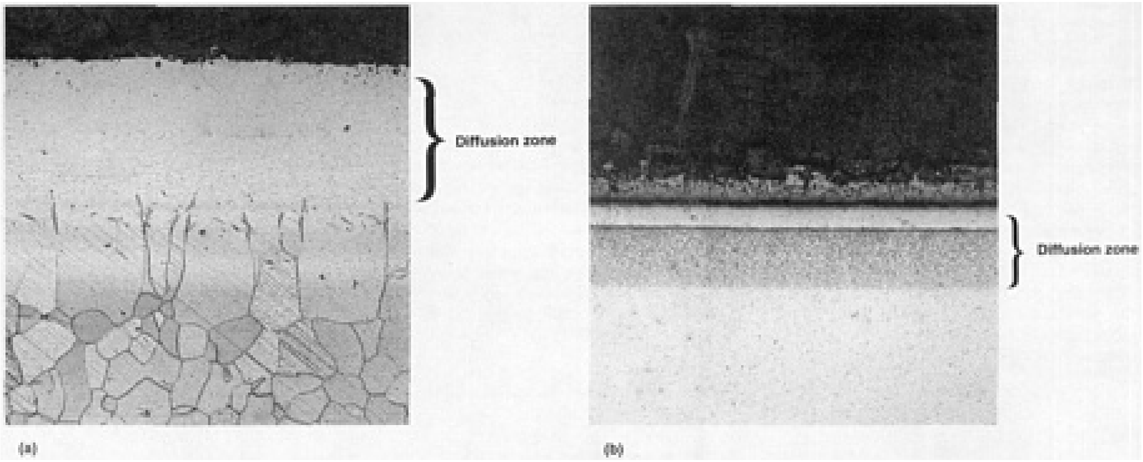

**Fig. 8 Photomicrographs showing the structure of pack aluminized (a) low-carbon steel and (b) type 304 stainless steel. Courtesy of Alon Processing, Inc.**

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## Processing Procedures

**Cleaning.** Prior to processing of parts, all surfaces should be cleaned to be free of oil, grease, mill scale, crayon, weld slag or spatter, and other foreign materials. A typical cleaning procedure might involve acid pickling to remove mill scale, removal of oil and/or grease by vapor degreasing, as well as abrasive or grit blasting. Grit blasting should be done using aluminum oxide abrasives (60 to 320 mesh, depending on surface finish) at 400 to 550 kPa (60 to 80 psi) from a 75 to 150 mm (3 to 6 in.) standoff. Residual grit should be blown off with a clean source of compressed air. From this point on until packing, parts should be handled with clean cotton gloves to prevent contamination.

**Powder Blending.** Depending on the material being processed and the desired aluminum activity of the pack, the aluminum pack cementation powder mix contains the following typical range:

- Aluminum (pure metal or ferroalloy): 4% to 25%
- Inert filler ($Al_2O_3$): 70% to 95%
- Halide activator: 0.5% to 4%

The two types of pack cycles are known as high activity and low activity (see the discussion on "Principles of Pack Diffusion Coating" in the previous Section of this article on "Diffusion Coatings for Gas Turbine Engine Hot Section Parts" ). A high-activity pack contains a relatively high fraction of pure aluminum (Table 2) as the source material, a halide activator, and an inert diluent, usually alumina; the process is performed at lower temperatures (650 to 815 °C, or 1200 to 1500 °F). This type of pack generally requires a subsequent high-temperature heat treatment under an inert atmosphere in order to complete diffusion and obtain the required surface aluminum content and diffusion depth. A low-activity pack contains a lower fraction of aluminum, usually in the form of an alloy with iron or chromium, and is performed at higher temperatures (815 to 1150 °C, or 1500 to 2100 °F) with no subsequent heat treatment.

**Packing.** Retorts can be constructed from a variety of alloys ranging from plain carbon steel to nickel-base superalloys, depending upon desired service life and acceptable costs. Retorts should be fabricated to best accommodate the job being processed. The parts to be coated in the retort should be completely covered with pack mix and should not be allowed to touch each other or the walls of the retort. Prior to sealing the retort, it is advised to make sure that the pack mix is well settled. Low-temperature (high-activity) packs can be run in air, but with high-temperature (low-activity) packs, a protective blanket of hydrogen or inert argon gas is required. For obvious reasons, the use of argon is preferable for safety considerations. High-temperature retorts must be constructed with provisions for gas input/removal kept in mind.

**Coating Cycle.** Depending on the base material to be pack aluminized, processing temperatures can range from 650 to 1150 °C (1200 to 2100 °F), as measured from a thermocouple inside the retort. At specific process temperatures, a maximum of ±14 °C (±25 °F) must be maintained. Process cycle times can range from 3 to $\geq$40 h, depending on process temperature and base material to be processed. Transport of aluminum as aluminum chloride through the pack and solid state diffusion of aluminum through the base material is more influenced by process temperature than process time. Although higher process temperatures generally increase surface aluminum content and overall diffusion depth, in some cases the higher processing temperatures can have undesirable effects on the mechanical properties of the base material. In these cases, parts are processed at lower temperatures for longer periods of time.

**Finishing.** Retorts should be cooled to below 95 °C (200 °F) before opening. Parts should be removed and cleaned by brushing or by a light wet or dry abrasive blast. Certain alloys require controlled cooling cycles to maintain mechanical properties.

## Classification of Materials

Pack compositions, process temperatures and process times depend on the type of base material to be aluminized. Materials fall into one of the following general classifications:

- Class I: carbon and low-alloy steels and copper
- Class II: ferritic and martensitic stainless steels and austenitic stainless steels with less than 20% Ni
- Class III: austenitic stainless steels with 21-40% Ni and iron-base superalloys

- Class IV: nickel-and cobalt-base superalloys

As a general rule, overall aluminum diffusion is slower as the nickel, chromium, and cobalt contents increase. Therefore, higher temperatures and longer process times are required to produce greater aluminum diffusion thicknesses as the base material goes from Class I to Class IV. (The Class IV materials are covered in the Section "Diffusion Coatings for Gas Turbine Engine Hot Section Parts" of this article.)

## Quality Control

Process quality is monitored by testing of coupons or test pieces which are run in the retort with the production materials during the process cycle. These test pieces are used to determine quality and depth of aluminum diffusion, and should be of the same or similar base material as the production parts. These pieces should be located in the hottest and coldest sections of the furnace loads. These locations should be determined prior to actual processing of parts through furnace surveys.

After the processing has been completed, the test pieces are removed from the retort and examined according to ASTM C 664-87, "Standard Test Methods for Thickness of Diffusion Coating." There are two procedures for measuring the thickness of diffusion coatings. Method A is the determination of the dimensional-change thickness, defined as the difference in the part before and after coating. This method employs a micrometer. Method B is the determination of total coating thickness, defined as the distance between the observably unaffected substrate and the exterior surface of the coating. This method employs standard metallographic specimen preparation equipment for mounting, polishing, and etching as well as a metallographic or optical microscope for observation of the diffusion layer at 100× and 500×.

Quality control reporting should include the maximum, minimum, and average coating thickness (in mils) of the individual measurements made on a specific part of the specimen surface. If Method B is used, a photomicrograph showing the bounds of a typical area of the coating is recommended. Depending on base materials and processing conditions, thicknesses from 1 to $\geq$40 mils (25 to 1000 μm) can be produced.

Additional mechanical testing may also be appropriate for processed materials which may undergo mechanical property changes due to the temperatures encountered in the process cycle. This testing could include hardness/microhardness measurements, as well as tensile testing to determine yield strength, ultimate tensile strength, and percent elongation.

## Properties of Pack Aluminized Steels

**Oxidation Resistance.** The action of pack aluminized steels under heat is similar to that of unprocessed stainless steels. Stainless steels owe their oxidation resistance to the formation of a thin chromium-rich oxide ($Cr_2O_3$) film which protects the underlying steel. A similar reaction occurs with aluminized steels, which form an even more protective oxide. $Al_2O_3$, from the aluminum in the coating. This oxide grows at a lower rate than $Cr_2O_3$ and does not exhibit volatility in the presence of oxygen above about 927 °C (1700 °F) as does $Cr_2O_3$. While a type 304 stainless steel scales excessively at temperatures of $\geq$870 °C ($\geq$1600 °F) in an oxidizing environment, a pack aluminized carbon steel exhibits only slight discoloration of the surface under these conditions. Figure 9 compares aluminized carbon steel with bare carbon steel, 5% Cr steel, 12% Cr steel, and 18Cr-8Ni steel with respect to the temperature at which scaling is less than 10 mg/cm$^2$ for oxidation in air. High-strength, highly alloyed stainless steels are also frequently aluminized to improve their oxidation resistance in elevated-temperature applications.

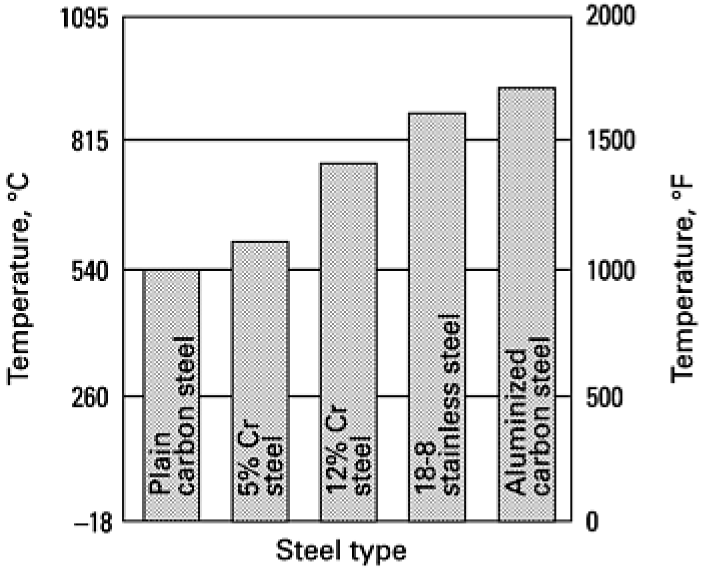

**Fig. 9 Oxidation of steels in air at the temperature at which scaling is less than 10 mg/cm$^2$. Source: Ref 60**

**Sulfidation Resistance.** Pack aluminized steels have remarkable resistance to the corrosive attack of gases such as hydrogen sulfide ($H_2S$), sulfur dioxide ($SO_2$), and sulfur trioxide ($SO_3$) as well as many other sulfur-bearing atmospheres at temperatures exceeding 230 °C (450 °F). The diffusion zone typically contains a minimum of 20% Al while the alloy surface is about 50 at.% Al and is far more resistant to high-temperature sulfide corrosion than stainless steels containing as much as 28% Cr. The maximum temperature at which these materials can be used in sulfur-bearing environments is limited by the high-temperature mechanical properties of the base steel. Figure 10 provides experimental data on the relative corrosion rates of bare and aluminized 9Cr-1Mo steel in $H_2S$ environments.

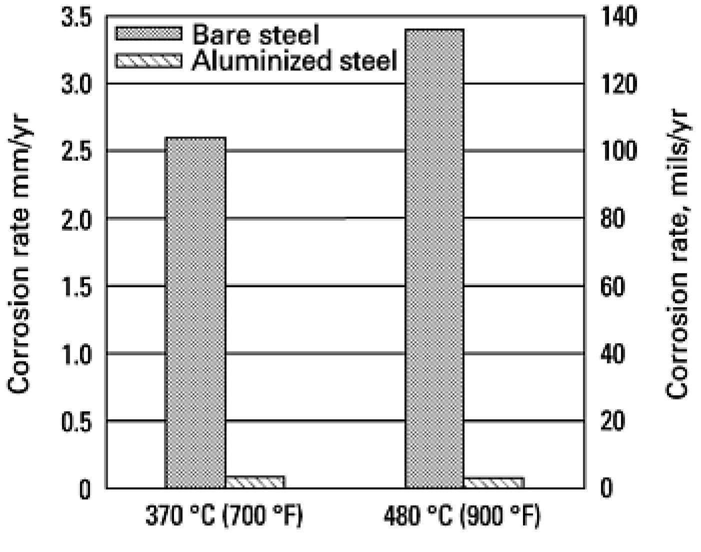

**Fig. 10 Relative corrosion rates of 9Cr-1 Mo alloy steel in 5 mol% $H_2S$ at 3550 kPa (515 psi) for 300 h. Source: Ref 61**

**Carburization Resistance.** When exposed at high temperatures to carbon-rich atmospheres, both stainless and alloy steels will carburize, become extremely brittle, and lose their heat- and corrosion-resistance properties. In certain environments, metal dusting associated with carburization will rapidly destroy the steel. Pack aluminized steels, however, suffer negligible deterioration from either carburization or metal dusting in high-temperature, carbon-rich atmospheres, thus greatly lengthening the service life of the steels in these environments. Figure 11 compares the carburization resistance of bare and pack aluminized austenitic stainless steels.

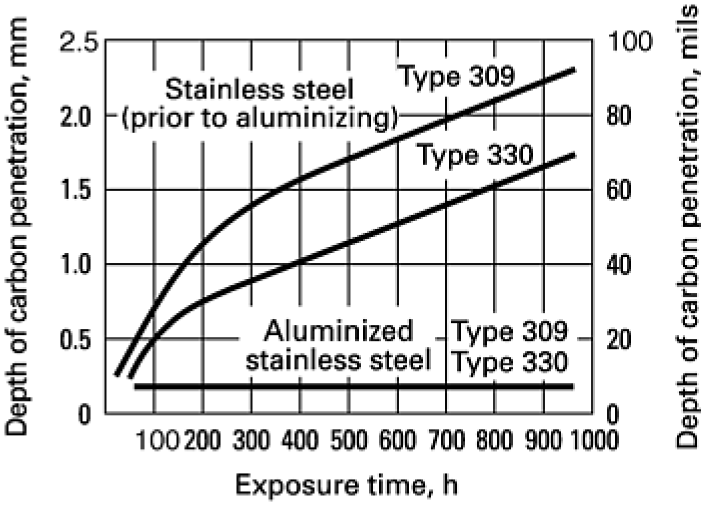

**Fig. 11 Carburization resistance of bare and aluminized stainless steels at 925 °C (1700 °F). Source: Ref 62**

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# Pulsed-Laser Deposition

**James S. Horwitz, Naval Research Laboratory**

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## Introduction

PULSED-LASER DEPOSITION (PLD) is a physical vapor deposition (PVD) technique that has gained popularity for the growth of high-quality multicomponent oxide thin films (Ref 1, 2, 3). Conceptually, PLD is an extremely simple PVD technique. The output of a short laser pulse (10 to 30 ns) is focused onto a solid target. The laser rapidly raises the surface temperature of a small portion of the target well beyond the vaporization temperature. A plume of evaporated material is ejected from the target and is collected on a nearby substrate. The congruent non-equilibrium evaporation of multicomponent materials and the transfer of the target composition to the deposited film make available high-quality thin films of materials that could not be deposited by other PVD techniques.

Much of the current research on PLD is due to the success realized with high-temperature superconductor (HTS) materials. In 1986 (Ref 4), the discovery of ceramic superconductors was soon followed by an intense search for a PVD technique that could be used to cast these materials in thin film form. Ceramic superconductors are generally complex multicomponent oxides containing three or more metals (e.g., $YBa_2Cu_3O_7$, or YBCO) with anisotropic electrical properties. PLD was among the techniques surveyed for possible application in the fabrication of thin-film superconductors at the time that bulk superconductors were being developed. Even though PLD was far from the advanced level of other film growth techniques, it was demonstrated that high-quality superconducting films could be reproducibly deposited by PLD. As a result, the technique became an integral component in the development of thin film applications of HTS materials.

Prior to 1987, there were very few research efforts in the area of PLD. This is despite the fact that literature references as early as 1965 (Ref 5) cite the capability of a short-pulse, high-peak power laser to "flash evaporate" a multicomponent target and transfer the composition of that target to a nearby substrate. PLD did not achieve widespread popularity at the time of its discovery, partly because the lasers required were not commercially available and the duty cycles ($\leq 1$ Hz) at which research laser systems operated were not suitable thin film production. At the time of its discovery, laser flash evaporation was not perceived to have any clear advantage over conventional evaporation techniques.

Between 1964 and 1987, research on the production of high-powered lasers was accompanied by studies of the interaction of the radiation field with solids, primarily to determine the origin of optical damage (Ref 6). These studies included an analysis of the vapor created by lasers focused to ablation energy densities. Film growth studies included the deposition of complex materials ($ReB_{22}$) (Ref 7), reactive deposition (Ref 8) (i.e., oxidizing ambients and enhanced gas-phase reaction due to high kinetic energies of evaporated material) (Ref 9), and the growth of high-quality II-VI semiconductor superlattices (Ref 10, 11, 12). However, research in these areas was still not sufficient to distinguish PLD as a new and important coating technology. The rapid development of the technique since 1987 is a combination of a materials need that could not be adequately met by conventional film growth techniques and the commercial availability of high-powered excimer lasers. Had high-temperature superconductivity been discovered in simpler, binary systems, PLD may have remained the interest of a relatively small research community. However, many of these new materials contain four or five elements, and the systems have extremely complex phase diagrams. These systems were the driving force in the development of this new technique.

The general attributes of PLD for thin film growth are summarized in Table 1. In addition to congruent evaporation and stoichiometric vapor transport, the high instantaneous growth rates lead to low impurity incorporation from the background. Although the pulsed lasers used generally have high peak powers, average power is low, and therefore the target remains thermally stable. PLD is a simple technique and therefore leads to reproducible deposition conditions. However, the technique is new, and it is difficult to predict optimum growth conditions. For most materials, it is still a trial-and-error process to determine optimum deposition conditions.

**Table 1 Attributes of PLD**

| **Attribute** | **Effect on film** |
|---|---|
| **Positive** | |
| Congruent evaporation | Stoichiometric deposition |
| Large range of deposition pressures | Control of vapor energy; control of volatile components |
| High instantaneous deposition rate | Low impurity incorporation |
| Low average power | Target remains thermally stable |
| Simple equipment | Reproducible properties |
| **Negative** | |
| Relatively new technique | Difficult to predict film properties |
| Line of sight | Difficult to coat nonplanar objects |

| | |
|---|---|
| High instantaneous evaporation rate | Particulates |

PLD research now covers a wide variety of conducting and insulating metal oxide thin films (e.g., ceramic superconductors, ferroelectrics, and ferrites) as well as nonoxide materials (e.g., semiconductors, metals, nitrides, and diamond-like carbon) (Ref 13). The areas of application range from electronics to biology, tribology, and optics. The list of materials successfully deposited as high-quality thin films is continuously growing. In spite of its success, the technique remains primarily a laboratory research tool, providing high-quality thin films and multilayers of complex materials for materials research and the development of new devices and applications based on these materials. This review describes the PLD technique and the components required for a simple system, examines the properties of the depositing vapor and how it is affected by the deposition parameters, and cites examples of classes of materials for which the technique offers a unique advantage over more conventional processes.

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## General Description

In PVD of multicomponent thin films, the preparation of a stoichiometric vapor is often difficult to achieve. When single-element sources are used, the arrival rate of each individual component must be calibrated and inter-regulated. In PLD, the composition of the vapor is the same as that of the target. Starting with the correct composition of the vapor greatly facilitates the growth of a desired phase in the depositing film. In addition, the absence of filaments or charged particles allows films to be grown by PLD in the presence of reactive gases. These gases can promote the growth of the desired thin film material through gas-phase reactions with the evaporated target material and gas-surface reactions with the growing film.

The pulsed laser ablation of materials can be viewed as taking place in several stages (Ref 6). The laser deposits energy into the target. Absorption of the radiation by the target material leads to surface heating and defect formation. The energy absorbed per unit volume depends on the optical penetration depth, the thermal diffusivity, and the rate at which the energy is deposited (Ref 14, 15, 16). The rate at which the energy is deposited is determined by the laser pulse width. The rise in surface temperature can be calculated from the ratio of the rate at which energy is deposited into the material to the rate at which the heat is conducted away. Typically, the laser is focused to a small spot (e.g., a few square millimeters) to minimize the volume of material being heated and to achieve surface temperatures that are greater than the melting temperature. If the optical penetration depth is small compared to the thermal diffusion length, surface heating is confined to the thermal diffusion length, and the change in temperature can be calculated from the energy absorbed, the volume of material irradiated, and the heat capacity. If the optical penetration depth is long, the rise in temperature is at a maximum at the target surface but decays exponentially as a function of depth below the surface (Ref 14, 15, 16).

Surface heating is followed by melting and evaporation. For most materials, there is a threshold laser fluence for the macroscopic removal of material from the surface (Ref 17). The high temperatures generated at the surface cause the emission of many species from the target, including ions and electrons generated by thermionic emission as well as atoms and molecules. Continued interaction of the laser pulse with the evaporated material causes the vapor to be ionized via nonresonant multiphoton processes, creating a plasma above the target. As the density of electrons increases, the laser radiation is absorbed preferentially in the plasma by inverse bremsstrahlung scattering (Ref 6). The absorption further heats the plasma and at the same time screens the laser pulse from further interaction with the target.

The high-pressure, high-temperature plasma expands rapidly into the vacuum. The dynamic behavior of the expansion has been compared to a supersonic or free-jet expansion (Ref 18, 19). In a free-jet expansion, the random motion of gas-phase particles in a high-pressure plasma is converted to a directed mass flow by expanding through a pinhole into a low-pressure region. Free-jet expansions are characterized by narrow, energetic velocity distribution about a center of mass velocity (Ref 20). A similar phenomenon is observed in PLD. A small high-pressure region is created at the target surface and then expands into the relatively low pressure of the vacuum system. The laser-generated plasma is a complex mixture of neutral and charged particles, each with different kinetic energies. Average neutral energies of $\approx 10$ eV are observed (compared to thermal evaporation particle energies of $\approx 0.1$ eV). Charged particle kinetic energies of as much as 10 to 100 times the neutral particle energies are also observed. The fraction of ionized material in the plasma is difficult to measure. Estimates vary between 1 and 10% (Ref 21).

The high energy content of the depositing vapor is believed to be one of the reasons for the success of PLD over other PVD techniques. The added energy can benefit film quality in several ways. First, gas-phase reactivity increases with atom kinetic energy. Enhanced oxidation cross sections are reported for laser-evaporated materials (Ref 22). For some materials, a correlation has been reported between the maximum concentration of metal oxides formed in the gas phase and optimum film properties (Ref 21, 29). Secondly, PLD films can typically be grown at a reduced substrate temperature in comparison to other PVD techniques. Substrates are usually heated to provide the arriving vapor with enough surface mobility for the atoms to build up on the surface in thermodynamically stable sites. Adding the energy to the vapor, as is done in PLD, means the substrate temperature can be lowered. This is desirable in cases in which the vapor can undergo a chemical reaction and the substrate or volatile components can be lost from either the film or the substrate.

Under optimized conditions, oriented thin films can be prepared by PLD in situ, minimizing the production of impurity phases, grain boundaries, and random orientations that might be formed during a postdeposition anneal. Although average film deposition rates for PLD are comparable to those in many other PVD techniques, the pulsed arrival of the vapor at the substrate results in instantaneous deposition rates of $\approx 1000$ to 10,000 Å/s. The instantaneous deposition rate minimizes the incorporation of background impurities into the depositing films, further improving the film quality.

**Plume Diagnostics.** A number of diagnostics have been used to characterize the laser-generated plasma (Ref 23): optical emission (Ref 24, 25, 26), absorption (Ref 27), laser-induced fluorescence (Ref 28, 29), resonance-enhanced multiphoton ionization (Ref 30), mass spectrometry (Ref 31, 32, 33 , 34), and ion probes (Ref 35). These diagnostics are being used to address several mechanistic issues relevant to film growth (Ref 23):

- The role of thermal versus nonthermal evaporation
- The extent to which the laser radiation interacts with the evaporated material
- The effect of the laser-generated plasma on the target
- The expansion mechanism responsible for the high initial particle energy
- The fraction of ionized material from the target surface out to the substrate surface
- The importance of clusters
- The role of the ambient in scattering, diffusion, shock front formation, and gas phase chemistry

The answers to these questions will come not from a single technique, but from a combination of the information provided by each of the diagnostics (Ref 23).

In the laser-generated plasma, the distribution of particles and the particle energy depend on the material, laser wavelength, laser fluence, and ambient composition and pressure. The characteristics are both temporally and spatially dependent. Presumably, this is the reason that optimized deposition conditions vary from system to system. An ideal vapor arrives at the substrate surface compositionally correct and with a kinetic energy that is high enough to allow adequate surface mobility, but not so high as to introduce defects or sputter the depositing vapor. The goal of these studies is to make a direct correlation between the vapor phase properties and the film properties.

Among the plasma diagnostics mentioned above, optical techniques have dominated the research efforts. These techniques are noninvasive and can be performed at the pressures under which films are deposited. Optical techniques have been used to identify the dominant components of the plume as being atomic and small molecular species. Dispersed emission spectra have been measured as a function of distance above the target from the vacuum ultraviolet through the visible (Ref 23, 24, 25, 26). Close to the target a continuum in the emission spectrum is observed, indicative of bremsstrahlung emission and a high density of free electrons. Several centimeters above the target, emission spectra are more characteristic of the isolated atomic species. The presence of electronically excited atoms and molecules at this distance is due to collisional, not optical, excitation. Secondary electrons generated from background gas ionization recombine with highly charged particles to form electronically excited species.

The dispersed spectra have been used to estimate the plasma temperature, which varies from 5,000 to 15,000 K (Ref 26, 36). Particle velocities ($v$) have been modeled using Maxwell-Boltzmann distributions $f(v) \sim \exp(-mv^2/2kT)$ and shifted distributions about a common center of mass $f(v) \sim \exp(-m(v-v_{cm})^2/2kT)$ (Ref 30). The shifted Maxwell-Boltzmann arises as a result of a Knudsen layer formed at the target surface (Ref 37, 38). Peak velocities are reported as $\sim 10^5$ to $10^6$ cm/s (Ref 21). Optical techniques have also monitored the formation of gas-phase species from the reaction of the ambient with the ablated material. In these studies, maximum gas phase production has been correlated with optimum film growth pressures. For example, in YBCO, the concentrations of YO and CuO are at a maximum at the optimum deposition pressure for high-quality films (Ref 21, 29).

Optical imaging techniques have also been used to detect the presence of a shock front (region where the plume and background gas pressure are the same) (Ref 39, 40, 41). The position of the shock front depends on the plasma temperature and pressure and the total system pressure. In vacuum, the shock front is relatively far from the target surface (several times the target substrate distance in typical deposition systems). As the ambient pressure is increased, the shock front moves in toward the target. The position of the shock front relative to the substrate is important for optimizing the properties of the deposited film.

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## Equipment

**Vacuum System.** Figure 1 is a schematic of a PLD system. The laser radiation is focused onto a rotating target at an angle of ~45°. The substrate is mounted at 90° with respect to the target normal. Typically, the target and substrate are separated by ~5 cm, but distances as large as 12 cm have been reported (Ref 42). The vacuum system requirements vary depending on the material. Generally, oxide films are deposited in an oxygen ambient at pressures <1 torr and do not require systems with ultrahigh vacuum base pressures. Gas flow rates of 10 standard cm$^3$/min at the desired deposition pressure can be achieved by gating the pump with the total system pressure controlled by a solenoid-activated leak valve that is controlled by a pressure transducer. At a minimum the vacuum chamber requires a pumping port, a gas inlet and pressure monitoring, a window transparent at the laser wavelength, and a viewport.

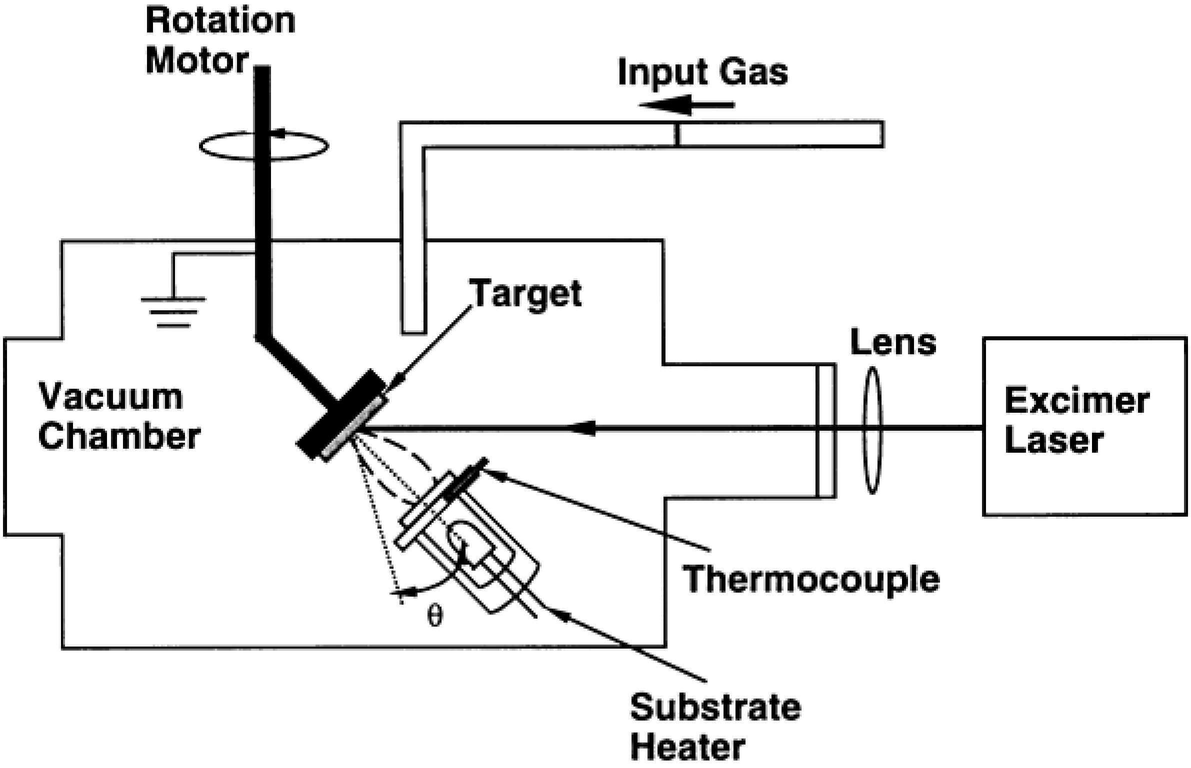

**Fig. 1 Schematic diagram of a typical pulsed laser deposition system**

**Laser.** The laser system and focusing optics are located outside the chamber. The focal length needs to be matched to the chamber size so that the required energy densities can be achieved at the target surface. Many different laser wavelengths have been successfully used. The excimer is the most commonly used laser because of its high peak power (> 40 MW) in the ultraviolet and ease of operation. In an excimer laser, the lasing medium is a rare gas/halogen mixture. A summary of rare gas mixtures and the output laser wavelengths is presented in Table 2. KrF (248 nm) is probably the most common excimer used for thin film deposition due to its stability and high peak power. In addition to excimer lasers, other gas laser systems ($CO_2$) and solid state laser systems (Nd:YAG) have been used to deposit thin films. The output wavelengths of these lasers can vary from 0.2 to 10 μm. Film quality as a function of laser wavelength has been compared (Ref 43), and it is generally accepted that film quality is significantly better for ultraviolet (UV) lasers (200 to 300 nm) than for infrared (IR) lasers (1 to 10 μm). This is due to a decreasing penetration depth of the laser radiation into the bulk material as the wavelength is reduced. The shallower penetration depth results in more energy being deposited per unit volume for comparable UV and IR pulse energies. As a result, UV lasers produce higher surface temperatures and more efficient evaporation of the solid target. IR lasers are often associated with thin films having rough surface morphologies, as a result of the incomplete vaporization of the target and the ejection of micron-size particles. Attenuation of the radiation by oxygen (in addition to the photochemical production of ozone) limits the use of laser wavelengths below 200 nm.

**Table 2 Excimer laser wavelengths**

| Wavelength, nm | Rare gas/halogen mixture |
|---|---|
| 157 | $F_2$ |
| 293 | $Ar\text{-}F_2$ |
| 222 | $Kr\text{-}Cl_2$ |
| 248 | $Kr\text{-}F_2$ |
| 308 | $Xe\text{-}Cl_2$ |
| 351 | $Xe\text{-}F_2$ |

An individual laser pulse transfers a large amount of material from the target to the substrate (~$10^{16}$ atoms per pulse), resulting in average deposition rates of ~1 Å/laser pulse (deposition rates are a strong function of the target composition and phase and the deposition conditions). To achieve a coating thickness on the order of 1.0 μm requires 5000 to 20,000 laser pulses. Commercial excimer systems operate at repetition rates as high as 150 Hz, and high-quality films 0.5 μm thick have been deposited at average growth rates as high as 150 Å/s.

**Substrate Heater.** For many materials, it is desirable to deposit at elevated substrate temperatures. Two problems are often encountered when trying to achieve uniform substrate temperatures $\leq 900$ °C in oxidizing environments. First, the heating element must be inert to the ambient. Second, the typical deposition conditions ($10^{-6}$ to 1 torr) do not allow for efficient gas-phase heat conduction from the radiating element to the substrate. Projection lamps serve as efficient heating elements because the filament is encapsulated in a quartz envelope. The lamps can be used to heat a small steel block to temperatures that approach the softening temperature of the quartz. The substrate is mounted onto the steel heater block. Transfer of the heat from the steel block to the substrate is usually done through a conductive bonding agent such as silver paint. This type of heater can be used for small substrates (up to ~1 in. diameter) and temperatures up to ~950 °C.

Alternatively, substrates can be heated using a pseudo-blackbody heater (Ref 42). Here the substrate is encased in a well-shielded heater with only a small opening for the depositing vapor. The substrate is not required to be in intimate thermal contact with the heater block because the temperature everywhere inside the blackbody is the same. Substrate heaters of this type have been successfully developed for the deposition of large-area films (>1 in. diameter). Rotation of the substrate inside the blackbody heater improves the temperature uniformity.

**Target Manipulation.** The target must be continuously manipulated to avoid having the laser strike the same spot on the target with successive shots. This is done exclusively by rotating the target during deposition. This minimizes problems associated with erosion at the target surface. Commercial systems are available that hold up to six rotating targets, 1 in. in diameter, that can be selected under computer control to be positioned in front of the laser focus. With this type of system, multilayer structures can easily be formed.

**Laser Beam Rastering.** Target rotation ensures uniform erosion. The laser beam can also be rastered across the target. In addition to minimizing problems associated with erosion, rastering of the laser beams increases the area of a substrate that can be coated. In PLD, the plume of evaporated material is highly forward-directed. If the position of the laser beam remains fixed in space, the plume of evaporated material is directed at a relatively small area on the substrate. For most deposition systems, a stationary laser beam produces a uniform coating over 1 cm$^2$. In its simplest form, the laser beam is moved by a motorized mirror mount across the target. The substrate and target are mounted so that their centers are on axis. The plume of evaporated material is swept across the substrate. The main limitation to this geometry is that the coated area is determined by the size of the target. Off-axis geometries have also been demonstrated (Ref 44). Offsetting the target center from the substrate center allows the same aerial coverage with a target that is only half the size of the substrate. Another scale-up technique is to raster the substrate in two dimensions while holding the laser position fixed on the target (Ref 45). This scheme has the advantage of not requiring large-area targets but suffers from the complications of having to move the heating elements.

Research efforts continue on the scale-up of PLD to large areas, although it is not yet clear what technological application will be the first to implement large-scale PLD in an industrial environment. Both ferroelectric and HTS thin films have been deposited over large areas as demonstrations. Uniform coatings have been successfully demonstrated on planar surfaces up to 5 in. in diameter. However, there is still a great deal of work to be done on the device structures based on these materials, and the demands for large-area coatings is relatively small. The versatility of the technique is simply not yet great enough to generate industrial acceptance.

**Deposition Parameters.** Typical deposition conditions are:

- *Laser wavelength:* 193 nm to 1.06 μm
- *Laser spot size:* 3-5 mm$^2$
- *Laser pulse energy:* 100-500 mJ
- *Laser pulse width:* 10-30 ns
- *Laser fluence:* 1-5 J/cm$^2$
- *Laser repetition rate:* 5-100 Hz
- *Substrate temperature:* Room temperature to 950 °C
- *Ambient pressure:* $10^{-6}$ to 1 torr

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## Deposition Characteristics

**Angular Distribution.** In general, the angular distribution of material from the laser-generated plasma is sharply peaked with respect to the target normal, with some tilting of the distribution toward the incident laser beam. Early studies on the PLD of multicomponent films indicated that the spatial distribution of deposited material was also accompanied by a spatial variation in film composition. In thermal evaporation, a small effusive source is described as having a cos(θ) distribution (θ is the angle at which the material is ejected from the target relative to the surface normal of the target; see Fig. 1). This results in a $\cos^4(\theta)$ thickness distribution of the film on the substrate. In a purely effusive source, there are no collisions from the evaporation region to the substrate surface. In PLD, a large number of collisions take place in the high-pressure plasma and are responsible for the forward peaking. It is difficult to generalize on the exact functional dependence of the angular distribution of material because it is sensitive to a number of the deposition parameters (e.g., laser wavelength, fluence, spot size and geometry, target-substrate distance, and background gas pressure). As an example, in vacuum the angular distributions, as determined from film thickness, for single and multicomponent materials have yielded values of $x$ ($\cos^x(\theta)$) ranging from 2.3 to 30 (Ref 46).

The angular distribution of ejected material is also sensitive to the shape of the laser spot on the target. The rectangular shape of excimer laser beams typically results in a rectangular focused spot on the target. In some systems, it has been observed experimentally that the deposited film has a rectangular image, with the long and short axis of the film reversed from the image on the target. The rotation of the image is an indication that plume expansion proceeds fastest along the shorter axis (i.e., there are fewer collisions and the particles can achieve greater velocities).

**Effects of Added Gas.** The addition of a background gas has a strong effect on the angular distribution of the evaporated material. Where direct comparison measurements have been made, the distribution has been less sharply peaked at an elevated pressure. Measurements on multicomponent oxides (e.g., YBCO) are complicated by gas-phase chemistry. For example, a comparison study has shown a reduction from $\cos^{23}(\theta)$ to $\cos^{17}(\theta)$ associated with a change from vacuum to 100 mtorr of oxygen (Ref 46).

The angular distribution changes nonlinearly with the added gas pressure. For elemental systems such as copper (Ref 47) or platinum (Ref 48), the initial addition of either argon (for copper) or oxygen (for platinum) leads to a forward focusing effect; that is, ejection of material occurs at smaller angles. Forward focusing is manifest as a narrowing of the angular distribution function (increasing $x$) and an increase in the average film deposition rate. This behavior reaches a maximum effect at low pressures (~1 to 50 mtorr). Above this pressure, scattering dominates and the average deposition rate decreases as material is scattered over larger angles.

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## Particulates

One of the most often cited drawbacks to PLD is the rough surface morphology of the deposited films. The observed surface roughness can originate from a variety of mechanisms. For the same deposition conditions (i.e., laser parameters), the particulate density (number of particles/$\text{cm}^2 \cdot \text{Å}$ of film) varies significantly from material to material (Ref 49). No one model is able to predict the size and distribution of the particulates. One of the main causes of surface roughness is the ejection of micron-size particles from the target. These particles can be problematic for electronic materials, especially those involving multilayers of conductors and insulators, as well as optical materials in which particles can serve as scattering centers. There are at least three mechanisms associated with formation of surface particulates: subsurface boiling (Ref 50), shock wave recoil (Ref 51), and exfoliation (Ref 52). Subsurface boiling occurs when the required heat transfer time is less than the evaporation time. The subsurface reaches a molten temperature before the surface layer has evaporated. The effect of subsurface boiling can be minimized by reducing the laser power, which also reduces the deposition rate. Above the target surface, a shock wave is formed at the boundary of the high-pressure region and the vacuum. Recoil pressure from the shock wave into the target can also result in the ejection of micron-size particles. These particles can be reduced by reducing laser power. Continuous heating and cooling of the laser target leads not only to erosion but also to modification of the target surface. Micron-size cones that point back at the direction of the incident laser beam are observed on the surface of ceramic targets and can be broken off by the shock of the laser. The presence of these structures can be minimized by mechanical polishing of the target surface.

**Mechanical Filters.** Although the presence of particulates seems to be an inherent property of the PLD process, careful control of deposition parameters can minimize their density. Additional particulate reduction can be achieved mechanically through the use of a particle filter (Ref 53). A velocity filter operates on the principle that particle size can be correlated with particle velocity. A shutter can be used to allow fast-moving ($10^6$ cm/s) atomic vapor to pass while blocking the slower-moving ($10^3$ cm/s) particulates (Ref 34). In practice, a rotating chopper (3000 to 10,000 rpm) can be synchronized to the firing of the laser. Mechanical filters are effective at reducing the aerial density of particulates regardless of the mechanism of origin.

**Off-Axis PLD.** The most common PLD geometry has the substrate facing the target, separated by a few centimeters. This is designed to maximize the film deposition rate. Recently, there have been a few reports of off-axis PLD. Non-normal geometries have been successfully used in the PLD of YBCO thin films, and two geometries have been reported. Mounting the substrate surface so that it is parallel to the target normal is essentially equivalent to an off-axis sputtering geometry (Ref 54). The majority of the ejected vapor (in addition to the particulates) travels across the substrate surface, without depositing. Although the deposition rate is decreased, there is substantial discrimination of the larger particulates in the depositing thin film. Additionally, substrates have been mounted facing away from the target surface (Ref 55). Films are deposited in high background pressures of reactive gases. Preferential slowing of the atomic vapor over the particulates allows deposition of smooth films and a substantial reduction in the average deposition rate. The required thermalization of the evaporated material and the absence of energetic ions in the depositing vapor does not seem to affect the properties of YBCO films.

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## Materials

PLD is currently being used to deposit thin films for a wide range of technological applications. These films vary from epitaxial superlattices of electronic materials to polycrystalline bioceramics. Several recent review articles have attempted to catalog research efforts to date ( Ref 15, 56, 57), indexing films by composition, phase, and the laser used to deposit the film. It would appear that the vast majority of research published to date on PLD has been directed at multicomponent oxides. The technique offers a clear advantage when the material contains more than two elements. The ceramic superconductors have provided the complex materials needed to accelerate research in PLD.

**High-Temperature Superconductors.** More research has been devoted to PLD of superconductors than to PLD of any other class of materials. There are two classes of oxide superconductors:

- *Cuprates:* Y-Ba-Cu-O, Bi-Sr-Ca-Cu-O, La-Sr-Cu-O, Nd-Ce-Cu-O, Tl-Ba-Ca-Cu-O
- *Noncuprates:* Ba-K-Bi-O, Ba-Pb-K-Bi-O

YBCO was the first of these materials to exhibit superconductivity above liquid nitrogen temperatures (Ref 58). Although other materials have since exhibited higher critical temperatures, YBCO still remains one of the more promising materials for applications because it is relatively easy to obtain in single-phase form. Crystallographically, the YBCO unit cell is based on a cubic perovskite structure. The superconductor is a triple layer of the cubic unit cell, with the corners of the perovskite either $CuO_4$ or $CuO_5$. The electrical properties of YBCO are highly aniostropic. Phase pure, polycrystalline materials have low critical currents ($10^3$ to $10^4$ A/cm$^2$) because of the poor electrical conductivity of the randomly oriented grains. Epitaxial or even textured thin films (with the *c*-axis normal to the substrate surface) provide alignment of the conduction planes and high critical currents on the order of $10^6$ A/cm$^2$. Current technological applications of YBCO thin films are divided into two classes: active components (based on Josephson junctions) and passive components (e.g., microwave wave guides) (Ref 59).

Currently, smooth YBCO films can be deposited by a large variety of PVD techniques (Ref 60), including single-source techniques such as sputtering as well as multisource techniques such as molecular beam epitaxy and chemical vapor deposition. In spite of the equivalent film properties of these techniques, PLD remains one of the preferred deposition techniques because of its minimal vacuum system requirements, high average deposition rate, and ease of optimization (see Table 1). However, most applications for superconductors require integration of the superconducting thin film with insulating thin films. The superconductor-insulator interface should be sharp, with the insulating material latticed matched to the superconductor. The deposition technique needs to be versatile to switch between the superconductor and the insulating material.

The first generation of passive microwave electronics based on HTS thin films were fabricated from patterned superconducting thin films deposited onto one side of low-dielectric substrates. MgO and $LaAlO_3$ substrates have been used in the majority of these applications. Advanced microwave devices will be fabricated from trilayer films: superconductor/dielectric/superconductor. In these multilayer structures, the dielectric films (2000 Å to 10 μm thick) must have a low dielectric constant, low loss tangent, and high resistivity, and they must provide a lattice-matched surface for the growth of the top superconducting thin films. Several dielectric films have been successfully deposited in trilayer structures by PLD. Insulating materials include $LaAlO_3$ (Ref 61), $NdGaO_3$ (Ref 62), and $PrGaO_3$ (Ref 63). The deposition of these multilayers can be achieved easily in situ simply by moving the laser beam from the superconducting target to the insulating target.

Barrier layers are also important for the application of HTS materials. Low-dielectric substrates, such as $Al_2O_3$, and semiconducting substrates, such as silicon or GaAs, react at the elevated deposition temperatures required for HTS thin films, leading to a degradation in the superconducting thin film properties. Barrier layers such as Y-$ZrO_2$ (Ref 64), $CoSi_2$ (Ref 65), $CeO_2$ (Ref 66), and $SrTiO_3$ (Ref 67, 68) eliminate substrate film interdiffusion and provide lattice-matched surfaces for superconducting thin film growth. Perhaps the most challenging barrier is that required for a Josephson junction. These barriers (deposited between two superconducting layers) must be on the order of the coherence length for the superconductor (for YBCO, ~10 to 30 Å). The nonsuperconducting praseodymium analog of YBCO is one of the candidate materials for this application (Ref 69, 70). For the application of high-temperature superconductors, PLD has been demonstrated to be capable of integrating many different materials into a multilayer structure.

**Ferroelectrics** are a class of high-dielectric materials that may also be piezoelectric and pyroelectric. These materials are suitable for a wide variety of thin film electronic applications, including displays, sensors, nonvolatile random access memories, optical switches, modulators, surface acoustic waves, and radio frequency electronics. Although the properties of ferroelectric materials have been known for some time, thin film applications are not very common due to a lack of availability of high-quality thin films. The rate of research into PLD of ferroelectrics is rapidly approaching the rate of research into PLD of HTS materials (Ref 71).

Many ferroelectrics have crystal structures that are based on a modified perovskite, similar to the ceramic superconductors, and as such have benefited from research in the area of PLD. Ferroelectric properties arise as a consequence of a nonsymmetric crystal lattice structure and the ability of that structure to be polarized in an applied electric field. Both the field-induced and spontaneous (or naturally occurring) polarization can be reversed by an applied field of the opposite polarity. A ferroelectric material will retain that polarization, even after the field is removed. Ferroelectric materials are characterized by a phase-transition temperature (Curie temperature). Below the Curie temperature is the ferroelectric phase. Above the Curie temperature is the nonferroelectric (polarizable but with no retained polarization) paraelectric phase.

Many of the electronic applications for ferroelectric thin films require integration with semiconductor electronics. Low processing temperatures are a desirable feature of the film processing technique. Ferroelectric thin films that have been deposited by PLD are:

- *Perovskites:* $PbTiO_3$, $BaTiO_3$, $PbZr_xTi_{(1-x)}O_3$
- *Nonperovskites:* $KTa_{(1-x)}Nb_xO_3$, $Bi_4Ti_3O_{12}$, $LiNbO_3$

Many of these materials contain volatile components such as lead (Ref 72), potassium (Ref 73), or lithium (Ref 74). These elements present unique problems for obtaining crystalline thin films. The crystallization temperatures (500 to 700 °C) can lead to changes in the film composition because of evaporation of the more volatile components. In spite of large differences between component vapor pressures, high-quality ferroelectric films have been successfully deposited by PLD.

In PLD, stoichiometric evaporation and transfer of the target material does not guarantee a stoichiometric thin film. That is to say, the surface temperatures required to ensure adequate surface mobility may give rise to nonstoichiometric films because of evaporation. One simple solution to this problem has been to overcompensate in the target for volatile species that may be lost from the film (i.e., add excess PbO to the target to minimize the loss of lead from the film) (Ref 75). The technique may work in some cases but is undesirable, because the compensating factors may change depending on the conditions.

It has been observed that in several systems the PLD deposition conditions can be adjusted to compensate for the loss of volatile components at elevated substrate temperatures. It appears that in these systems, higher ambient pressures ($\geq 300$ mtorr) minimize the loss of these components. This is probably the result of several factors. Higher gas pressures lead to a reduction in the kinetic energy of the arriving vapor (increasing the sticking coefficient). Higher pressures favor increased oxidation, either in the gas phase or as a result of gas-surface collisions. In the case of lead, it is believed that PbO has a lower equilibrium vapor pressure than lead and is therefore retained at elevated oxygen deposition pressures.

As with HTS materials, single-layer ferroelectric films by themselves are not easily incorporated into a device. The ferroelectric properties of interest arise as a result of electric field effects and as such have presented a unique challenge for their implementation. Electrodes are required that are noninteracting under film growth conditions and that do not degrade the ferroelectric film behavior under repeated cycling. Although noble metals such as platinum or gold are commonly used, the interface between the metal and the ferroelectric film causes the ferroelectric to degrade in time. Oxide conductors such as YBCO (Ref 76), $(La,Sr)CoO_3$ (Ref 77), and $(Sr,Ca)RuO_3$ (Ref 78) are ideally suited for ferroelectric integration. These oxide conductors are lattice-matched perovskites. Multilayer structures have been successfully deposited by PLD that have demonstrated superior characteristics over noble metal structures.

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# Film Thickness Measurements Using Optical Techniques

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## Introduction

MEASURING THE THICKNESS of thin films can be accomplished in many ways, but this article will focus on the optical method of single-wavelength ellipsometry (SWE) and two multiple-wavelength methods of reflectometry and spectroscopic ellipsometry (SE). Single-wavelength ellipsometry and reflectometry are relatively inexpensive methods that excel when a single film on a substrate is to be measured. Single-wavelength ellipsometry is particularly effective for films a few nanometers thick to a few hundred nanometers thick, and reflectometry is particularly effective for films thicker than a few hundred nanometers. Spectroscopic ellipsometry is a more expensive and more complex method that can be readily used with multiple films.

In this article, the general capabilities and principles of ellipsometry and reflectometry are discussed in terms of nondestructive methods for measuring the thickness of thin films. The film thicknesses to be considered will be from a few. nanometers to a few micrometers. Emphasis is placed on the methods that are available commercially rather than methods that require more specialized development.

In their rudimentary form, the initial expenses for purchasing the equipment for SWE and reflectometry are roughly the same. Although SE has been used in research laboratories for over a decade, it has only been used regularly in industry since the early 1990s. The initial cost of SE in its rudimentary form is three or five times that of the other two techniques. Very few users in industry purchase these techniques in their rudimentary form, however, and the additional options can often double or triple the cost.

This article does not discuss methods such as optical microscopy of cross-sectioned samples or the shift of interference fringes at a purposely fabricated step. The thickness of a thin evaporated metal on a microscope slide can be determined by measuring the fraction of transmitted light, after suitable calibration. This requires a special substrate, however; it is not an in-line technique and will not be considered here.

## Acknowledgements

The author would like to acknowledge Mark Keefer, Prometrix Corp.; William Henderson, SOPRA, Inc.; and John Woollam, J.A. Woollam Co. for useful discussions. In addition, Tom Wetteroth, Motorola, Inc., was very helpful in reading the manuscript and making numerous useful suggestions. His careful attention to detail is appreciated.

## General Background

A basic requirement for using optical methods for determining the thickness of a film is that the light must be able to reach the bottom of the film and interact with the underlying layer. Transparent materials such as most oxides qualify throughout the above-mentioned thickness range up to a few micrometers. Many semiconductors are nearly transparent and also easily qualify. Metals, however, must be very thin for these optical methods to be applicable.

The intensity change upon reflection for very thin films is quite small. On the other hand, the phase shift differences are significant. For this reason, ellipsometry is one of the most powerful techniques for very thin films. Other traditional thickness measuring techniques such as stylus profilometry and interferometry are ineffective for films thinner than 50 nm. Electrical phenomena. such as eddy currents are sometimes used for thickness measurements of metal films. These techniques require significantly greater calibration efforts, however, and always depend on assumptions wit regard to microstructure.

Ellipsometry and reflectometry basically involve the measurement of changes in phase shift or intensity, respectively, as light reflects from material. Optical properties and film thicknesses of the samples are then calculated based on a chosen model. Regression software is able to determine the thicknesses that give the best fit to within a few angstroms. In many cases, the regression software also gives a "goodness-of-fit" parameter. The "goodness-of-fit" parameter provides a test of the model describing the sample. If the value is outside the acceptable range, then another model may be required. In any event, thickness is not determined directly; the assumption of a model allows calculation of the ellipsometry or reflectometry parameters and subsequent. comparison of calculated values and measured values. Differences between the results of an analysis and reality are more often due to an oversimplified model than to limitations in the capability of the measuring instrument.

## Basic Theory

For general information on electromagnetic waves and optics, the reader should refer to textbooks (Ref 1, 2, 3, 4, 5) and reference books (Ref 6) on the subjects. Some of the salient features that are directly applicable to reflectometry and ellipsometry (Ref 7, 8) are reviewed here.

The electromagnetic wave is a transverse wave consisting of both an electric field vector and a magnetic field vector that are mutually perpendicular and perpendicular to the propagation direction of the wave. The wave can be specified with either the magnetic field vector or the electric field vector. For simplicity, the electric vector only is considered. The light wave can be represented mathematically as a sine wave with amplitude $A$. Waves transport energy, and the amount of energy per second that flows across a unit area perpendicular to the direction of travel is called the *intensity* of the wave and will be denoted as $I$. The intensity, or energy density (Ref 7), is proportional to the square of the amplitude.

**Reflection.** For a single film on a substrate (Fig. 1), reflections rather than transmission, are the primary concern. As shown in Fig. 1, some of the light is reflected and some passes into the material at the air-to-solid interface. At the second interface, again, some is reflected and some is transmitted. The various rays that leave the material from the top surface combine to make the outgoing wave. For reflectometry, the ratio of the intensity of the outgoing wave to the intensity of the incoming wave is measured. Reflectometry measurements are often made at normal (perpendicular) incidence. The various rays give constructive or destructive interference, depending on the wavelength of the light, the thickness of the film, and the optical properties of the various materials. For the reflectometry technique, one measures the reflected intensity versus the wavelength of light to deduce the film thickness.

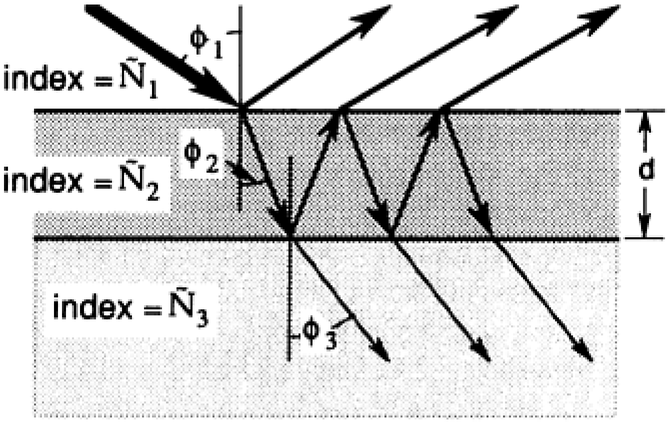

**Fig. 1 Schematic of light reflected and transmitted at film interfaces. The outgoing beam is a combination of all of the rays emerging from film from the top interface. Each material is characterized by the index of refraction $N_1$. The thickness of the film is *d*. Source: Ref 8**

For ellipsometry, the measured parameter is the ratio of the wave amplitude parallel to the plane of incidence versus the wave amplitude perpendicular to the plane of incidence. The reflection process also causes a phase shift between these two waves, and this phase shift is measured during ellipsometry. The amplitude ratios and phase shifts are functions of the wavelength, thickness, optical properties of the various materials, and angle of incidence.

**Polarized Light.** Most light sources emit unpolarized light, or light with electric-field components oriented in all possible directions perpendicular to the direction of travel. If all the photons in a light beam have the electric field oriented in one direction, the light is referred to as *polarized light* or, more completely, *linearly polarized light.* Some light sources emit polarized light. In addition, one can obtain polarized light by passing the light beam through an optical element or by causing the beam to make a reflection under some specific conditions.

Figure 2(a) illustrates two light beams with the same frequency moving along the same path, one polarized in the vertical plane and the other polarized perpendicular to the vertical plane. In this case, the maxima of the two beams coincide (i.e., the phase is the same). These two beams can be combined to give a resultant light beam that is also linearly polarized. The key point here is that *when two linearly polarized waves with the same wavelength (or frequency) are combined in phase, the resultant wave is linearly polarized and lies in a plane*.

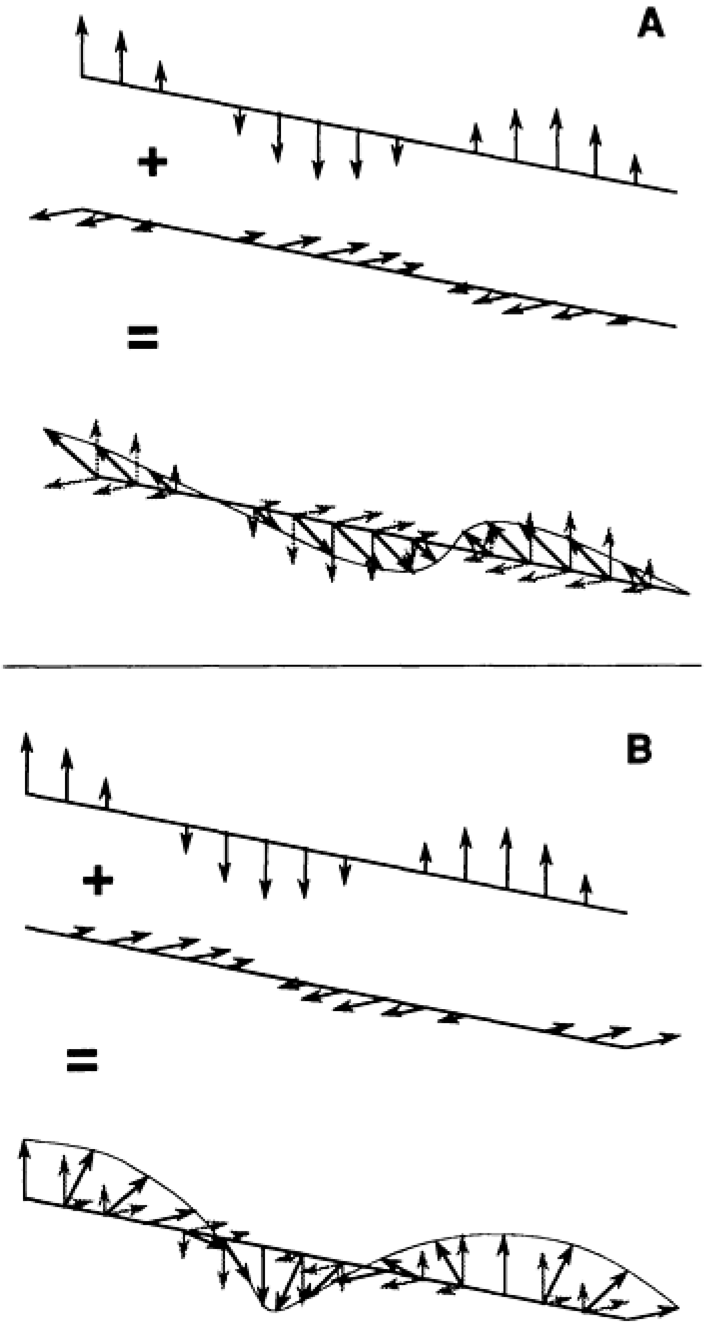

**Fig. 2 Linear and elliptical polarization. (a) If two linearly polarized light beams that are in phase are combined, the resultant light beam is linearly polarized. (b) If two linearly polarized light beams that are out of phase are combined, the resultant light beam is elliptically polarized. In this particular example, they are out of phase by 90°. Because the amplitudes are equal, the resultant beam is circularly polarized. Source: Ref 8**

Figure 2(b) shows two beams where the maxima do not coincide, but are out of phase. When these two waves are combined, the tips of the arrows do not move back and forth in a plane as in the previous example. This is, in general, elliptically polarized light. The key point is that *when two linearly polarized waves with the same wavelength (or frequency) are combined out of phase, the resultant wave is elliptically polarized or spiraling in three-dimensional space*.

In ellipsometry the important fact is that when linearly polarized light makes a reflection on a metal surface, there is a shift in the phases of both the components (parallel and perpendicular to the plane of incidence). For non-normal incidence, the shift is, in general, not the same for both components, and hence the resultant light will be elliptically polarized. The induced amount of elliptical polarization depends on various factors including the optical properties of the substrate as well as the thickness and optical properties of overlying films. From this concept of elliptical polarization, the term *ellipsometry* takes its name for the measurement of induced ellipticity.

**The Complex Index of Refraction.** When light passes from one medium (e.g., ordinary room air) into another medium that is not totally transparent (Fig. 1), several phenomena occur at the interface. Some of the light is reflected back and does not enter the second medium, while an unreflected component enters the second medium. The unreflected component will be considered first.

The parameter used to describe the interaction of light with the material is the complex index of refraction, $N$, which is a combination of a real part and an imaginary part and is given as

$$N=n - \mathrm{j}k \qquad \textbf{(Eq 1)}$$

where $n$ is also called the *index of refraction* (sometimes leading to confusion), $k$ is called the *extinction coefficient,* and j is the imaginary number $\sqrt{-1}$.

For a dielectric material such as glass, none of the light is absorbed and $k= 0$. In this case, only $n$ is being considered. Both $n$ and $k$ are functions of the wavelength. It is not uncommon for a material to have $k = 0$ for a range of wavelengths and $k \neq 0$ for another wavelength range.

The index of refraction $n$ is defined to be:

$$n = c/v \qquad \textbf{(Eq 2)}$$

where $c$ and $v$ are the velocities of light in free space and in the material, respectively.

The extinction coefficient $k$ is a measure of how rapidly the light is absorbed as a function of depth in the material. A transparent material such as glass has an extinction coefficient of zero. Metals typically have values ranging from $k = 2$ to about $k = 6$.

**Dispersion.** It should be noted that $n$ and $k$ are not simple constants for a given medium, but are in fact functions of the wavelength, $\lambda$. This is the reason that white light entering a prism emerges with the various colors separated.

The term *dispersion* is used to describe the way in which the optical constants change with wavelength. Figure 3 shows how $n$ and $k$ vary for a metal such as nickel and for a dielectric such as silicon nitride (Ref 9). The index of refraction $n$, for both materials, is near 2 for the entire range of wavelength. From an optical point of view, the quantity that differentiates these two materials is not $n$, but $k$. In a material with $k \neq 0$, the intensity of light $I$ decreases as a function of distance into the material. The functional form is:

$$I/I_0 = \exp(-\alpha z)$$

where $z$ is the distance into the material and $\alpha$ is the absorption coefficient (related to the extinction coefficient, $k$). Because the intensity continuously decreases, the concept of how far the light goes into the material has no meaning. Instead, to illustrate penetration, the distance $z$ is used where the quantity $\alpha z$ is equal to unity and $I/I_0 = \exp(-1) \approx 0.37$.

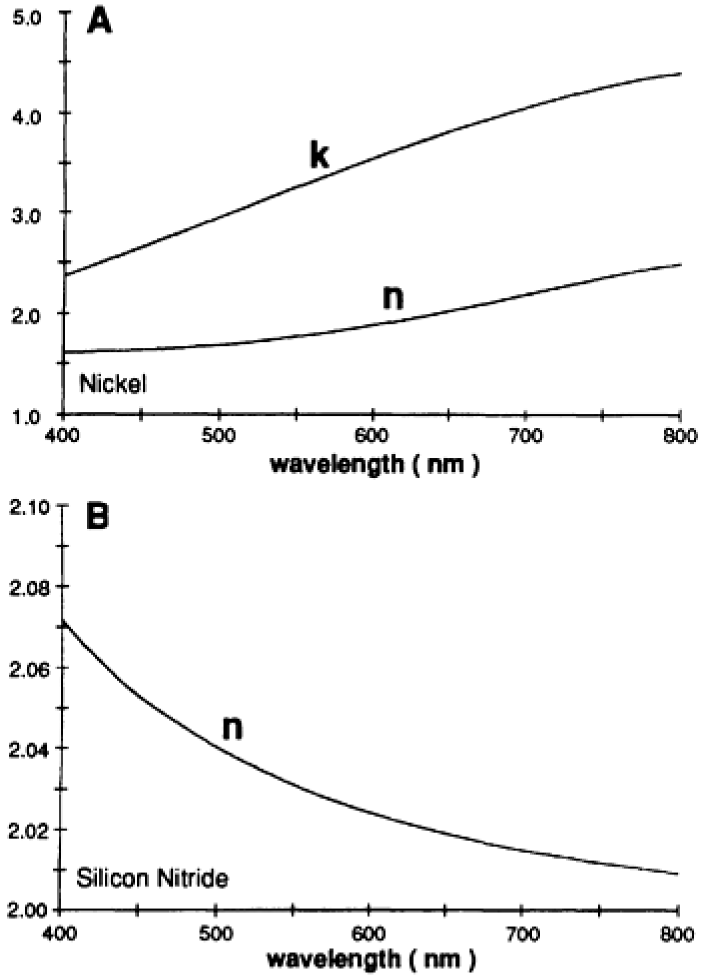

**Fig. 3 Optical constants for (a) nickel and (b) silicon nitride. The value of *k* for silicon nitride is zero in the wavelength range shown. Source: Ref 9**

Nickel has a value of *k* that is greater than 2 for the entire range. The thickness where the intensity drops to 37% is about 13 nm. For thicknesses three times this value, or about 40 nm, the material is essentially opaque. For silicon nitride, the value of *k* is zero for the entire range. This material is transparent.

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## Single-Wavelength Ellipsometry (SWE)

Ellipsometry was first practiced by Paul Drude (Ref 10) just prior to 1890. The name *ellipsometry* was introduced by A. Rothen (Ref 11) in 1945. Clearly, this is not a recently developed technique. Ellipsometry uses monochromatic light, optical elements that change the polarization state of the light, some sort of detector, and some calculation facilities. Although rudimentary forms of these requirements have been present throughout this century, the development of the photomultiplier, the laser, and the desktop computer have greatly enhanced the use of this technique to the point that it is now routinely used as a metrology tool in semiconductor wafer manufacturing.

**Instrumentation.** Figure 4 shows the basic requirements for SWE. The figure shows the arrangement of a manual null ellipsometer. The source generates monochromatic light, and the polarizer passes only light that is polarized in a particular direction. The quarter-wave plate (QWP) then converts the light to elliptically polarized light. If the polarizer and QWP are positioned correctly, the ellipticity is reversed by the reflection, giving linearly polarized light. The analyzer nulls out the light so that the intensity at the detector is zero. The optical elements used for the polarizer and analyzer are both polarizers. The terminology describes function, in that it is the function of the element called *polarizer* to cause the light to be polarized, and it is the function of the *analyzer* to determine the polarization state of the light.

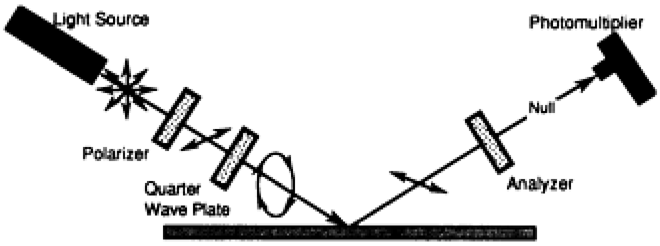

**Fig. 4 Schematic of manual null ellipsometer. The quarter-wave plate is fixed at either ± 45° and the polarizer and analyzer are rotated to find the null. The positions of the polarizer and analyzer are then used to calculate the ellipsometric parameters *Del* and *Psi.* Source: Ref 8**

Operation of this instrument requires iterative adjustment of the polarizer and the analyzer until the null positions are located. The angular position of the polarizer and analyzer are then used to calculate the ellipsometric parameters, *Del* and *Psi. Del* is the reflection-induced phase shift between the waves that are perpendicular and parallel to the plane of incidence, and *tan* (*Psi*) is the amplitude attenuation ratio of the parallel wave to the perpendicular wave.

Although the manual null instrument illustrates the concepts reasonably well, most commercial instruments are rotating-element instruments. In some cases, the polarizer and analyzer are rotated by the instrument, under microprocessor control, until null is found. In other cases, only the analyzer is rotated, and *Del* and *Psi* are calculated from photometric measurements, rather than null positions.

**Analysis of Films.** Regardless of whether the measurement is made with a manual null instrument, a rotating-element null instrument, or a rotating-element photometric instrument, the parameters that an ellipsometer measures are *Del* and *Psi.* For a film-free surface (a substrate), *Del* and *Psi* can be converted to the values of the optical constants for the substrate material, $N = n - jk$. The value of *Del* for a substrate will be between zero and 180° and the value of *Psi* will be between zero and 45°. In Fig. 5, the film-free value of *Del*/*Psi* for silicon is about 178°/10.5°. If a dielectric film (i.e., $k = 0$) with index $N = 1.46$ is added, the location of the *Del*/*Psi* joint begins to change on the *Del*/*Psi* domain. When the film thickness is 20 nm, the *Del*/*Psi* location is about 129.9°/13.7°. As the thickness increases, the *Del*/*Psi* trajectory is traced out until the value of thickness reaches the period thickness. At this thickness, the *Del*/*Psi* point has returned to the film-free location. For added thicknesses, the *Del*/*Psi* point simply retraces the trajectory. For the particular example given in the figure, the period thickness is 283.2 nm.

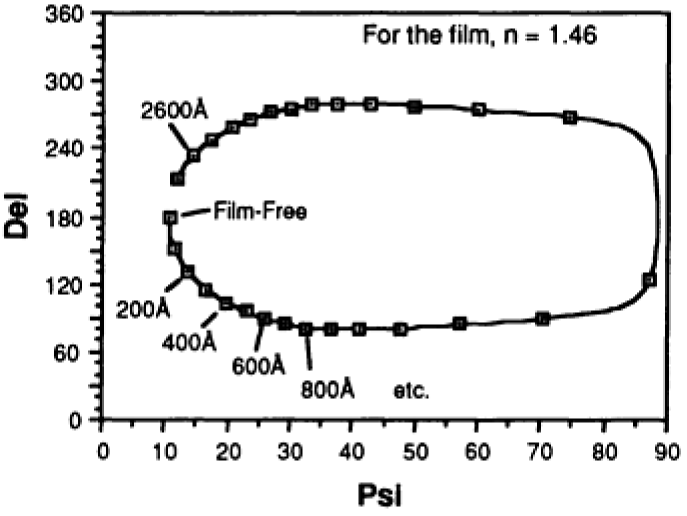

**Fig. 5 The *Del/Psi* trajectory for silicon dioxide on silicon with angle of incidence of 70° and wavelength of 632.8 nm. Source: Ref 8**

The physics and mathematics for converting ellipsometric measurements to optical constants and film thicknesses are beyond the scope of this article. The reader should refer to books by Azzam and Bashara (Ref 7) and Tompkins (Ref 8) for details. The important point to remember is that the technique relies on differences in phase shift and reflectance for the two directions of polarization, and on changes in these differences as a function of film thickness.

The trajectory that is traced out depends on the index of refraction of the film. Figure 6 shows the first part of trajectories for films on silicon, with *n* values 1.46, 1.6, 1.8, and 2.0. If an unknown film were measured and the resulting values of *Del*/*Psi* were 70.0°/28.9°, it could be determined by inspection from Fig. 6 that the *Del*/*Psi* point falls on the *n* = 1.8 trajectory, and the position on this trajectory indicates that the thickness is 60 nm. Although the calculations to plot these trajectories can be made (Ref 8), normally the microprocessor in the ellipsometer makes the calculations and provides the values of *n* and thickness. This has led to the common misconception that ellipsometers measure the index of refraction and thickness. In fact, ellipsometers measure *Del*and *Psi*, and the values of *n* and thickness are calculated based on a model. The model is implicitly chosen when the program on the microprocessor is chosen (e.g., single film or substrate).

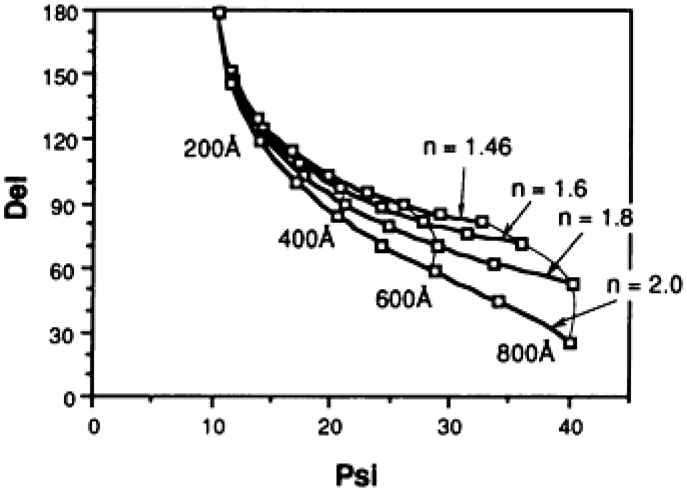

**Fig. 6 The *Del/Psi* trajectories for films with several different indices of refraction on single crystal silicon substrates. The first 80 nm is shown. Source: Ref 8**

Because of the periodicity, the resulting thickness value is not unique. A *Del*/*Psi* point of 129.9°/13.7° could represent a film 20 nm thick, 283.2 + 20 nm thick, 2 × 283.2 + 20 nm thick, and so on. In many cases, other processing information can be used to deal with this matter. The deposition or film formation rate can often be used to estimate the film thickness to well within one period thickness. For a totally unknown film, however, other methods must be used. The period thickness depends on the index of refraction of the film, the angle of incidence, and the wavelength of light being used. By using another wavelength of light or another angle of incidence, the question of period can often be resolved. If unknown film stacks are routinely encountered, spectroscopic ellipsometry might be a more appropriate technique.

For non-dielectric films, the *Del*/*Psi* trajectory does not close on itself. An example is shown in Fig. 7. Conceptually, with no film present, the *Del*/*Psi* point represents the substrate. When there is a thick film of an opaque material present, the *Del*/*Psi* point will represent a substrate of the film material. The *Del*/*Psi* trajectory during film growth is simply the movement of the *Del*/*Psi* point between the location for the original substrate to the location for a substrate of the film material. In Fig. 7 the growth of a tungsten film on silicon is shown. As long as the film is thin enough that light reaches the silicon substrate, ellipsometry can be used for film thickness measurements. For tungsten, the method could be used for films up to about 20 nm thick. Beyond that, the points are too close together for the method to be useful.

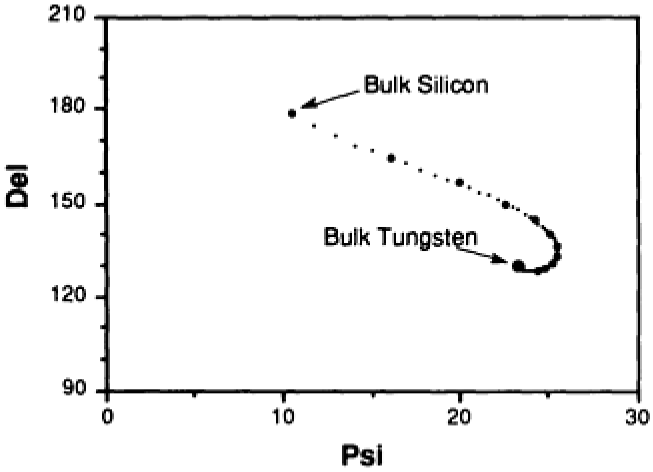

**Fig. 7 The *Del/Psi* trajectory when a film of tungsten is deposited onto silicon. The small dots are at 1 nm intervals. The large dots are at 5 nm intervals from zero thickness. Source: Ref 8**

**Areas of Applicability.** Ellipsometers can measure *Del*/*Psi* to a few hundredths of a degree. A change in film thickness (with $n$ = 2.0) of 0.1 nm represents about 0.25° in *Del.* This technique therefore can be used to measure monolayer changes. This is a particularly powerful technique in the thickness range from about 1 nm to a few hundred nanometers. When the thickness is greater than several period thicknesses, other techniques such as reflectometry may be more appropriate for thickness measurements. Even in this case, however, ellipsometry may be used to provide index of refraction information for the reflectometry instrument.

When multiple films are present, information about the top film can be determined if information is available for all of the underlying films. In metrology situations, this is often the case, but for totally unknown films, other methods normally must be used.

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## Reflectometry

Reflectometry is normally done at normal incidence and is simply the measure of the ratio of the intensity of the reflected light to the intensity of the incident light (Ref 12). This is usually done at various wavelengths over the visible, ultraviolet, and/or infrared region. Figure 8 shows the schematic setup of a typical instrument used for this measurement. Measurements are often made on patterned wafers, hence it is necessary to have an image detector for proper positioning of the sample. The diffraction grating separates the light into its various wavelengths. As this is rotated, the photometric detector is used to measure the reflectance spectrum.

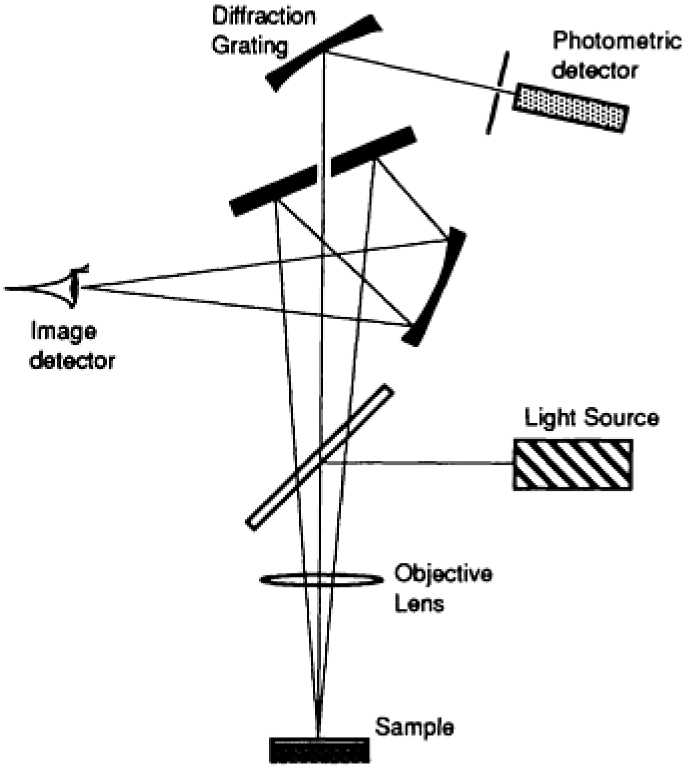

**Fig. 8 Schematic of reflectance instrument**

Rudimentary instruments scan between about 400 and 800 nm and contain the software to determine film thickness for several specific film/substrate materials (with the optical constants included in the software). More advanced instruments allow the introduction of other values for the indices of refraction and give plots of the calculated spectrum versus the measured spectrum. Other advanced features include regression analysis of thicknesses and optical constants for multiple films and extended wavelength ranges.

**Spectral Interpretation.** The equipment is basically an interferometer that scans wavelength for a fixed interference path rather than scanning distance at a fixed wavelength. The technique relies on interference between light reflected from the film and light reflected from substrate surfaces. Figure 9 shows a generic reflectance spectrum. When the wavelength/film thickness ratio is large, no interference occurs. As the wavelength/film thickness ratio decreases, the first order minimum is approached. Here, light reflecting from the lower interface destructively interferes with light reflecting from the upper interface and gives a minimum in intensity. As the wavelength/film thickness ratio decreases further, constructive interference causes the first order maximum to be reached. Further decreases in the wavelength/film thickness ratio cause the intensity to pass successively through various minima and maxima. Figure 9 can be described as a generic reflectance spectrum that shows interference phenomena but does not include the influence of dispersion of the index of refraction of either the film or the substrate. What is shown is a rather wide range in wavelength/film thickness. In an actual measurement, only a part of the entire spectrum would be observed because the wavelength range of available instruments is limited.

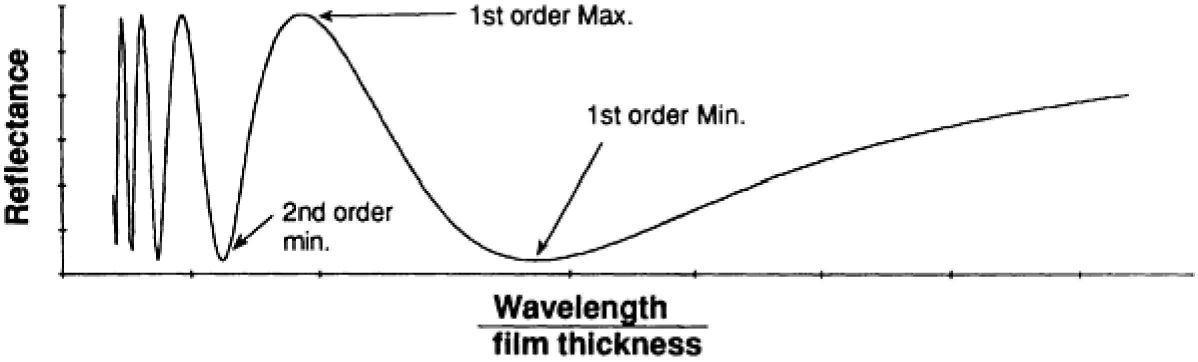

**Fig. 9 Generic interferogram plotting reflectance vs. the wavelength/film thickness ratio. Optical constant dispersion is ignored. Note that for a finite wavelength range, a given instrument will not measure the entire interferogram**

Moving from the generic to the specific, Fig. 10 shows calculated reflectance spectra for a $Si_3N_4$ film on a nickel substrate. In Fig. 10(a) the film thickness is 2 µm and in Fig. 10(b) the film thickness is 0.2 µm. Note that there are many maxima and minima in the spectrum from the thicker film. Some instruments simply determine where the maxima and minima occur and use this information for calculating the film thickness. When there are insufficient numbers of maxima and minima for this method (e.g., as in Fig. 10b), curve fitting is used to determine the film thickness. In some instruments, curve fitting is used for all thicknesses. In still other instruments, the reflectances at predetermined wavelengths are used in a lookup table. When the film thickness is below a few tens of nanometers, the curve shapes are insignificantly different from each other, and spectral reflectometry is insufficient for film thickness measurements.

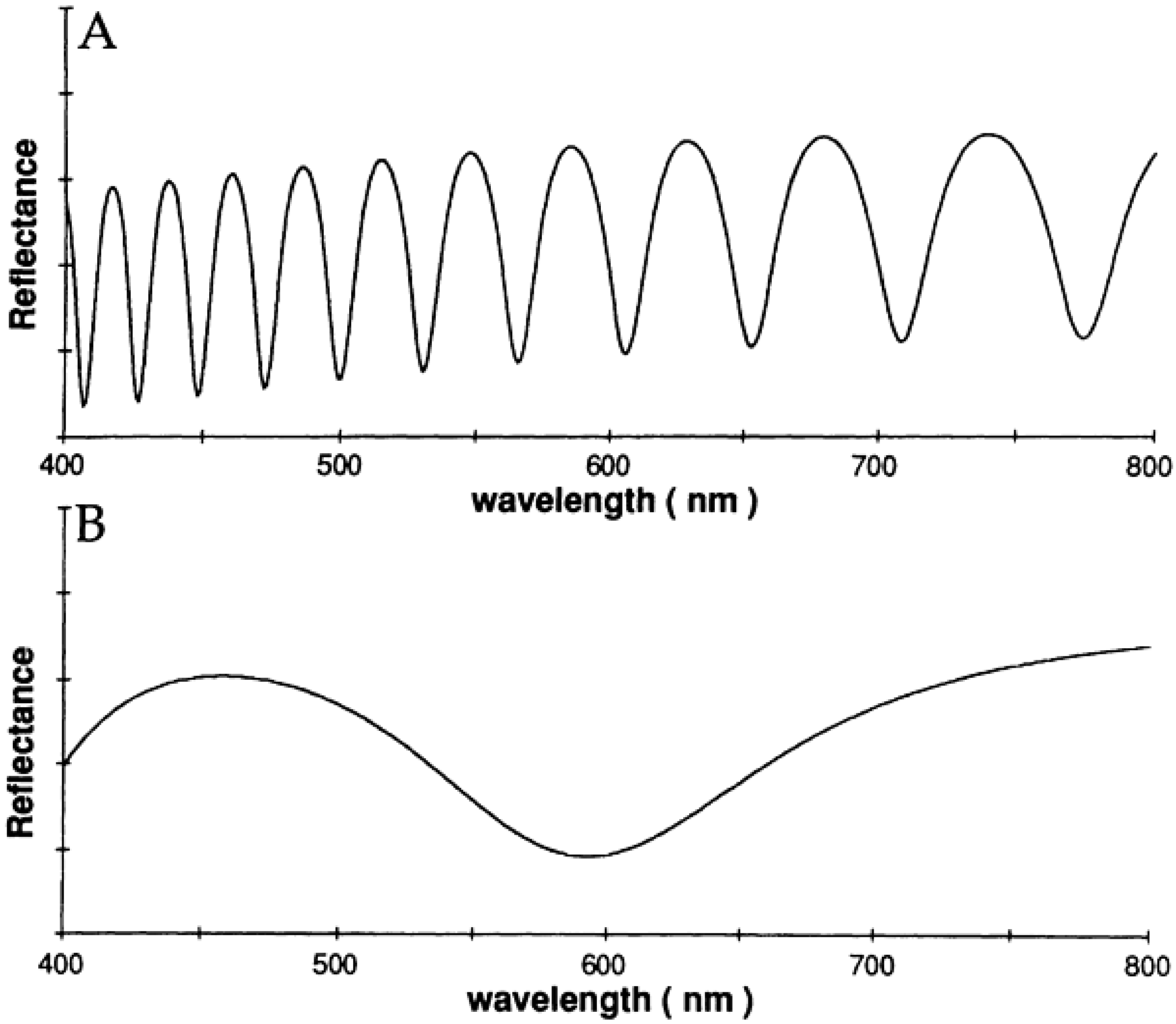

**Fig. 10 Interferogram for $Si_3N_4$ on nickel. (a) The film thickness is 2 μm. Note that there are many maxima and minima in the wavelength range. (b) The film thickness is 0.2 μm. Note that there are only one maximum and one minimum in the wavelength range.**

**Applicability.** The uncertainty due to periodicity found in SWE is not present in reflectometry. The method works best when the optical constants of both the film and the substrate are known and the only quantity to be determined is the film thickness. It is particularly appropriate for films thicker than several hundred nanometers. Some of the latest models make it possible to determine material constants for materials not preprogrammed into the software.

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## Spectroscopic Ellipsometry

**Contrasted to SWE and Reflectometry.** Both SWE and reflectometry excel when the sample of interest is a single film on a substrate. For samples with two layers on a substrate, both SWE and reflectometry can be used if many of the optical parameters are known, with only a few to be determined. These are special cases, however. Spectroscopic ellipsometry, on the other hand, is designed specifically to be used with multiple layers (Ref 13).

The function of the SE instrument, like that of the SWE instrument, is to measure the ellipsometric parameters. The primary difference is that for SE, the measurements must be made at many wavelengths. Because a QWP used in SWE is specific to a given wavelength, it cannot conveniently be used for SE. In addition, the light source gives out radiation with all of the wavelengths of interest, and they are sampled one at a time by using a monochromator. Because many measurements must be made for a single spectrum, the photometric method is used rather than the null method, because it is faster. For rotating-element instruments without QWPs, the quantities measured are *tan*(ψ) and *cos*(Δ) rather than ψ and Δ as in SWE.

**Multilayer Example.** As an example of the use of SE, Fig. 11 shows the SIMOX structure (Ref 14, 15, 16, 17, 18). This structure is fabricated by implanting oxygen into silicon and then annealing the structure at temperatures above 1200 °C (2200 °F). The anneal helps segregate the implanted oxygen into a well-defined oxide layer and reduces defectivity in the layers. The top silicon retains its crystallinity due to elevated sample temperatures during the implant. One side effect is the formation of the silicon nodules shown near the bottom of the oxide. Any oxide formed on the top silicon layer during the anneal is removed as a final processing step. The usual native oxide then forms upon exposure to the atmosphere.

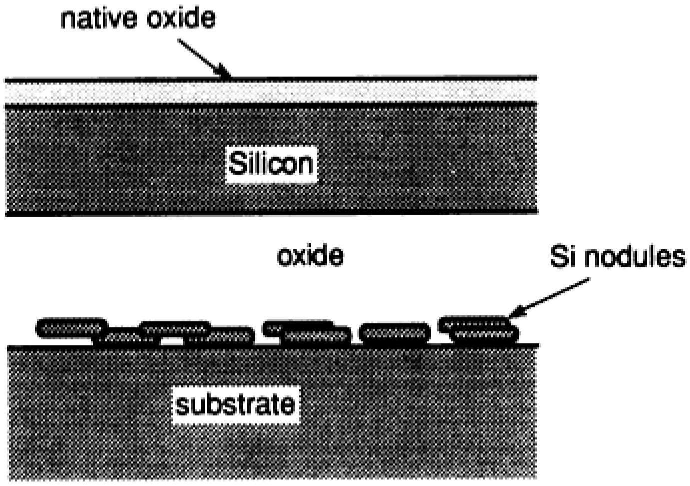

**Fig. 11 Film structure formed by implanting silicon with oxygen (SIMOX structure) and then annealing at a temperature greater than 1200 °C (2200 °F)**

Analysis with SE consists of measuring the parameters *tan*(ψ) and *cos*(Δ) for the wavelengths of interest and then determining the thicknesses and optical constants of all the layers by regression analysis. In many cases, the optical constants are known and preprogrammed into the analysis software. Figure 12 shows the SE spectra along with the best regression fit when the nodule layer is ignored and the sample is modeled as silicon wafer/oxide/silicon/native oxide.

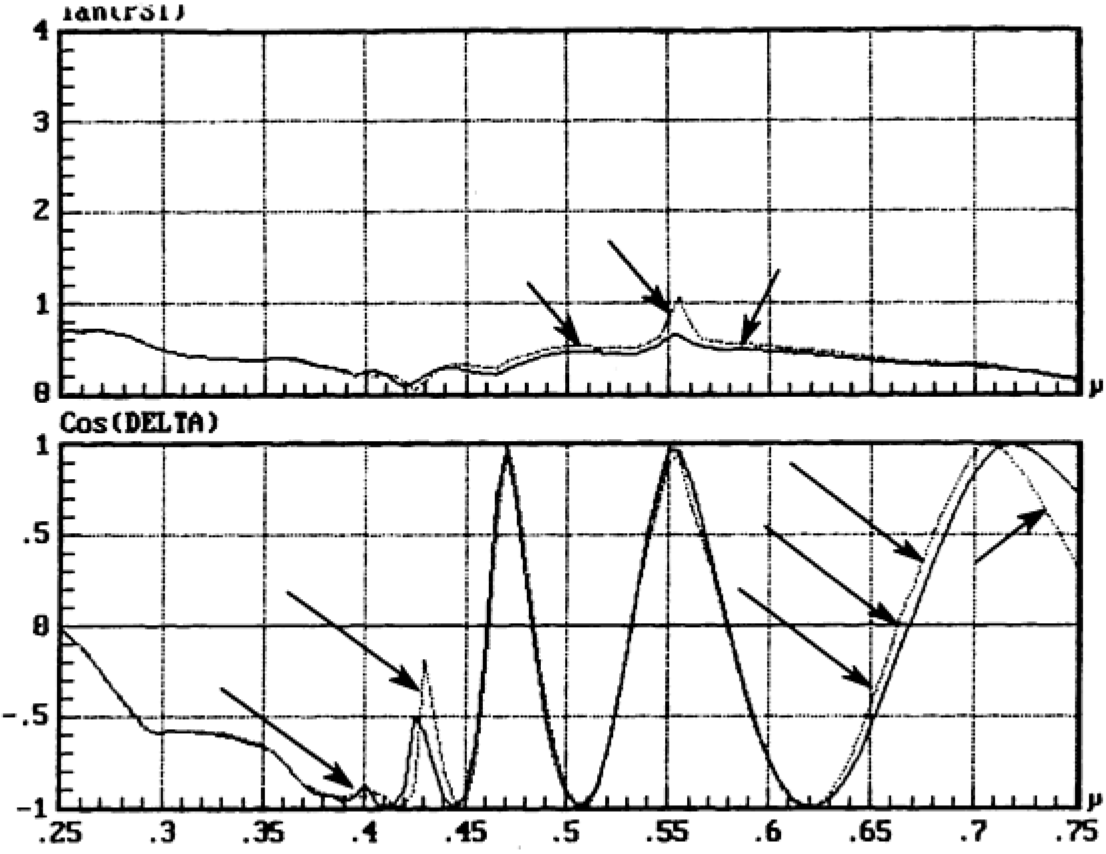

**Fig. 12 The measured spectroscopic values for a SIMOX sample along with the calculated values using a model that ignores the silicon nodules. The arrows indicate regions of serious lack of fit.**

For this fit, the thicknesses are 360.1, 211.2, and 1.8 nm for the oxide, silicon, and native oxide, respectively. Although the regression analysis curve matches the measured curve in many places, there are several locations where the misfit is noticeable, and these are indicated by arrows.

To improve the fit, the oxide can be modeled as two layers. The top layer is simply the oxide, and the bottom layer (to deal with the nodules) is a mixture of oxide and silicon. The concentration of the silicon in the mixture is one of the quantities to be determined, along with the thicknesses of the various layers. Figure 13 shows the regression fit best for this model, showing that the fit has been improved. Goodness of fit is measured by comparing the calculated curve to the measured curve and is significantly better for the curve shown in Fig. 13 than in Fig. 12. The thicknesses of the layers with this model are 32.9, 325.2, 210.9, and 1.8 nm for the mixture, oxide, silicon, and native oxide, respectively. The concentration of the silicon in the bottom oxide layer is 46%.

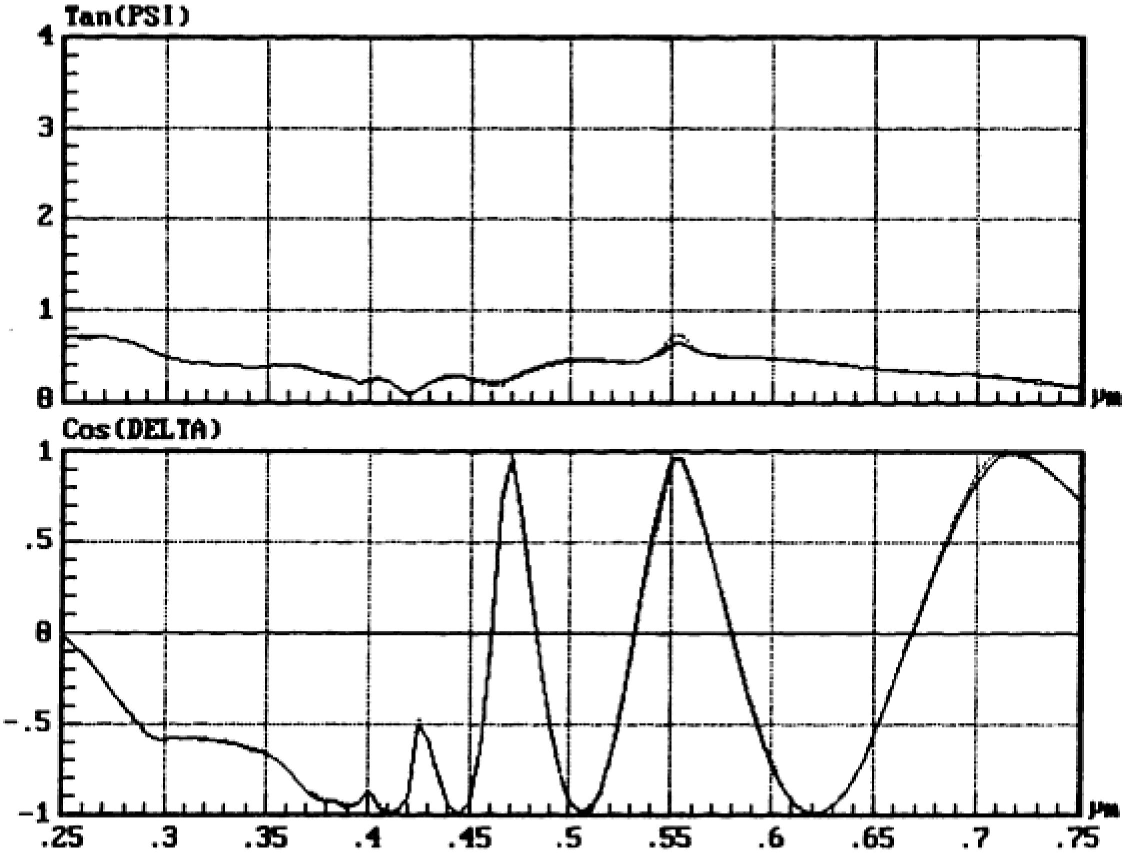

**Fig. 13 The measured spectroscopic values for a SIMOX sample along with the calculated values using a model that includes a layer of a "mixture" consisting of oxide and silicon**

**Applicability.** Spectroscopic ellipsometry can be used to measure layers in thicknesses ranging from a few nanometers to a few micrometers. The optical constants of many materials make them opaque in part of the spectral region and transparent in other parts of the spectrum. This feature can be used to advantage to distinguish between top layers and underlying layers. The most important feature of SE is that multilayers can readily be measured.

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## Corrosion Testing of Coatings

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## Introduction

CORROSION, according to the *ASM Materials Engineering Dictionary*, is "the chemical or electrochemical reaction between a material, usually a metal, and its environment that produces a deterioration of the material and its properties." Because corrosion is related to the material and its environment, it occurs under an immense variety of conditions. The environment includes not only the gas atmospheres or liquid media in their actual composition surrounding the piece, but also temperature and its changes and specific conditions of flow. This means that corrosion is a materials behavior in a specific environment.

Increasingly, corrosion resistance must be provided even by decorative coatings and those used for wear resistance. Numerous corrosion protection techniques have been developed (e.g., conversion coatings, organic coatings, and metallic thin and thick films). These techniques introduce a new system property, the coating-substrate behavior. The major requirements for good corrosion protection are high corrosion resistance of the coating material, a pore-free structure, and good adhesion. Additionally, production costs play an important role in the selection of a coating-substrate for a given problem.

This article discusses the testing and typical corrosion behavior of coating-substrate systems in aqueous solutions and humid aggressive atmospheres. There is a short review of the fundamentals of corrosion, followed by discussion of specific system behavior, electrochemical and laboratory accelerated tests, and simulated service tests. Finally, the article gives examples of types of corrosion damage and guidelines for improving corrosion resistance by coatings. A more detailed description of general corrosion phenomena, corrosion testing and evaluation, corrosion protection, corrosion of specific alloy systems, and corrosion in specific industries and environments is given in *Corrosion*, Volume 13 of the *ASM Handbook* (Ref 1), as well as in other review books and articles (Ref 2, 3, 4, 5). The behavior of nitride hard coatings deposited by physical vapor deposition or chemical vapor deposition is summarized in Ref 6.

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## Fundamentals of Corrosion of Coating-Substrate Systems

**Corrosion Processes.** Corrosion is based on the reaction of a metallic material or layer with its environment. The metal atoms of a component change from the metallic state into an oxidized state. The products may be dissolved species or solid corrosion products. The driving force of this process is the tendency of the system to lower its free energy.

Corrosion in aqueous media is a surface reaction that takes place as an electrochemical process. In terms of electrochemistry, the metal and the corrosive medium are the electrode and the electrolyte, respectively. The electrolyte is conductive due to the presence of dissolved cations and anions. Hence, the corrosion reaction is a closed electrical circuit in which the current is based on the electrical conductivity of the metal on one hand, and on the ionic conductivity of the electrolyte on the other hand. Corrosion results from a direct electrical contact between the metal and the electrolyte. In the case of the formation of a nonconducting, pinhole-free surface layer (e.g., aluminum oxide on aluminum), no corrosion current is possible.

This type of corrosion involves at least two or more separate electrochemical reactions that take place simultaneously. The transfer of a metal atom into a metal forms free electrons, which leads to the reduction of the corresponding oxidant. The deciding factor governing the corrosion reaction is the electrochemical equilibrium between the metallic surface and the aqueous corrosive medium in contact with it. This equilibrium is influenced by which materials are in contact and the activity of the reacting species.

In the case of a very low metal ion concentration in the electrolyte, the corrosion current is anodic to its major part (i.e., the metal is corroded by its dissolution in the electrolyte). Under closed-system conditions, the current exists only as long as the system has not reached its equilibrium state. In the dynamic equilibrium the sum of the anodic and cathodic currents becomes zero (i.e., the rate of metal dissolution equals the rate of metal deposition), and no loss of mass can be observed any longer by microscopy. In practice, the equilibrium state is normally never reached, so corrosion proceeds continuously.

The standard electrochemical potential of metals is defined as the potential in the equilibrium state. The measurement of the electrode potential is only possible relative to that of a second electrode, so all potentials are related to the potential of a standard hydrogen electrode, which is by definition set to zero as reference. Standard potentials can be listed for all metals and for specific electrochemical reactions. Table 1 shows the standard potentials of selected metals. Additionally, potentials are listed for these metals under different conditions. As can be seen, the order of the different metals changes. For corrosion processes, such tables indicate which metal of a pair in contact is more noble or less noble. Factors influencing the actual potential values are temperature, concentration of the electrolyte, and alloy composition of the metal.

**Table 1 Electrochemical potential of selected metals under three different conditions**

| **Metal** | **Potential, mV** |
|---|---|
| **Versus standard hydrogen electrode** | |
| Gold | +1360 |
| Silver | +800 |
| Copper | +350 |
| Hydrogen | 0 |
| Tin | -140 |
| Nickel | -230 |
| Iron | -440 |
| Chromium | -560 |
| Zinc | -760 |
| Aluminum | -1670 |
| **In artificial seawater** [(a)] | |
| Gold | +243 |

| | |
|---|---|
| Silver | +149 |
| Nickel | +46 |
| Copper | +10 |
| Chromium | -290 |
| Iron | -450 |
| Aluminum | -670 |
| Zinc | -800 |
| **In water** [(b)] | |
| Gold | +306 |
| Silver | +194 |
| Copper | +140 |
| Nickel | +118 |
| Aluminum | -169 |
| Chromium | -249 |
| Tin | -275 |
| Iron | -400 |
| Zinc | -790 |

(a) pH 7.5, 1 bar (DIN 50907).

(b) pH 6, 1 bar

In practice, where different metals are present as alloy components or in coating-substrate systems, the different electrochemical reactions take place simultaneously, resulting in a mixed or galvanic couple potential. The corrosion behavior of a specific system is determined by the relation of the respective metals in contact. Furthermore, environmental conditions such as pH value, temperature, concentration of the electrolyte, and the hydrodynamic conditions at the electrode affect the actual behavior (Ref 1, 2, 3, 4).

**Corrosion of Coating-Substrate Systems.** In principle, the corrosion behavior of a coated part (i.e., a coating-substrate system) is determined by the corrosion resistance of the coating material in the respective medium. However, this holds only for absolutely dense coatings that completely separate the aqueous corrosive medium from the underlying substrate material. In practice, coatings and thin films show pores, pinholes, and other defects after their deposition, or they may be damaged by scratches or other wear mechanisms. Both types of defects allow the corrosive medium to contact the substrate material or the interlayers and underlayers.

Depending on the materials combination, the coating material is either *more* noble or *less* noble than the substrate material. The behavior of the two adjacent layers and the interlayers can be characterized in the same way. The relative corrosion behavior depends on the corrosion medium and the specific conditions. Their order can vary markedly, as shown in Table 1.

The electrochemical reactions are schematically illustrated in Fig. 1. In the case of a more noble coating (Fig. 1a), the corrosion medium reaches the substrate material, and a galvanic cell is formed between the anodic substrate material and the cathodic coating material. This results in strong local corrosion of the substrate. The anodic metal ion current density is rather high because of its very small surface area, whereas the cathodic $H^+$ discharging or oxygen reduction takes place over the entire coating surface. This explains why defects can be so detrimental. If a system cannot be deposited without defects, a fine and homogeneous distribution of them reduces local corrosion. This explains why the well-known microcrack network is used in electrolytic chromium plating.

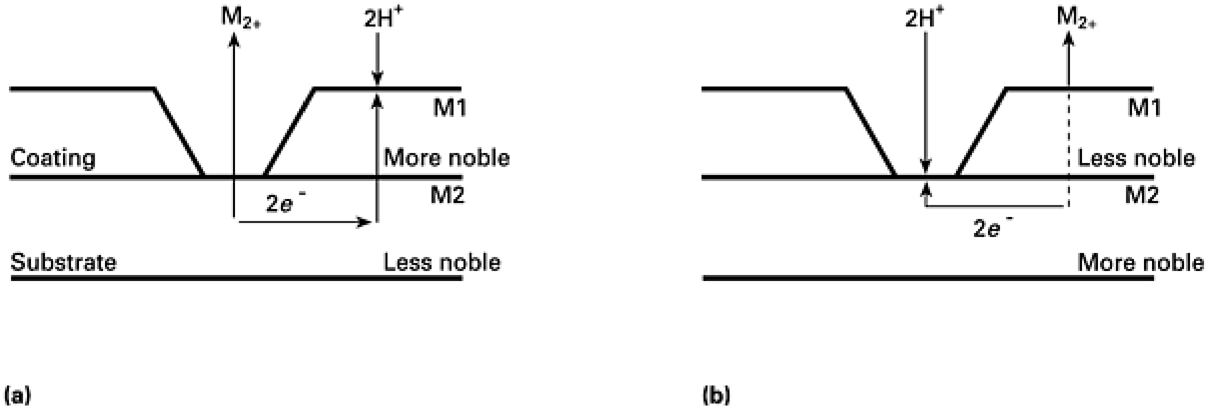

**Fig. 1 Schematic illustration of corrosion of coating substrate systems in the presence of pores. M, metal. (a) More noble coating on less noble substrate (galvanic corrosion). Increased corrosion of substrate material, small anodic area, large cathodic area. (b) Less noble coating on more noble substrate (anodic corrosion). Cathodic protection of substrate material, coating material dissolved, large anodic area, small cathodic area**

In the case of a less noble coating material (Fig. 1b), anodic protection of the substrate is observed. The anodically polarized coating is uniformly dissolved, and in general the relatively small cathodic area yields a low rate of corrosion.

Figure 2 schematically illustrates some typical examples of corroded coating-substrate systems, demonstrating the system effects in the corrosion performance of a part.

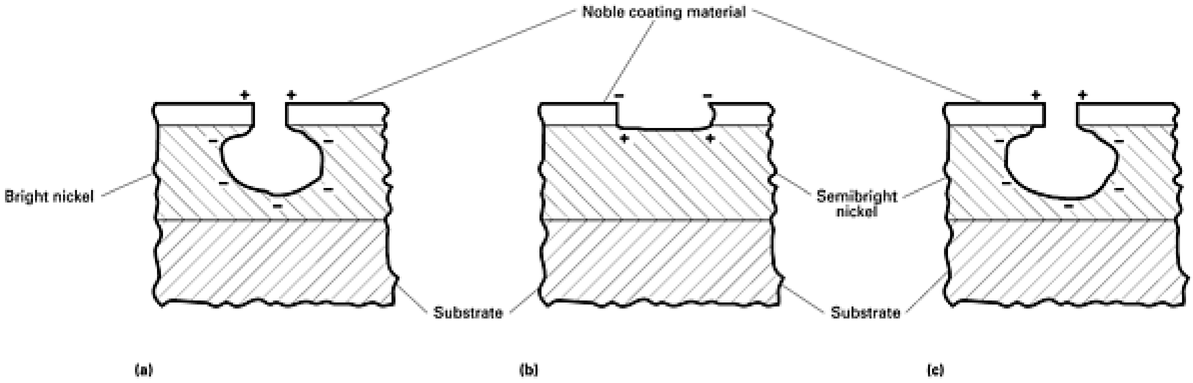

**Fig. 2 Corrosion of coating-substrate systems showing the different behaviors with respect to system and electrolyte. Solution 1, $Cl^-$. Solution 2, $SO_4^{2-}$. (a) Solutions 1 and 2. (b) Solution 1. (c) Solution 2**

As a consequence of these two types of coating-substrate corrosion behavior, two methods for improving corrosion resistance are applied in practice:

- *A more noble coating* protects the less noble substrate. The coating should have high corrosion resistance and be highly defect-free; otherwise, severe local galvanic corrosion can degrade the material. Examples are copper, nickel, and chromium plating.
- *A less noble coating* is deposited as sacrificial protection material. Corrosion protection is virtually guaranteed as long as coating material is present. Examples are zinc and cadmium coatings.

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## Electrochemical Corrosion Tests

Because corrosion of metals is an electrochemical process, electrochemical measurements are especially suited to it. As described above, the corrosion reaction occurs between the cathodic and anodic parts of a corroding system, resulting in an electric current in the metal and an ionic current in the electrolyte at the metal-electrolyte interface. The amount of current produced is a measure of the oxidation or reduction reaction, so it provides information about the rate of the corrosion process.

In principle, electrochemical methods of corrosion measurements can be divided as follows:

### Without external electrical source

- Current measurements
- Potential measurements

### With external electrical source

- Polarization measurements

- Tafel extrapolation
- Polarization resistance measurements
- Impedance measurements

In the first type, different electrical parameters can be present. In the latter type, only system-adjusted values are measured (Ref 1, 2, 7, 8, 9). All measurements are performed in different electrochemical cells (Fig. 3). The following paragraphs describe these techniques in more detail.

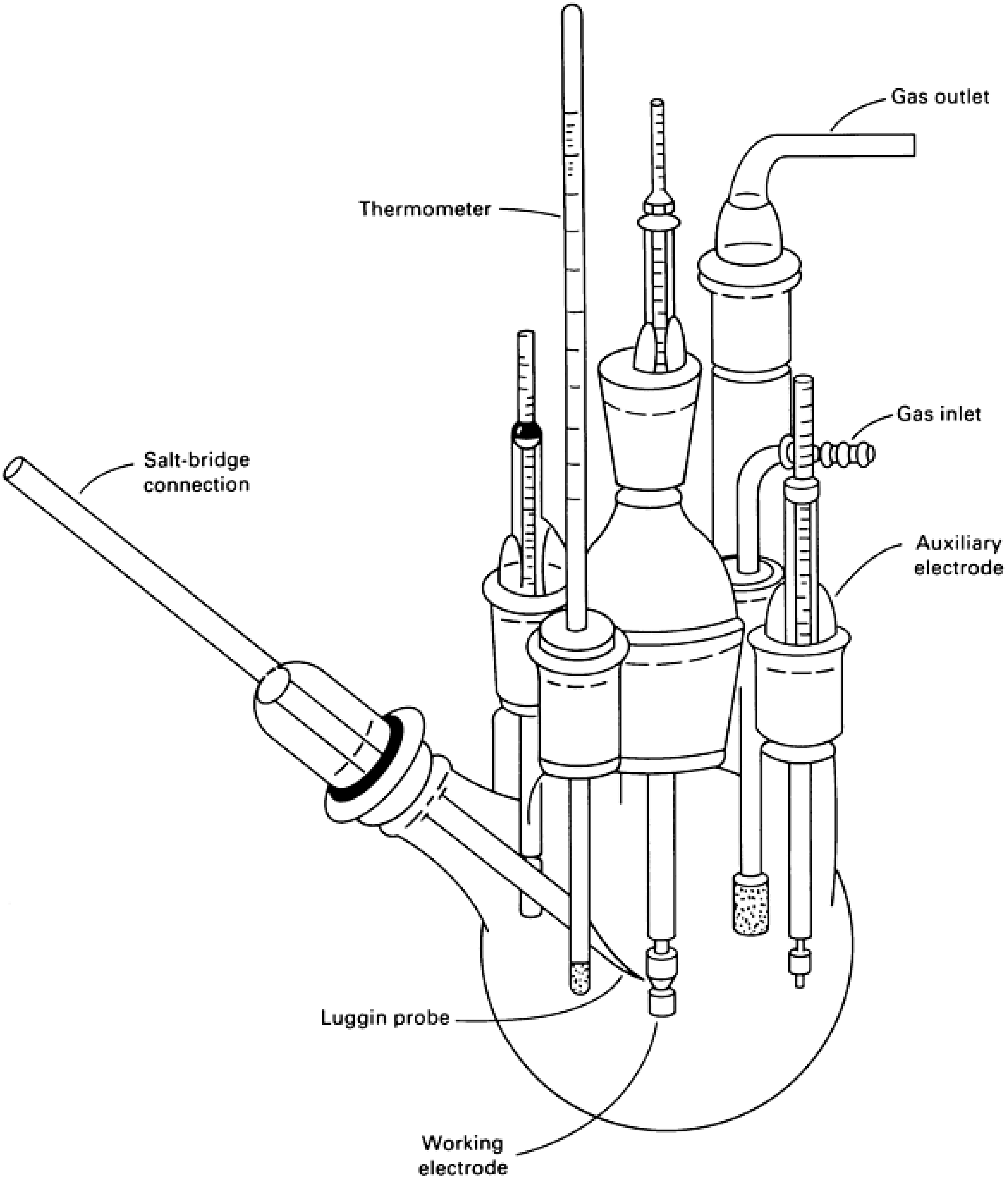

**Fig. 3 Electrochemical measurement cell for corrosion investigations. Source: Ref 10**

**Current Measurements.** The calculation of the corrosion rate of metal-electrolyte systems is based on Faraday's law if the reaction follows an electrochemical mechanism:

$$m = \frac{l.t.M}{n.F} \qquad \textbf{(Eq 1)}$$

where $m$ is the amount of substance (in mol%) liberated or deposited by the passage of an electric current $I$ (in amperes); $t$ is time in seconds; $M$ is the molecular weight of the electroactive species; $n$ is the number of electrons involved in the electrochemical reaction; and F is the Faraday constant. Thus $m$ is directly proportional to the quantity of charge passed, $Q$, where $Q = I \cdot t$.

The corrosion current of a homogeneous mixed electrode cannot be measured directly, because the surface is composed of a large number of "short-cut" corrosion elements uniformly distributed over the surface. In contrast, for electrode systems with separate areas of cathodic and anodic processes (e.g., different metals in contact), the corrosion current can be determined directly.

**Potential measurements** determine the potential established at the (working) electrode versus that established at the electrolyte. A standard reference electrode is used, such as Ag-AgCl-$Cl^-$ (Argental) or Pt-Hg-$Hg_2Cl_2$-$Cl^-$ (standard calomel electrode). These open-circuit measurements are made under equilibrium conditions (i.e., absence of current flow) to describe the thermodynamic equilibrium of an electrochemical system.

In the case of homogeneous mixed electrodes, the position of the reference electrode is of no importance because of the uniform potential distribution of the working electrode (sample). In contrast, potential measurements on heterogeneous mixed electrodes have to be performed locally. The Haber-Luggin capillary electrode is one of the easiest to use because it is positioned with its capillary tip close to the sample surface.

Potential measurements make it possible to describe the behavior of an electrode-electrolyte system (active or passive state) and the potential distribution of the corroding electrode.

**Polarization measurements** are based on the application of an external electrical load. The different methods are distinguished by the presetting of a potential or current that is controlled by a potentiostat. Methods using constant or time-dependent potentials are called potentiostatic and potentiodynamic, respectively. Likewise, current-controlled methods are called galvanostatic or galvanodynamic. The variation of the potential or current values can be performed continuously or in stepwise fashion. In the static methods, measurements need to be taken for a long enough period to reach steady-state conditions. In the dynamic measurements, parameters can be changed, such as scan rate or form of scan function. Quasi-steady-state conditions can be reached in the case of stepwise alterations at long holding times.

These polarization measurements involve three electrodes: a measurement electrode, a reference electrode, and a counter electrode. In this system the sample represents the measurement electrode (working electrode). The current flows only between the working electrode and the counter electrode, while the reference electrode is connected to a potentiostat or a high-impedance voltmeter and, hence, is without load. In potential-controlled measurements, the potential of the working electrode is kept constant or is definitely varied; in current-controlled measurements, a defined current flow is applied. In both methods, the potential of the measurement electrode is measured by use of the reference electrode.

**Tafel Extrapolation.** An application of polarization measurements is the determination of corrosion current density using the Tafel extrapolation. Under the conditions of a pure charge transfer-controlled process, the current density/polarization curves are given by:

$$j = j_{corr}\left[\exp\left(\frac{2.3h}{b_A}\right) - \exp\left(-\frac{2.3h}{b_c}\right)\right] \qquad \textbf{(Eq 2)}$$

where $j$ is the applied current density, $j_{corr}$ is the corrosion current density, $\eta$is the polarization, and $\beta_A$ and $\beta_C$ are the anodic and cathodic Tafel slopes.

In the case of a highly anodic polarization, the second part of Eq 2 becomes very small, and in the case of a highly cathodic polarization, the first part becomes small. These relationships can be shown as:

$$j_A = j_{corr} \exp\left(\frac{2.3h}{b_A}\right) \qquad \textbf{(Eq 3)}$$

$$j_C = j_{corr} \exp\left(-\frac{2.3h}{b_C}\right) \qquad \textbf{(Eq 4)}$$

The plotting of polarization versus the logarithm of the current density shows a linear relationship. The extrapolation of these Tafel straight lines to the open-circuit potential can be used to determine the current density of the corrosion process (Fig. 4).

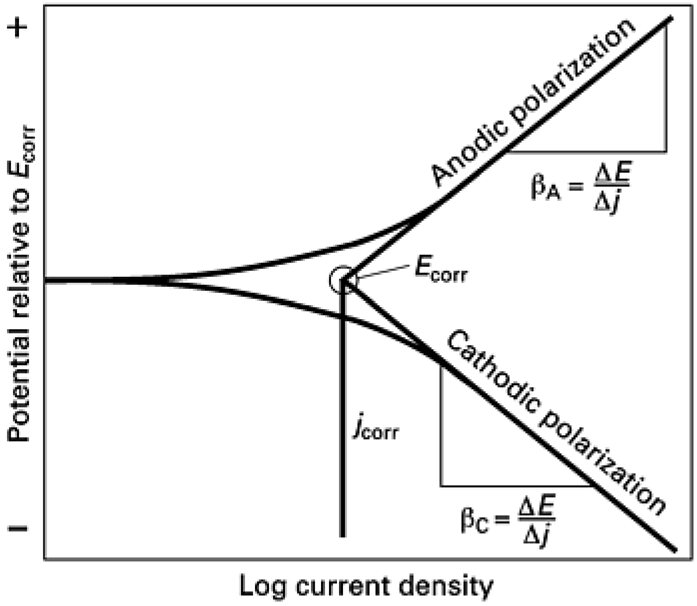

**Fig. 4 Tafel plot to determine corrosion current density. $\beta_A$ and $\beta_C$, anodic and cathodic Tafel coefficients; *j*, applied current density; $j_{corr}$, corrosion current density *E*, potential;$E_{corr}$, corrosion potential**

These equations can be used only in the case of a pure charge transfer-controlled reaction. Therefore, it must be guaranteed that other polarization effects are negligible (e.g., concentration polarization or polarization resulting from the resistivity of the electrolyte depending on the distance of the used reference electrode from the sample surface).

**Polarization Resistance.** Another polarization technique is the determination of polarization resistance, $R_p$. This method is based on the fact that the cathodic or anodic current density change is approximately linear with the polarization in the range near the corrosion potential (Ref 11, 12). These relationships can be described by:

$$R_p = \frac{b_A.b_C}{2.3.j_{corr}(b_A + b_c)} \qquad \textbf{(Eq 5)}$$

The advantage of measuring polarization resistance is that only a very small potential range has to be scanned, and thus the measurements take less time. On the other hand, a charge transfer-controlled condition can be reached with very low scan rates without a large increase in total measuring time.

**Impedance measurements** involve applying a small-amplitude sinusoidal potential to the measurement system and registering the current response to the signal's amplitude and the phase. A corrosion process can be described by an equivalent electrical circuit model. A simple corrosion reaction can be viewed as a circuit, as illustrated in Fig. 5. The impedance of this circuit can be described by:

$$Z = R_{\Omega} + \frac{R_p}{(1+v^2.R_p{}^2.C^2)} - \frac{j.v\,.C.R_p{}^2}{(1+v^2.R_p{}^2.C^2)} \qquad \textbf{(Eq 6)}$$

where ω is the frequency of the applied signal. To determine *R*Ω and $R_p$ in Fig. 5, it is necessary to make measurements over a wide range of frequencies and to plot the impedance of the system as a function of frequency. A Bode plot for the equivalent electrical circuit in Fig. 5 is shown in Fig. 6. To describe the system it is also necessary to measure the current response that is in phase with the alternating potential wave form, as well as the current response that is out of phase with the applied potential. From these data one can calculate the real and imaginary part of the impedance for each frequency. The plot of imaginary versus real impedance over a range of frequencies, the Nyquist plot, is shown in Fig. 7. When interpreted correctly and applied appropriately, impedance measurements are a powerful tool for describing corrosion processes (Ref 8, 13, 14, 15).

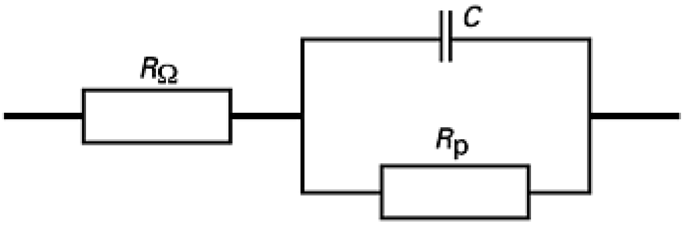

**Fig. 5 Equivalent electric circuit model. *R*Ω, resistance between the reference electrode and the working electrode; $R_p$, polarization resistance of the electrochemical reaction; *C*, capacitance of the double layer**

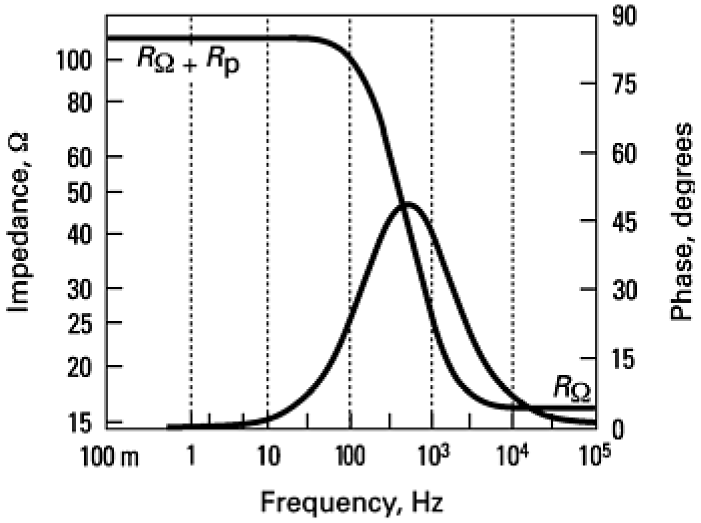

**Fig. 6 Bode plot of the electrical circuit in Fig. 5. *R*Ω, resistance between the reference electrode and the working electrode; $R_p$, polarization resistance of the electrochemical reaction**

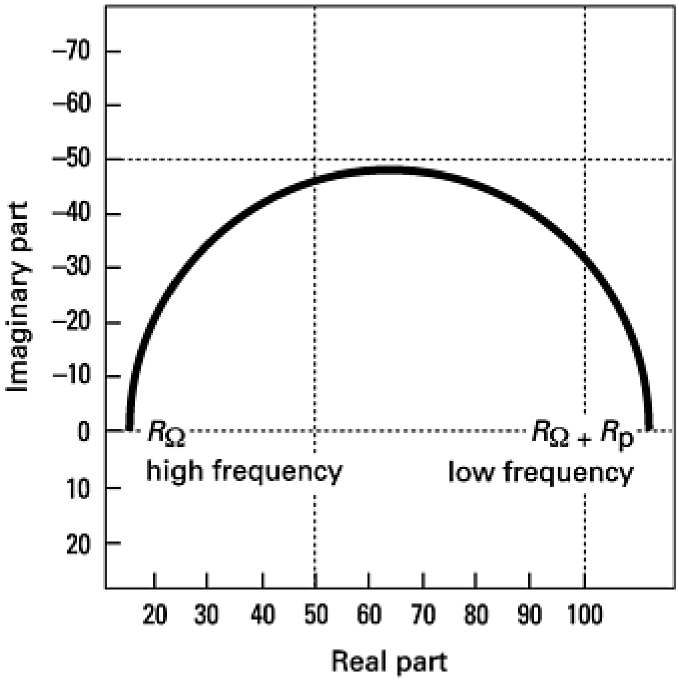

**Fig. 7 Nyquist plot of imaginary versus real impedance over a range of frequencies. $R_\Omega$, resistance between the reference electrode and the working electrode; $R_p$, polarization resistance of the electrochemical reaction**

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## Laboratory Corrosion Tests

To get information on the long-time corrosion behavior of parts, accelerated (short-time) tests have been used for decades. The environment used might simulate a humid tropical area, the salty air of a seaside area, a salted road in winter, a highly industrialized area, or one of many others. Even these few examples show the tremendous variety of aggressive environments that have to be considered.

Laboratory tests can easily compare the performance of materials and systems. They involve continuous exposure or increased corrosion activity so that results will be available within a short period of time. This means, however, that the mechanism of the corrosion reaction may be changed. It is not known for certain that lifelong corrosion can be simulated by a short-time test, considering that real conditions vary greatly and are sometimes much more complex. Nevertheless, laboratory tests are most widely accepted as a tool for ensuring uniformity and quality of coatings. In general, they have to be verified by field tests.

Laboratory tests are standardized in part, but a huge number of specific test conditions can be applied, depending on the actual conditions of exposure. In principle, three types of tests can be distinguished: wetting of the surface by condensing media in humid atmospheres (simulated atmospheres), spraying of aggressive media, and immersion into corrosive liquid. All tests can be modified by certain intervals or changing conditions. In Table 2 the major laboratory corrosion tests are characterized by their media, procedures, and simulated environments. In general, laboratory corrosion tests are the same as those applied to bulk materials, although the type of deterioration is different.

**Table 2 Laboratory corrosion tests**

| **Test** | **Conditions** | **Information** |
|---|---|---|
| **Simulated atmospheres** | | |
| Condensed water climate test | Saturated water vapor | Behavior in humid environment |
| Condensed water alternating climate test | Water vapor + $SO_2$, temperature change | As in condensed water climate test, with polluted gas |
| **Salt spray tests** | | |
| Salt spray test | NaCl solution | Ocean climate |
| Acetic acid salt spray test | NaCl + $CH_3COOH$ | Salted roads |
| Copper-accelerated acetic acid salt spray test | As in acetic acid salt spray test | As in acetic acid salt spray test, but more aggressive |
| **Immersion tests** | | |
| Artificial sweat test | . . . | Wearing of decorative parts |
| Immersion tests | Solutions of HCl, $HNO_3$, etc. | Wearing of decorative parts, corrosion in aqueous media |

The samples treated in short-time tests normally are visually or optically inspected. The major information to be obtained is whether the coating or substrate material (at the defects) is corroded, the type of corrosion, if any, and the local distribution of the defect-related corrosion attack. The nature and color of the reaction product may be hints about the type of corrosion. The density and extent of corrosion give information about the coating properties (defect distribution) and coating quality (e.g., homogeneity of thickness).

**Simulated atmosphere tests** are performed in closed cabinets (humidity-temperature chambers). The samples are hung above the water-covered cabinet floor. The standard test procedure is to dry the samples and visually inspect them after a certain period (cycle), after which the test is repeated several times.

**The simple condensed water climate test** consists of 24 h cycles performed in saturated water vapor at 40 °C (104 °F) (Ref 16). A more aggressive atmosphere is produced by the addition of $SO_2$ gas. Alternating conditions may be chosen.

**The condensed water alternating climate test** consists of 24 h cycles of changing temperature conditions (e.g., water vapor plus 0.07 to 0.7 vol% $SO_2$ at 18 to 28 °C, or 64 to 82 °F, and 40% humidity, then 75 to 100 °C, or 166 to 212 °F, and 40% humidity) (Ref 17).

**Salt spray (fog) tests** have long been used to determine the corrodability of metals and the degree of protection provided by inorganic or organic coatings. The reproducibility of these tests and their correlation to actual service performance have been extensively discussed. However, they are easily performed, acceptable standards for comparing the behavior of materials and coatings. In several regulations the test procedures and specific conditions are standardized, but some companies and institutions have established their own standards and procedures.

All variations of the salt spray test are used to evaluate coatings for uniformity of thickness and degree of porosity. They are considered the most useful accelerated laboratory corrosion tests. In particular, they are used to evaluate different lots (for quality control in production) or different samples (for coating development in research). As can be seen from Table 2, the neutral salt spray test has been modified into acidified tests.

**The neutral salt spray test** is applied for periods ranging from 8 to 3000 h. A 5% NaCl solution of pH 6.5 to 7.2 is used that does not contain more than 200 ppm total solids. The temperature of the salt spray cabinet is kept at 35 °C (95 °F) +1.1 or -1.7 °C (+2.0 or -3.0 °F) (Ref 18).

**The acetic acid salt spray test** is normally applied for 144 to 240 h or more, but it can be applied for periods as short as 16 h. As in the neutral salt spray test, a 5% NaCl solution is used, but pH is adjusted to a value from 3.1 to 3.3 by adding acetic acid. The temperature is the same. This test is especially useful for decorative chromium platings (Ref 19).

**The copper-accelerated acetic acid salt spray (CASS) test** is applied for 6 to 720 h. Once again, a 5% NaCl solution is used, but with 1 g $CuCl \cdot H_2O$ (Cu-II chloride) per 3.8 L salt solution. The pH value is adjusted to a value from 3.1 to 3.3 by adding acetic acid. The temperature is somewhat increased, 49 °C (120 °F) +1.1 or -1.7 °C (+2.0 or -3.0 °F) (Ref 20).

**Immersion Tests.** In certain cases, complete immersion of the test sample in a corrosive solution is the best simulation. However, the test conditions need to be controlled to ensure reproducible results. The solutions are usually selected according to the actual problem (e.g., seawater or wastewater, liquids used in technical processes, or biological agents such as sweat or saliva). They are often of increased concentration in order to accelerate the corrosion process. For the most part, standardized test conditions are applied (Ref 21, 22). The parameters are solution composition, temperature, aeration, velocity, duration, and cleaning at the conclusion of the exposure.

Immersion of the test samples can be complete or partial (the latter simulates local corrosion, especially at the liquid line). It can also be continuous or intermittent (the latter simulates the moving of liquids in chemical plants, for example). The evaluation of immersion tests is by visual inspection.

An example of a specific test is alternate immersion in 3.5% NaCl. The samples are tested in 1 h cycles that include 10 min of immersion in 3.5% NaCl, followed by 50 min of immersion (Ref 23). The total test period can reach 90 days or longer.

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## Field Corrosion Tests

Field tests show the real performance of a coated part that is exposed to all the variations in environmental conditions that cannot be simulated by laboratory tests. As with laboratory tests, the same field test procedures are applied for coating-substrate systems as for bulk materials. Evaluation is by visual inspection or surface analytical techniques. For reliable predictions of corrosion behavior, a thorough comparison of field test results with accelerated laboratory tests and electrochemical tests is indispensable.

## Corrosion Performance of Coated Parts

Deposition of a more noble material provides good corrosion protection in the case of a pore-free or defect-free coating. Defects, however, may allow severe local corrosion to occur. As shown schematically in Fig. 2, corrosion of the substrate or interlayers may result in caves underneath the coatings. This effect is further illustrated in Fig. 8 for TiN deposited by physical vapor deposition onto NiP deposited on brass by electrochemical deposition. Already dezincification can be detected. Similar results are found in coatings and thin films deposited by other techniques, such as electroplating or electroless plating, plasma spraying, or chemical vapor deposition.

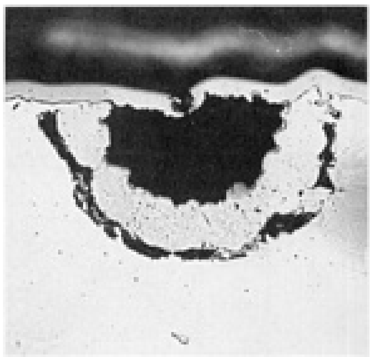

**Fig. 8 Pitting corrosion after salt spray testing of the coating-substrate system TiN deposited by physical vapor deposition NiP electrochemically deposited on brass. Source: Ref 24**

Polarization (electrode potential versus current density) curves provide useful information about the corrosion behavior of coating-substrate systems. The more noble and defect-free the coating, the greater the reduction in the measured current density. In general, thicker films exhibit fewer defects penetrating from the surface to the base material. Figure 9(a) shows polarization curves for TiN films deposited by plasma-assisted chemical vapor deposition onto 304 stainless steel. Even at a coating thickness of 10 μm, the behavior of the coated steel does not correspond to that of pure TiN deposited on glass (Ref 25). The deposition parameters also influence the coating morphology; this holds true for all deposition techniques. For PVD coatings, the substrate temperature, among other factors, determines the morphology (porosity) of the coatings (Fig. 9b).

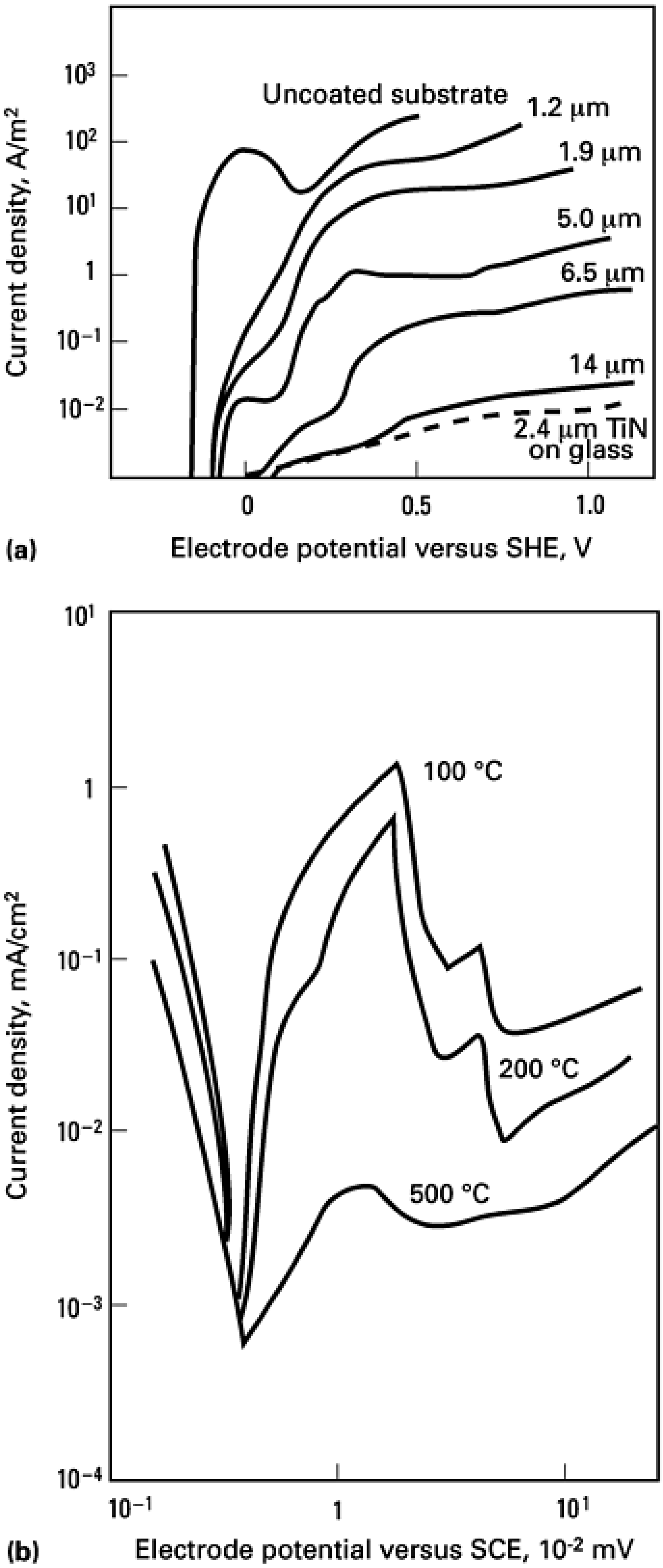

**Fig. 9 Anodic polarization curves for selected coating systems. (a) TiN deposited on 304 stainless steel by plasma-assisted chemical vapor deposition. Curves for TiN deposited on glass and for the uncoated base metal are provided for comparison. Environment: 1 *M*/L HCl. Source: Ref 25. (b) TiN ion-plated onto ball bearing steel. Environment: 1 *N* $H_2SO_4$. Source: Ref 26**

Polarization curves also show that corrosion resistance can be improved by the deposition of dense electrochemical or physical vapor deposition interlayers, alone or in combination. The polarization curves for reactively magnetron-sputtered

TiN on brass in Fig. 10 demonstrate the marked influence of interlayers. The coating with a 5 μm thick electrochemically deposited 80Pd-20Ni interlayer performs almost as well as pure TiN deposited on glass. The coating with a 2 μm PVD titanium interlayer does not perform quite as well, but much better than the TiN coated on brass without an interlayer. The titanium film was sputter-etched before the TiN was deposited.

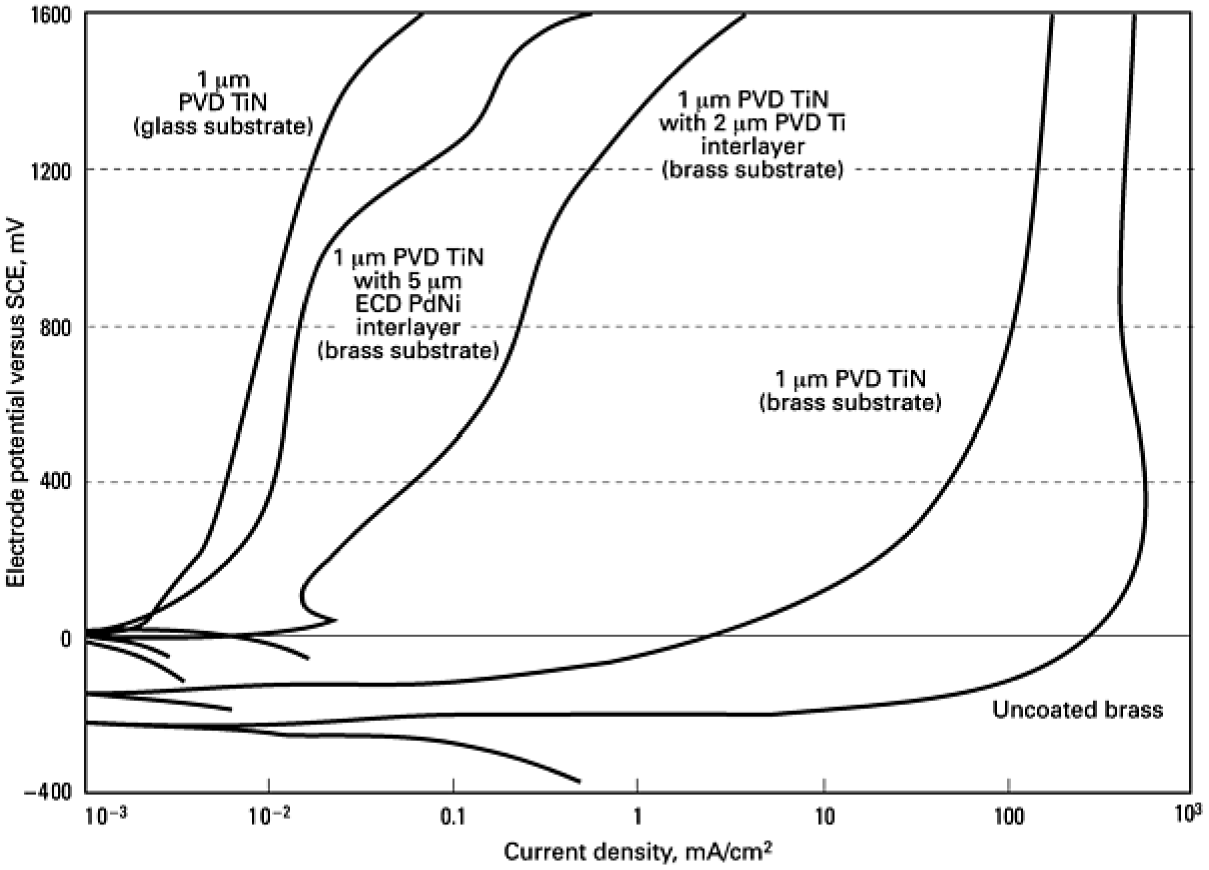

**Fig. 10 Polarization curves for selected coating systems with and without interlayers. Environment: 0.8 *M* NaCl. Source: Ref 6**

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### Conclusion

Electrochemical measurements provide useful information about the fundamental corrosion behavior of coating-substrate systems in particular environments. However, it is not valid to draw conclusions about one aspect of a system from the results of one test. For example, a relatively low current density measurement for one coating system in a specific environment does not necessarily mean that the coating material is better than the others being tested. For a fairly complete analysis of corrosion mechanisms and behavior of a particular system, a combination of tests and measurements is needed.

Accelerated tests can only partially simulate the actual corrosion behavior of a given system. However, they are able to provide qualitative and reproducible results for the development and quality assurance of coating systems. Often, a combination of tests is used in practice.

In general, the corrosion resistance of a system can be improved by producing dense coating structures through the optimization of deposition techniques and process parameters, by selecting noble coating materials, and by using dense and noble interlayers.

## Evaluation of Mechanical Properties of Thin Films

**Franz R. Brotzen, Rice University**

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### Introduction

THE TERM "THIN FILMS" is usually applied to metallic and nonmetallic layers of thickness of the order of microns or fractions of microns that are deposited on a variety of substrates. Their mechanical resistance is of particular interest, because high stresses often develop in the films during deposition or in service as a result of differences between the thermal expansion coefficients of the films and their substrates. This is a matter of special concern in the manufacture of microelectronic devices, where metallic films having high thermal expansion are often deposited on low-expansivity semiconductor substrates and where service temperatures vary by several hundred degrees Celsius. Similar conditions may prevail when thin films are deposited on bulk materials for the purpose of providing protective coatings.

The mechanical behavior of a given material in the form of thin films may differ substantially from that of the same material in bulk. Consequently, specialized thin-film testing methods have been developed. In these methods, one must differentiate between testing of freestanding films, that is, films removed from their substrates, and in situ films, that is, films still adherent to their substrates. Substantial differences may be observed between test results obtained from the two types of samples, mainly because of epitaxial and interfacial effects on adherent films.

### Evaluation of Freestanding Films

Testing of freestanding films requires that the films be removed from their substrates without impairing their integrity. A relatively simple procedure can be applied in which the films are deposited on substrates or intermediate layers that will readily dissolve in water or some other medium. Alkali halides, such as sodium chloride or cesium iodide, have been used to this end. Organic substances (e.g., collodion or certain polymers) have also been used as substrates. However, inherent properties of films deposited on different substrates may vary, so it is often desirable to use films deposited on a specific substrate. This is particularly true of microelectronic circuits in which metallizations, such as aluminum, are deposited on silicon or silicon oxide. In these cases, the metal films are separated from the substrate by exposure to a stream of fluorine in an inert carrier gas. The silicon is removed in the form of gaseous silicon tetrafluoride, while the metal is covered by a very thin protective metal fluoride film. As the substrate is consumed, a freestanding film is produced.

**Uniaxial Tensile Testing of Films.** The most direct way to obtain the stress-strain relations of thin films in tension is by uniaxial testing. In principle, this procedure is analogous to conventional tensile testing of bulk materials, yet the fragility of the films and their extreme sensitivity to even the smallest flaws make uniaxial tensile testing a difficult and often frustrating task. In view of the high surface-to-volume ratio in thin films, specimens must be virtually free of surface flaws, because even the smallest defects will lead to premature failure. Tensile specimens usually have the form of a "dog bone." This shape, which has proved to be most advantageous, is obtained either by covering the substrate with a mask during deposition or by standard photolithographic techniques.

Problems are caused also by internal stresses that are created in the films during the deposition process. When the films are separated from the substrates, the stresses often cause films to wrinkle or to curl severely, rendering them useless for testing. To alleviate this condition, special devices have been developed that keep the films stretched during ablation (Ref 1).

Equipment used for uniaxial tensile testing of thin films is generally based on the simple principle of deforming a freestanding film by a known amount through the application of a known force to the ends of the specimen. The testing devices can be divided into two categories:

- *"Soft" machines*, in which the loading rate is constant and the ensuing elongation is measured
- *"Hard" machines*, in which the elongation rate is constant and the applied loads are measured

An example of tensile curves obtained by uniaxial testing of plasma-deposited aluminum films of 1μm thickness is given in Fig. 1. The initial portion of the curves often contains a clearly noticeable "unwrinkling" stage that can be ignored or discarded.

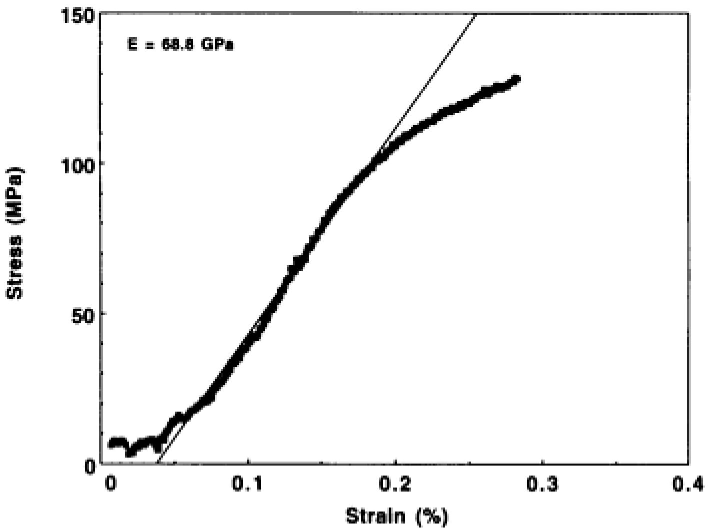

**Fig. 1 Stress-strain curve obtained by uniaxial testing of a freestanding 1 μm thick annealed aluminum film**

The absence of a well-defined yield point is characteristic for aluminum in bulk and, as evidenced by Fig. 2, for thin films.

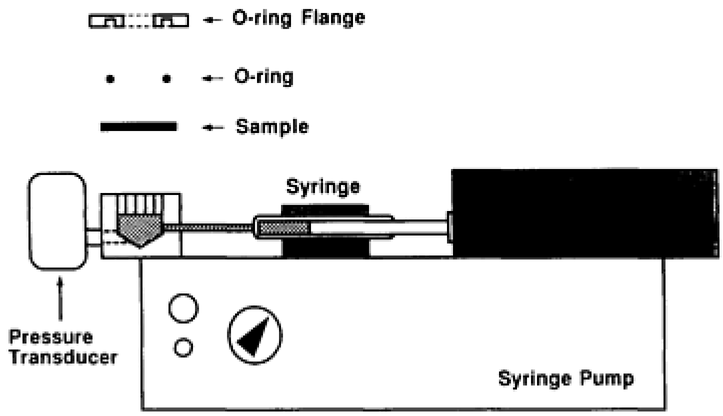

**Fig. 2 Schematic drawing of a bulge-testing device. Source: Ref 3**

The effect of film thickness on film strength has been the subject of intense study. Tests indicate that the strength of metallic films rises dramatically when the thickness falls below about 0.3 μm. There is evidence that the strength of films obeys the Hall-Petch relation:

$$\mathit{Strenght} = K + \frac{b}{\sqrt{t}}$$

where $K$ and $b$ are constants and $t$ is the film thickness. However, the details concerning the thickness effect in films are still open to question and appear to be greatly influenced by the deposition conditions.

Whereas the elastic properties of metal films closely approach those of metals in bulk form, some investigations reveal a substantially higher fracture-strength level for thin films than for the corresponding bulk materials. The fracture stress of metallic polycrystalline and single-crystal films tends to rise sharply as the film thicknesses drop below 0.2 μm.

**Uniaxial Creep Testing of Films.** Uniaxial testing equipment can be readily employed in creep tests of freestanding thin films by keeping the load constant. In such tests, characteristic creep curves consisting of a primary and a secondary stage are obtained. The stress and temperature dependence of the secondary creep rates is very similar to that of bulk materials. For high strain rates, secondary creep rates are modeled as:

$$\varepsilon = B \exp - [(Q_0 - \beta\sigma) / kT] \qquad \textbf{(Eq 1)}$$

For low strain rates, the relation is:

$$e = \frac{ADGb}{KT}\left(\frac{s}{G}\right)n \qquad \textbf{(Eq 2)}$$

where $B$, $A$, $\beta$and $n$ are constants, $Q_0$ is the activation energy at zero stress, $\sigma$is the applied tensile stress, $k$ is Boltzmann's constant, $T$ is the absolute temperature, $D$ is the diffusion coefficient (i.e., $D_0$ exp [$Q_D/kT$]), $G$ is the shear modulus, $b$ is the interatomic distance, $D_0$ is a constant, and $Q_D$ is the activation energy for self-diffusion. The values of the stress exponent $n$ are usually in the range between 4 and 10 and are highly sensitive to the grain structure of the material. The material constant $\beta$in Eq 1 for thin aluminum films, for example, is close to $10^{-27}$ $m^3$/atom and about half of that in aluminum-silicon alloy films of 1 μm thickness. The activation energy at zero stress, $Q_0$, for steady-state creep in unannealed, vapor-deposited copper films is about 1.3 eV. In sputtered 1 μm thick aluminum and aluminum-1% silicon-alloy films, $Q_0$ is 0.56 and 1.10 eV, respectively (Ref 2). The low activation-energy value for aluminum approaches that of grain-boundary diffusion of vacancies in that metal.

In summary, the uniaxial testing method provides an excellent means for obtaining readily interpretable results in terms of tensile stress and strain. These results can be applied to well-known descriptions of the fundamental processes of plastic deformation. On the other hand, the uniaxial testing technique requires extreme care in specimen preparation and handling, and the elongations that can be obtained are often limited.

**Biaxial Testing of Films.** The bulge-testing technique is a biaxial testing method that can be applied to freestanding thin films. A film whose edges are fixed may be viewed as an impermeable membrane. Applying a known fluid pressure, liquid or gas, to one side of this membrane will cause it to bulge, so that the film material is strained biaxially. By monitoring the bulge expansion as a function of the fluid pressure, a stress-strain relationship is obtained. In principle, bulge testing is a straightforward technique by which problems associated with defects on the sample edges are eliminated. However, the interpretation of bulge-testing results is far more complex than that of uniaxial-test results.

Bulge testing can be performed by applying fluid pressure through a hole drilled on the back of the substrate without damaging the deposited film. An alternative procedure (Fig. 2) employs films that are removed from their substrates (Ref 3). The films are fastened by an O-ring on top of a small cylindrical chamber. A syringe pump then injects glycerol into the chamber at a constant rate. The glycerol pressure is monitored by a pressure transducer, and the injected volume is determined by the elapsed time. The bulge extension can be determined either by the displaced fluid volume or by the height of the bulge. In general, when designing bulge-testing equipment, the ratio of the bulge orifice to the film thickness should be at least between 200 and 300, so that the effect of flexural rigidity is minimized.

Films used in the bulge-testing technique must be separated from their substrates. The film-ablation techniques are identical to those described in the preceding section. It should be noted that metal films, such as aluminum or aluminum alloys, deposited on a silicon substrate tend to dissolve silicon, which often precipitates in the form of silicon-rich nodules. These nodules are removed during the ablation process together with the silicon substrate, producing very fine pinholes in the film that vitiate the bulge-testing procedure.

The analysis of the pressure-bulge deformation is generally based on a model proposed by Hill (Ref 4), which gives the meridional stress as:

$$s_m = \frac{\mathrm{Pr}_0}{2t} = \frac{Pa^2}{4th} \qquad \textbf{(Eq 3)}$$

where $P$ is the fluid pressure, $r_0$ is the radius of curvature at the top of the bulge, $t$ is the thickness of the film, $a$ is the radius of the orifice, and $h$ is the height of the bulge. This is an approximate expression that is predicated on the bulge height's being much less than the radius of the orifice. The calculation of the meridional strain, also based on Hill's work, is:

$$e_m = a\,\frac{h^2}{a^2} \qquad \textbf{(Eq 4)}$$

where $\alpha$ is a constant that is generally taken to be $\frac{2}{3}$. This, too, is an approximation based on the premises that the bulged film assumes a spherical shape and that the film is a plane at zero tension. The realization of true sphericity is questionable, but experimental results have shown that the meridional strain may be accurate within about 8% for strains up to 1% (Ref 5).

A serious criticism of bulge testing centers about the initial state of the film, that is, its flatness at zero pressure. Whenever bulge testing is carried out on films adherent to the substrate by removing the substrate over a given area, there may be residual compressive or tensile stresses in the film. In the former case, this results in buckling or wrinkling of the film, and in the latter case, in a film stressed in tension (Ref 6). These conditions must be taken into account when calculating the stress-strain relations obtained from the tests.

The bulge test presents an attractive method for determining mechanical properties of thin films, mainly because--in contrast to the uniaxial test--flaws at the edges of the film specimens do not affect bulge-test results. It is seen from the above comments, however, that the value of this method for the accurate determination of mechanical behavior of freestanding thin films is diminished because of the many imponderables with which the interpretation of bulge-testing data is fraught.

**Beam-Bending Methods Applied to Free-standing Films.** When a specimen in the shape of a beam is bent, the portion on one side of a longitudinal "neutral" plane is strained in tension, while the portion of the other side of the plane is strained in compression. If the specimen has a uniform composition, such as a freestanding film, the stress-strain relation of the material can be readily calculated from the load-deflection data determined during bending. In this technique, very small cantilever-beam specimens are used, which are produced by microelectronic fabrication methods. In such test, a Nanoindenter device can be employed that applies the load to the free end of the cantilever beam and simultaneously measures the deflection (Fig. 3). The elastic modulus and the yield strength of the material are determined from the load-deflection curve. The specimens for the microbeam method are prepared by creating the required pattern of the film and the subsequent removal of the substrate. Microbeam fabrication and testing are briefly reviewed in Ref 8. A detailed review of micromachining of beam specimens is given in Ref 9.

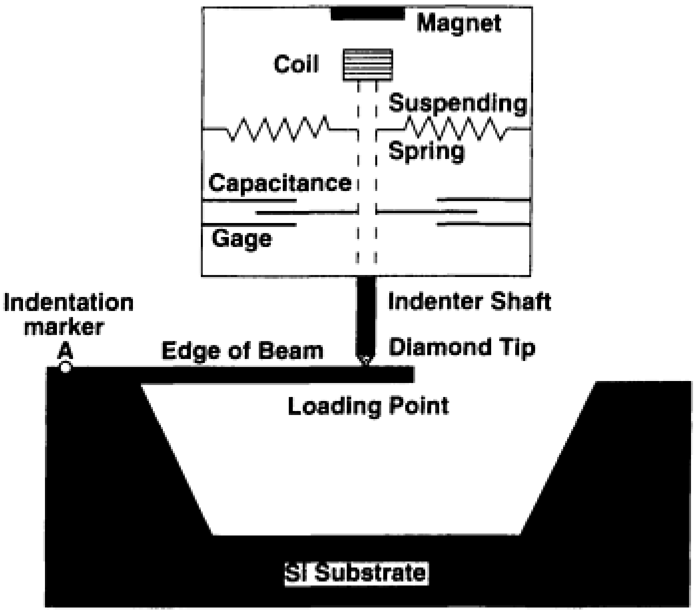

**Fig. 3 Schematic drawing of a Nanoindenter used as a loading device on a microcantilever beam. Source: Ref 7**

When the deflections are small and the material is considered to be uniform and isotropic and to deform elastically, the well-known equation for the cantilever-beam deflection δ under a load $P$ applied to the free end of a beam is given by:

$$d = \frac{PL^3}{3EI} = \frac{4PL^3}{bEh^3} \qquad \textbf{(Eq 5)}$$

where $L$ is the length of the beam, $E$ is Young's modulus, $I$ is the moment of inertia, $b$ is the width of the beam, and $h$ is the thickness of the beam. This equation is modified, for the case of thin and broad plate-like specimens ($b$ **?** $h$), where plane stress is applied in the direction of the beam thickness and plane strain is applied in the direction of its width, to read:

$$d = \frac{4(1-v^2)PL^3}{bEh^3} \qquad \textbf{(Eq 6)}$$

where ν is Poisson's ratio. Young's modulus is derived from the slope of δ($P$).

The simple beam theory described above can also be employed in the determination of the yield strength of the beam material. When the beam is bent under a downward load applied to its free end, the maximum tensile stress occurs at the fixed end. When this stress reaches the yield strength, the load-deflection curve ceases to be linear. The load that marks this deviation from linearity is denoted by $P_v$, so that the yield stress is (Ref 7):

$$s_y = \frac{6LP_v}{bh^2} \qquad \textbf{(Eq 7)}$$

An interesting modification of the simple curved-beam method has led to a resonance technique for the determination of the elastic modulus. Specimens similar to the ones used in the technique described above were vibrated electrostatically, and Young's modulus was obtained from the observed natural frequency (Ref 10).

The beam-bending method is well suited for the determination of elastic and some plastic properties of freestanding films. The principal drawback to this technique is the inherent difficulty of specimen preparation.

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## Evaluation of Films Adherent to Their Substrates

**Indentation testing** of thin films resembles in many aspects the well-known hardness measuring techniques, such as the Vickers and Brinell hardness tests. However, in the "nanoindentation" technique, the indentations extend only to extremely shallow depths, often as low as nanometers. A hard indenter, usually an accurately ground diamond, is gradually pressed into the film, which is deformed first elastically and then plastically. Upon gradual removal of the load, the elastic deformation is recovered (Fig. 4). Analysis of the load-displacement curves provides information not only on the hardness, but also on the elastic and creep properties of the films. In contrast to traditional hardness measurements, the nanoindentation technique furnishes a continuous record of both load and indentation depth during loading and unloading, so that imaging of the indentation is no longer required.

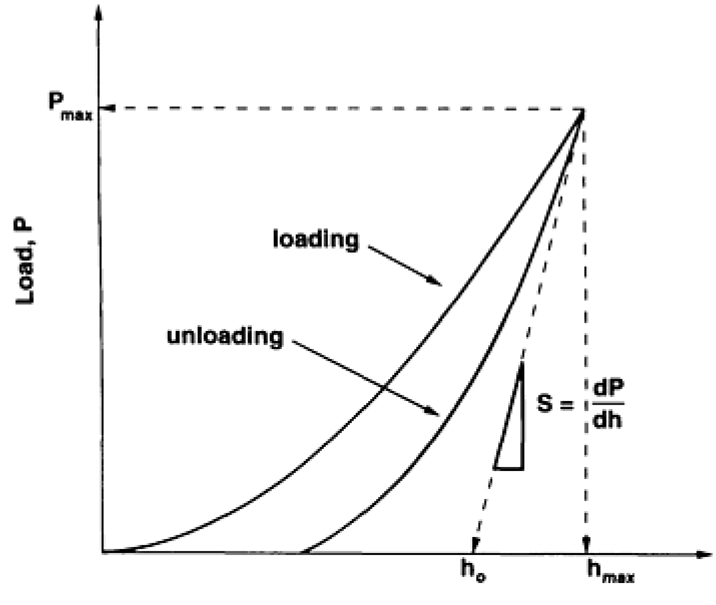

**Fig. 4 Typical curve of load as a function of indenter-penetration depth. Source: Ref 11**

The determination of mechanical properties of thin films by nanoindentation has gained widespread use in recent years. Its popularity stems not only from the high spatial resolution of the indentations--less than 1 μm$^2$--but also from the simplicity with which mechanical properties of surface layers on bulk materials and of films adherent to their substrates can be determined under essentially compressive conditions. Details of nanoindentation testing techniques and equipment can be found in the literature (see the "Selected References" in this article. The most common means of applying the load in nanoindentation equipment is through electromagnetic or piezoelectric devices, in which the resolution obtained is often better than 0.01 μN. The displacements are typically measured by a capacitive device giving resolutions as small as 0.1 nm. The most commonly used indenter is a diamond of the Berkovich type, a triangular pyramid with the same depth-to-area relation as the standard Vickers indenter (square pyramid)--that is, the cross-sectional area varies as the square of the depth of the indentation.

**Determination of Elastic Properties by Indentation.** The indentation technique provides a simple means for determining the elastic modulus of the film. During penetration of the film by the indenter, both elastic and plastic deformations occur. Upon withdrawal of the indenter, the depth of the permanent indentation changes as a result of the elastic recovery of the film. Repeated applications of the load generate a truly elastic recovery for which mathematical solutions are known, so that the unloading curves can be related effectively to the elastic properties of the material, that is, the elastic modulus, $E$, and Poisson's ratio, $\nu$. The effective modulus is obtained from the slope of the unloading curve:

$$S = \frac{dP}{dh} = \frac{2}{\sqrt{p}} b \sqrt{AE_r} \qquad \textbf{(Eq 8)}$$

where $S$, $P$, and $h$ are given in Fig. 4, $A$ denotes the contact area of the indenter, $E_r$ is the effective elastic modulus, which takes into account the small deformation of the indenter, and $\beta$is a dimensionless parameter that depends on the geometry of the indenter. For any indenter that can be described as a solid of revolution of a smooth function, $\beta = 1$. Although neither the Vickers nor the Berkovich indenters falls into this category, $\beta$deviates only very slightly from unity for these indenters. To compute the modulus $E_r$, according to Eq 7, the slope of the unloading curve $dP/dh$ must be known and the projected contact area, $A$, at the maximum load would have to be known as well. The area is obtained from an area function F($h$), which relates the cross section of the indenter to the appropriate depth, $h$, of the indentation measured from the tip of the indenter. As an example, for an ideally sharp Berkovich indenter the area function is $F(h) = 24.5\ h^2$. In reality, this function is much more complex because of the impossibility of achieving ideal tip sharpness. To determine the appropriate depth of indentation, various models for elastic unloading were proposed (Ref 11). An improved method for determining the contact area at peak load uses the contact depth $h_c$ found by the equation

$$h_c = h_{\max} - e \frac{P_{\max}}{dP/dh} \qquad \textbf{(Eq 9)}$$

whose terms are defined in Fig. 4. The value of $\varepsilon$ depends on the geometry of the indenter and can be taken to be 0.75 for the Berkovich indenter. Once $h_c$ is determined from the above equation, the appropriate contact area can be calculated from the area function $A = F(h_c)$. The effective elastic modulus, $E_r$, can now be determined from the unloading curve in accordance with Eq 7.

**Indentation Hardness Testing of Films.** The indentation technique is very well suited for determining the hardness of films adherent to their substrates. Hardness is a measure of resistance to local deformation and is defined by the ratio $H = P(\max)/A$, where $P(\max)$ is the peak load applied to a given type of indenter and $A$ is the projected area of the hardness impression. In general, the determination of the contact area $A$ follows the procedure outlined in the preceding section.

The effect of indentation depths on hardness measurements has been a matter of concern. It has been shown, however, that a variation in the applied load has little effect on the hardness of several different materials, provided that the projected area has been properly determined. When the hardness of films deposited on a substrate is measured, the region deformed by the indentation may extend to the film/substrate interface, which affects the hardness measurements. As the plastic zone under the indentation in the film reaches the substrate, the measured hardness becomes a function of the ratio of maximum penetration depth to film thickness and ceases to be the true hardness of the film. A rule of thumb suggests that the indentation depth should not exceed 10% of the film thickness.

It should be noted that silicon, as well as ceramic materials, may develop cracks when indentation strains are not accommodated by plastic deformation. These cracks affect the measured load-displacement relations. To overcome the troublesome substrate effects in very thin films, extremely shallow indentation techniques have been applied successfully.

**Strength Measurements by Indentation Testing.** It would be, of course, very desirable to derive plastic properties, such as the ultimate tensile strength or the yield strength, from indentation measurements. Because of the complexity of the mechanics of the indentation process, such a task is very difficult. In 1951, Tabor (Ref 12) formulated an equation that related the ultimate tensile strength, $\sigma_{UT}$ (in kg/mm$^2$), to the Vickers hardness number, $H_v$, for a material whose work-hardening exponent ($n$) is as follows:

$$\frac{s_{UT}}{H_v} = \frac{1-n}{2.9}\left(\frac{12.5n}{1-n}\right)^{n} \qquad \textbf{(Eq 10)}$$

This equation yielded reasonable agreement with experimental data.

Actual stress-strain curves were obtained by indentation of 1 μm thick gold and aluminum-copper metallizations deposited on silicon (Fig. 5). Here, spherical diamond indenters of radii of 5, 10, and 22 μm were used. The analysis of the load displacement data was based on Tabor's work and presupposed a strain-hardening equation in which the flow stress, $\sigma$, was exponentially related to strain, $\varepsilon$, such that $\sigma \approx \varepsilon^n$. While the application of Tabor's analysis has been helpful, correlations fo pressure-indentation results with stress-strain curves of ductile materials have not been promising.

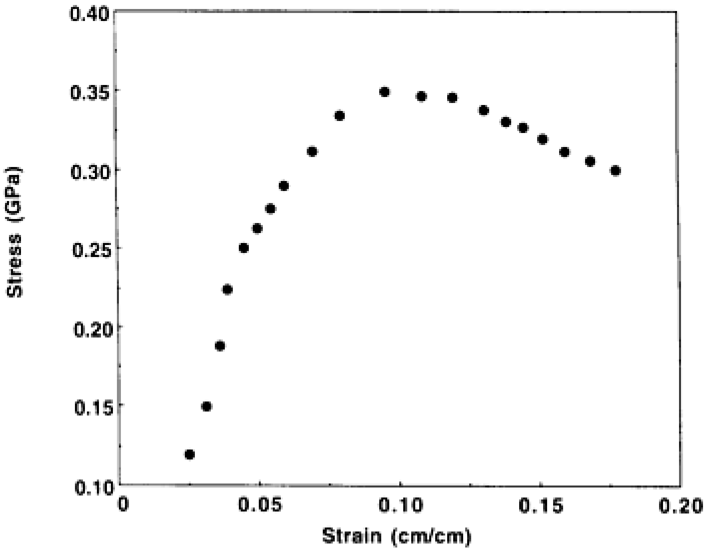

**Fig. 5 Stress-strain curve for an annealed gold film, obtained by the indentation technique using a spherical-tipped diamond indenter of 20 μm radius. Source: Ref 13**

**Creep and Stress-Relaxation Testing by Indentation.** Modern indentation equipment is designed to monitor the movement of the indenter under a given load as a function of time as well as the changes in load at a fixed depth of penetration. The equipment is therefore capable of measuring the equivalents of creep and stress relaxation.

When recording the penetration rate under a constant indenter load, curves are obtained that bear a strong resemblance to typical creep curves of bulk materials (Fig. 6). The classical stress dependence for secondary creep rate ($\varepsilon$) = constant $\sigma^n$ can be applied, where $\varepsilon$ is the stain rate, $\sigma$is the stress, and $n$ is the stress exponent. The latter is close to the one found by uniaxial creep testing of films (see the section "Uniaxial Creep Testing of Films" in this article).

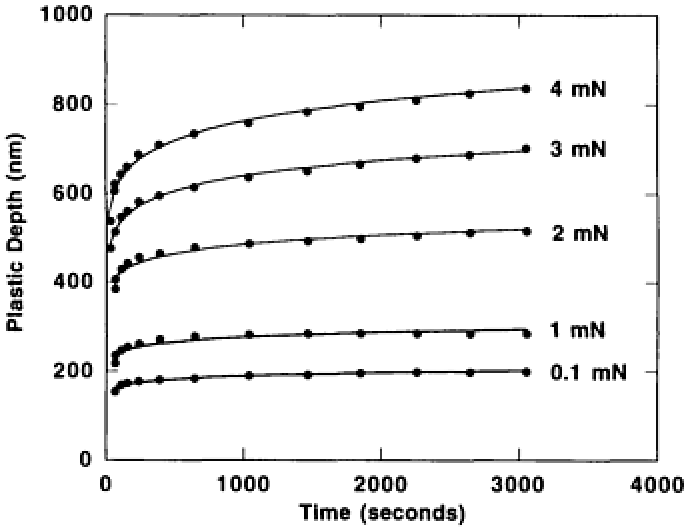

**Fig. 6 Penetration depth (plastic deformation only) in a 1.6 μm thick sputtered aluminum film at constant indenter loads. Source: Ref 14**

Valuable information can also be obtained from stress-relaxation experiments. In a typical experiment of this kind, the indenter is pressed into the specimen at a constant rate, usually of the order of 10 nm · $s^{-1}$, to a predetermined depth while monitoring the change in load. After the displacement is halted, a record is made of the relaxation effected by the specimen and the elastic reactions of the testing equipment. The modulus describing these elastic reactions is obtained from the initial slope of the unloading curve at a constant displacement rate. The relaxation curve yields data on the plastic strain rate, $\varepsilon$, as a function of stress, $\sigma$, the strain-rate sensitivity being defined by:

$$m = \frac{\partial \ln e}{\partial \ln s} \qquad \textbf{(Eq 11)}$$

One concludes from the above that the indentation method provides a consistent picture of elastic modulus, hardness, and strain-rate sensitivity measurements of surface layers of bulk materials, including thin films deposited on substrates. It is particularly well suited for use with hard surface films, in which plastic deformation plays only a minor role. Indentation testing is attractive in view of its simplicity and the absence of complex sample preparation. The principal drawbacks of the indentation method lie in uncertainties of interpretation, particularly in ductile materials.

**Beam-Bending Methods Applied to Adherent Films.** This technique is based on the same principles as the beam-bending technique applied to freestanding films, described earlier. In the case of testing of adherent films by the beam-bending technique, the specimen is a composite of two materials, the film and the substrate. If the mechanical characteristics of the substrate are known, the stress-strain relation for the deposited material can be inferred from the load-deflection curve.

The elastic deflection at the free end of a bilayer cantilever beam under an external load is related to the elastic constant by an equation similar to Eq 6:

$$d(L) = \frac{PL^3}{3(EI)_{eff}} \qquad \textbf{(Eq 12)}$$

where Young's modulus *E*, and the moment of inertia, *I*, are replaced by the product of the effective modulus and the effective moment of inertia:

$$(EI)_{eff} = b\left[\frac{1}{3}(E_{ps}h_s^3 - E_{pf}h_f^3) - C_i^2(E_{ps}h_s - E_{pf}h_f\right] \qquad \textbf{(Eq 13)}$$

Here, the subscripts "p," "s," and "f" refer to "plate," "substrate," and "film,"respectively, and $E_p = E/(1 - u^2)$. The distance between the film/substrate interface and the neutral plane of the beam is given by:

$$C_i = \frac{(E_{ps}h_s^2 - E_{pf}h_f^2)}{2(E_{ps}h_s - E_{pf}h_f)} \qquad \textbf{(Eq 14)}$$

A comparative beam-bending technique can also be employed, in which the load-deflection curve of a cantilever-beam sample consisting only of the substrate is registered. This operation is repeated after a film is deposited on the substrate. The difference between the two tests is used to find the elastic modulus of the film. The modulus can be evaluated by this method without prior knowledge of the properties of the substrate material, as shown in Ref 9.

Elastic properties of thin films adherent to the substrates are sometimes investigated by subjecting the specimen to temperature changes. In this case, calculable thermal stresses are introduced that produce an observable curvature in the specimen. It is possible to derive elastic and certain plastic properties of thin films from the curvature-vs.-temperature records by techniques shown in Ref 15.

The cantilever-beam technique in its different forms is a useful tool for determining elastic and yield properties in films. However, although it provides a means to determine these properties in situ, that is, properties of films adherent to their substrates, it suffers from the difficulty of specimen preparation.

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### Stress Determination for Coatings

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## Introduction

COATINGS AND THIN FILMS can be produced by a large variety of deposition techniques. Typical processes are physical vapor deposition (PVD), chemical vapor deposition (CVD), electroplating, electroless deposition, anodizing, thermal growth, and thermal spraying. Since the early 1980s, considerable progress has been made in improving deposition processes for a wide range of high-technology applications. Consequently, many new ceramic coatings and films have been introduced in various industries. Typical examples are metal-oxide semiconductors for microelectronics; titanium nitride, titanium carbide, aluminum oxide, and silicon nitride for machining tools; and thermal-sprayed tungsten carbide/cobalt, M-chromium-aluminum-yttrium (where M stands for iron, cobalt, or nickel), and yttrium oxide/partially stabilized zirconia coatings for aerospace applications.

Residual stresses, which are internal and therefore locked in, are contained in materials that are produced by nearly every mechanical, chemical, and thermal process, either alone or in combination. As a result, most coatings are in a state of internal stress, including metallics and ceramics. The stress can be either compressive or tensile. It is generally recognized that compressive stresses in coatings are more favorable than tensile stresses, because they increase resistance to fatigue failure. However, extremely high compressive stresses may cause either coating separation from the base metal or intra-coating spallation. Generally, if a tensile stress causes strain that exceeds the elastic limit of the coating, then it will cause cracking in the coating perpendicular to the direction of the stress. Therefore, understanding the formation of residual stress in the coating is important to prevent the coating from peeling or cracking during service. Furthermore, residual stresses have significant influences on the mechanical and physical properties of the coatings, particularly electrical resistivity, optical reflectance, fatigue, and corrosion.

There are three types of residual stresses:

- Macrostresses, which are nearly homogeneous over macroscopic areas of the material
- Microstresses, which are nearly homogeneous over microscopic areas, such as one grain or subgrain
- Inhomogeneous microstresses, which are inhomogeneous even on a microscopic level

Residual macrostresses are the ones of most interest in engineering practice, because they can substantially affect component service performance. Both residual and inhomogeneous microstresses are of more interest in material science.

This article intends to provide a useful guide for measuring residual macrostress on a coating. The most commonly used measurement methods are mechanical deflection, x-ray diffraction, and hole-drilling strain-gage. After a discussion on the origins of residual stress, the fundamental principles, as well as examples of practical measurements, are described for each method.

## Origins of Residual Stress

Residual macrostress in a coating combines the intrinsic stress and the thermal stress acting in the coating plane parallel to the coating/substrate interface:

$$\sigma_t = \sigma_i + \sigma_{th} \qquad \textbf{(Eq 1)}$$

where $\sigma_t$ is the total macrostress, and $\sigma_i$ and $\sigma_{th}$ are intrinsic stress and thermal stress, respectively. Intrinsic stress results from the growth processes, depending primarily on deposition parameters, whereas thermal stress arises from a mismatch in coefficients of thermal expansion between the coating and the substrate.

Many phenomenological models have been proposed to explain the occurrence of intrinsic stresses by correlating them with a variety of coating microstructure and process features. To varying degrees, the intrinsic stress of a coating is associated with these deposition conditions and coating features:

- Incorporation of residual gas atoms in the coating
- Grain size, microvoid, and dislocation density in the coating
- Energetic particle bombardment during coating growth
- Lattice misfit between the substrate and the growing coating
- Combined effect of surface tension and growth process at grain boundaries
- Deposition temperature relative to the melting temperature of the coating material
- Annealing and shrinkage of disordered material buried behind the advancing surface of a growing coating

Although many studies have described the intrinsic stresses, information on the corresponding structural details is limited. It seems unlikely that one can formulate a generalized model of intrinsic stress for various coating materials and deposition processes.

Any coating that is prepared at elevated temperatures ($T_2$) and then cooled to room temperature (stress measurement temperature, $T_1$) will be thermally stressed because of the difference in the coefficients of thermal expansion between the coating and the substrate. Assuming no deformation of the substrate, the magnitude of the thermal stress in the coating is:

$$\sigma_{th} = (\alpha_c - \alpha_s)\,(T_2 - T_1)\,E_c/(1 - u_c) \qquad \textbf{(Eq 2)}$$

where $\alpha_c$ and $\alpha_s$ are the coefficients of thermal expansion for the coating and the substrate, respectively, and $E_c$ and $\nu_c$ are the Young's modulus and Poisson's ratio of the coating, respectively. A coating deposited at an elevated temperature exhibits compressive stress if $\alpha_s > \alpha_c$, but tensile stress if $\alpha_s < \alpha_c$. In the case of $\alpha_s > \alpha_c$, the substrate shrinks more than the coating does during cooling from the deposition temperature and compresses the coating to maintain dimensional compatibility.

In some cases, thermal stress is the primary residual stress of the coating. For example, a titanium nitride coating can be deposited on a cemented carbide substrate (tungsten carbide-1 wt.% tantalum-10 wt.% cobalt) via a CVD process at 1000 °C (1830 °F). With the values of $\alpha_s = 5 \times 10^{-6}$/K, $\alpha_c = 9.54 \times 10^{-6}$/K, $E_{TiN} = 411$ GPa ($60 \times 10^6$ psi) and $\nu_{TiN} = 0.24$, the stress in the coating, as calculated from Eq 2, is 2.39 GPa ($0.35 \times 10^6$ psi) in tension at 25 °C (77 °F).

## Deflection Method

The deflection method is the most widely used technique for determining the residual stress in a coating. In terms of basic principles, it involves measuring the amount of bending in a strip that is due to the deposition of the coating. A formula for calculating the residual stress in an electrodeposited coating was first derived by Stoney (Ref 1) in 1909. Subsequent researchers have derived more complex formulas to improve the accuracy of the stress evaluation. Comparative studies on those stress-evaluation formulas are reviewed and discussed elsewhere (Ref 2, 3, 4). Nearly all formulas are variants of Stoney's formula.

Consider a coating deposited on one side of a strip substrate. Both coating and substrate are assumed to be homogeneous. A mismatched force at the coating/substrate interface results in residual stress in the coating, which bends the strip either upward (concave) or downward (convex), depending on whether the stress is tensile or compressive. For overall force and moment equilibrium of the coating/substrate composite, it can be shown that the residual stress in the coating is (Ref 5):

$$\sigma_c = (E_s d_s^2) / [6(1 - \nu_s) R d_c] \, (d_s \; ? \; d_c) \qquad \textbf{(Eq 3)}$$

or, in general,

$$\sigma_c = \{E_s d_s^2 / [6(1 - \nu_s) R d_c]\} \\ \{(1 + \Gamma \Theta^3) / (1 + \Theta)\} \qquad \textbf{(Eq 4)}$$

where

$$\Gamma = [E_c(1 - \nu_s)] / [E_s(1 - \nu_c)], \ \Theta = d_s / d_c, \\ \text{and } R \approx L^2 / 8f \approx L^2 / 2\underline{\underline{\delta}} \qquad \textbf{(Eq 5)}$$

where *E* is Young's modulus; $\nu$ is Poisson's ratio; *d* is thickness, with the subscript c denoting coating and s denoting substrate; *R* is the radius of curvature of the bent strip, *L* is the length of the strip, *f* is the deflection from the free end of the strip, and $\delta$ is the deflection at the center of the strip (Fig. 1).

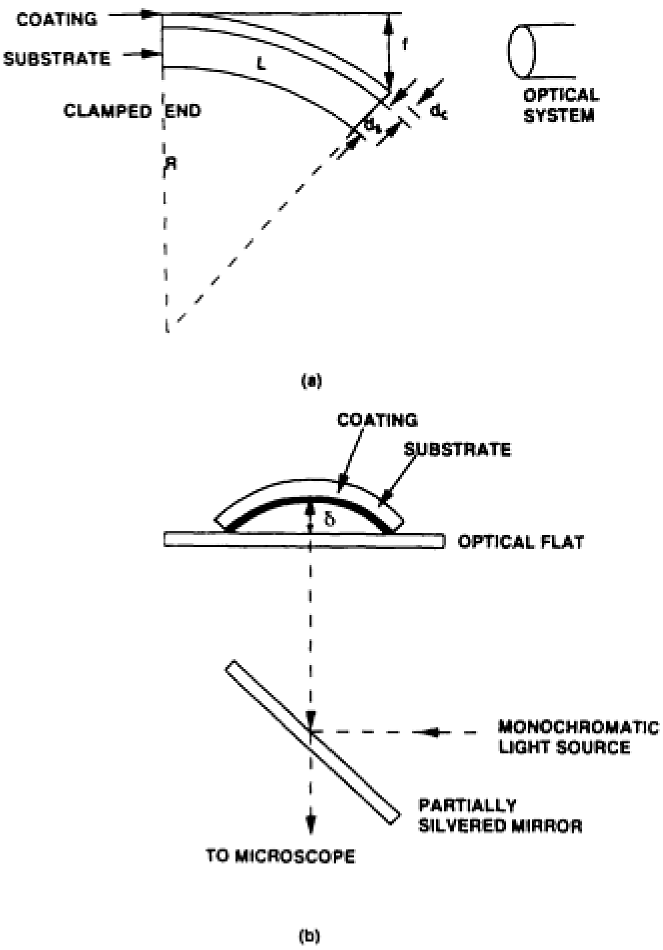

**Fig. 1 Stress measurement techniques. (a) Bending of cantilever beam. (b) Disk deflection. Source: Ref 7**

Although Eq 3 is most often used in practice and represents a generalized Stoney's formula for a planar state of stress, it tends to overestimate the value of measured stress. However, it does not require knowledge of the elastic properties of the coating. Equation 4 provides a much better approximation than Eq 3, but it does require knowledge of elastic properties. Equation 4 differs from Eq 3 in terms of a correction factor $[(1 + \Gamma \Theta^3)/(1 + \Theta)]$. Table 1 compares stresses as a function of $d_s/d_c$, calculated from both Eq 3 and 4. In the calculation, it was assumed that $E_c$ = 400 GPa (60 × $10^6$ psi), $E_s$ = 200 GPa (30 × $10^6$ psi), and $\nu_c = \nu_s$. It is clear that both equations are in good agreement when $d_s/d_c > 50$. By choosing a large value of $d_s/d_c$, the error can be minimized if Eq 3 is used.

**Table 1 Comparison of average residual stress calculated using Eq 3 and 4**

| $d_s/d_c$ | **Calculated stress** | | | |
|---|---|---|---|---|
| | **Eq 3** | | **Eq 4** | |
| | **MPa** | **ksi** | **MPa** | **ksi** |
| 200 | -1143 | -165.7 | -1137 | -164.9 |
| 100 | -571 | -82.8 | -565 | -81.9 |

| | | | | |
|---|---|---|---|---|
| 50 | -286 | -41.5 | -280 | -40.6 |
| 20 | -114 | -16.5 | -109 | -15.8 |
| 10 | -57 | -8.3 | -52 | -7.5 |

**Cantilever Beams.** To measure the deflection of cantilever beams, various techniques have been developed (Ref 6), including optical, capacitance, mechanical, electromechanical, interferometric, and electromechanical or magnetic restoration. Figure 1(a) shows the setup for the deflection measurement when an optical system is used. In this example, a titanium nitride coating was deposited on a quartz beam via a PVD process, and the average residual stress in the coating was determined by measuring the amount of deflection at the free end, $f$, of the bent beam, according to the relation:

$$\sigma_c = [4E_s d_s^2 f] / [3(1 - \nu_s)L^2 d_c] \qquad \textbf{(Eq 6)}$$

With the values of $E_s$ = 71.7 GPa (10.4 × $10^6$ psi), $\nu_s$ = 0.16, $d_s$ = 3 mm (0.12 in.), $d_c$ = 3 × $10^{-6}$ m (1.2 × $10^{-4}$ in.), $L$ = 50 mm (2 in.), and $f$ = 2 × $10^{-6}$ m (8.0 × $10^{-5}$ in.), the stress in the coating is determined to be 273 MPa (40 ksi) in compression.

**Disks.** The average stress in the coating on a disk substrate can be determined from the amount of deflection, $\delta$, at the center of the disk caused by the deposition of a coating on one side. This value can be measured optically by interferometry or microstylus profilometry. Figure 1(b) shows a typical interferometry apparatus setup. Either technique measures deflection at the same position, across a diameter of the disk, both before and after coating deposition. The stress in the coating is then calculated:

$$\sigma_c = \{E_s d_s^2\ [(\Delta\delta_x + \Delta\delta_y) / 2]\} / [3(1 - u_s)r^2 d_c] \qquad \textbf{(Eq 7)}$$

where $\Delta\delta_x$ and $\Delta\delta_y$ are deflection changes measured before and after coating deposition, and $r$ is the radius of the disk. Whether the stress is tensile or compressive, it is determined by the curvature of the disk before and after coating deposition, as determined by a depth microscope. When the change in curvature is upward (concave), viewed from the coating side, the stress in the coating is tensile. The opposite change in curvature indicates a compressive stress in the coating.

Typical interference fringe patterns are shown in Fig. 2. Figures 2(a) and 2(b) correspond to equal and unequal principal stresses of the same sign, whereas Fig. 2(c) corresponds to a biaxial stress state with principal stresses of opposite signs. Using Fig. 2(a) as an example, the measured defection, $\delta$, is equal to the wavelength of monochromatic light multiplied by the number of light fringes ($\delta$ = 632.8 nm × 17).

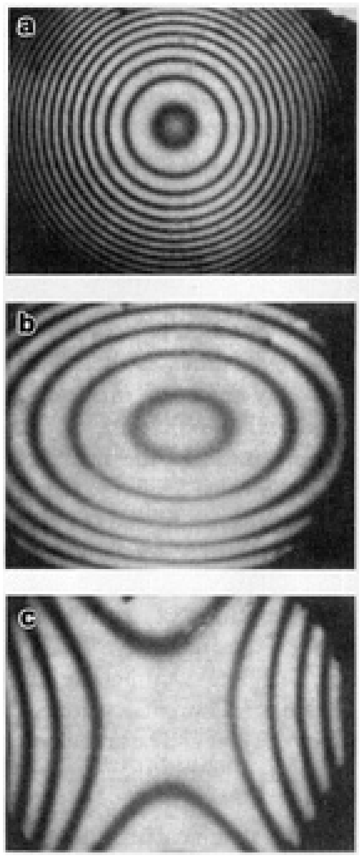

**Fig. 2 Typical patterns of interference fringes. (a) $\sigma_x = \sigma_y$. (b) $\sigma_x \neq \sigma_y$, where both components are in compression or tension. (c) $\sigma_x \neq \sigma_y$, where one component is in compression and the other is in tension. Source: Ref 8**

Figure 3 shows typical microstylus traces on the titanium nitride coated surface of an AISI 304 stainless steel disk, both before and after coating deposition. The curvature of the coated surface was downward (convex), viewed from the coated side. With the values of $E_s$ = 193 GPa (28 × $10^6$ psi), $\nu_s$ = 0.28, $d_s$ = 4.74 mm (0.186 in.), $r$ = 11.94 mm (0.4700 in.), $d_c$ = 20 μm (800 μin.), and the deflection $\Delta\delta$= 6.3 × $10^{-6}$ m (2.5 × $10^{-4}$ in.), the stress in the titanium nitride coating is 4.44 GPa (0.644 × $10^6$ psi) in compression. The measurement errors from both the optical and the microstylus trace setups are within one-half light band and ±0.1 μm (4 μin.), respectively.

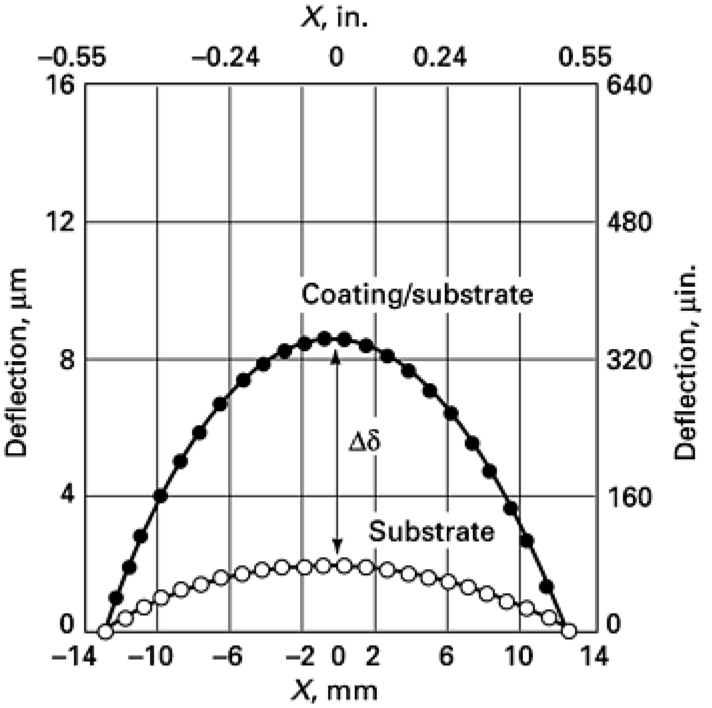

**Fig. 3 Typical microstylus trace on titanium nitride-coated AISI 304 stainless steel disk before and after coating deposition**

**Practical Considerations.** First, either strip or disk-shape substrate specimens should be parallel within 0.02 mm (0.001 in.) over their length or diameter. Specimen edges should be free from visible flaws and chips. In addition, the surfaces on which the deflection measurements (interferometer or profilometer) will be performed should be ground and lapped to a finish better than 0.08 µm $R_a$ (3 µin. $R_a$).

Second, the dimensions of a strip of length $L$, width $w$, and substrate thickness $d_s$ should obey $L > 10\ w > 10\ d_s$. The substrate thickness of a strip or disk depends on the coating thickness to be deposited. The thickness ratio of the substrate to the coating, $d_s/d_c$, should be greater than 50 to ensure the accuracy of the stress calculation from Eq 3.

Third, substrate specimens should be stress relieved before coating deposition. They should be placed between two stainless steel surface plates under at least an 8.8 kPa (1.3 psi) normal load, at an annealing temperature, in a vacuum furnace for at least 1 h. The annealing temperature is dependent on the substrate material.

Fourth, for coatings with an inherently smooth surface, such as those produced by PVD and CVD, the deflection can be determined either by interference fringe or microstylus profilometer measurements on the coated surface. For a coating with a relatively rough surface, such as those produced by thermal spraying and electroplating, the measurements can be made on the surface that is opposite the coated surface.

***Significance and Use.*** The deflection measurement method is recommended for determining the average stress in the cross section of a coating with a thickness ranging from several hundred angstroms to several hundred micrometers. Typically, the elastic constants of a thin coating are much different from those of a bulk material. Equation 3 provides a means for stress measurement on a thin coating without any knowledge of its elastic constants. The measurement normally applies only to a test sample. The disk deflection method is particularly useful for the direct inspection of silicon wafers used in solar cells or integrated circuits.

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## X-ray Diffraction Method

**Basic Principles.** Stress measurement, using the x-ray diffraction method, is based on the change in the interplanar spacing (strain) close to the surface of the specimen material. The details of the theory and interpretation of residual stress measurements are well described in the article "X-Ray Diffraction Residual Stress Techniques" in Volume 10 of the *ASM Handbook*, as well as in Ref 9, 10, and 11. Consider an isotropic material with a lattice parameter $d_0^{hkl}$ for unstressed material in the sample plane normal. The strain in a direction inclined by an angle y to the surface normal of the coating and the stress acting in the surface plane of the coating at an angle φwith the principal axis of the specimen are related by:

$$\begin{aligned} e_{jy}^{hkl} = ( d_{jy}^{hkl} - d_0^{hkl} ) / d_0^{hkl} = [(1 + \nu^{hkl}) / E^{hkl}] \\ (\sigma_x \cos^{2\varphi} + t_{xy} \sin^{2\varphi} + \sigma_y \sin^{2\varphi} - \sigma_z) \sin^2\psi \\ + [(1 + \nu^{hkl}) / E^{hkl}]\, \sigma_z - (\nu^{hkl} / E^{hkl})\, (\sigma_x + \sigma_y + \sigma_z) \\ + [(1 + \nu^{hkl}) / E^{hkl}]\, (t_{xz} \cos\varphi + t_{yz} \sin\varphi) \sin^2\psi \end{aligned} \qquad \textbf{(Eq 8)}$$

where *h*,*k*, and *l* are the indices of the Bragg reflection; $e_{jy}^{hkl}$ and $d_{jy}^{hkl}$ $d\varphi\psi$ are the strain and interplanar spacing of (*hkl*) in the direction of (φ, ψ) respectively; $\nu^{hkl}$ and $E^{hkl}$ are Poisson's ratio and Young's modulus in (*hkl*) in the coating; $\sigma_x$, $\sigma_y$ and $\sigma_z$ are normal stresses; $t_{xy}$, $t_{yz}$, and $t_{xz}$ are shear stresses; $\sigma_x$ is the normal stress acting in the *x* direction on a plane perpendicular to the *x* axis; and $t_{yz}$ is the shear stress on a plane normal to the *y* axis (the first subscript) in the *z* direction (the second subscript). Residual stresses of the coating in various stress states can be determined using Eq 8.

***Biaxial Stress.*** At a free plane, the out-of-plane stress components $\sigma_z$, $\tau_{xz}$, and $\tau_{yz}$ are all zero, at a free surface. Because the penetration depth of x-rays is very small, the resulting measurements refer specifically to near-surface material. Plane stress conditions therefore often apply to x-ray measurements, and Eq 8 is simplified to:

$$\begin{aligned} e_{jy}^{hkl} = ( d_{jy}^{hkl} - d_0^{hkl} / d_0^{hkl} = [(1 + \nu^{hkl}) / E^{hkl}] \\ \sigma\varphi \sin^2\psi + (\nu^{hkl} / E^{hkl})(\sigma_x + \sigma_y) \end{aligned} \qquad \textbf{(Eq 9)}$$

where $\sigma\varphi = \sigma_x \cos^2\varphi + \sigma_y \sin^2\varphi$ is the macrostress in the coating parallel to its surface at an angle φwith the principal axis of the sample.

For a biaxial stress state, $\sigma_x = \sigma_y = \sigma\varphi$, and at $\psi = 0$,

$$( d_{j,y}^{hkl} = 0 - d_0^{hkl} )/ d_0^{hkl} = 2\nu^{hkl} \sigma\varphi / E^{hkl} \qquad \textbf{(Eq 10)}$$

From Eq 9 and 10,

$$d_{jy}^{hkl} = d_{j,y}^{hkl} = 0 + \sigma\varphi\, d_0^{hkl}\ [(1 + \nu^{hkl}) / E^{hkl}] \sin^2\psi \qquad \textbf{(Eq 11)}$$

In practice, high-angle diffraction peaks of an (*hkl*) reflection are obtained from -ψ to +ψ at a given angle φ. Lorentz polarization, absorption, and background corrections are applied to the diffraction peak profile. The peak positions are determined by profile fitting or other methods and are subsequently converted to interplanar spacing $d_{jy}^{hkl}$ for stress analysis.

In the linear plot of $d_{jy}^{hkl}$ vs. $\sin^2\psi$, the intercept is $I = d_{jy}^{hkl} = 0$ and the slope is $M = \sigma\varphi\, d_0^{hkl}\ [(1 + \nu^{hkl})/E^{hkl}]$ .The stress of the coating can then be determined by:

$$\sigma\varphi = M / \{ d_0^{hkl}\ [(1 + \nu^{hkl}) / E^{hkl}]\} \qquad \textbf{(Eq 12)}$$

***Triaxial Stress State Without Shear Stress.*** For a material in a three-dimensional (triaxial) stress state without shear stress, but with the stress component $\sigma_z$ having a finite value within the x-ray penetration volume, Eq 8 becomes (Ref 9, 11, 12):

$$\begin{aligned} e_{jy}^{hkl} &= ( d_{jy}^{hkl} - d_0^{hkl} ) / d_0^{hkl} \\ &= [(1 + \nu^{hkl}) / E^{hkl}](\sigma_x\cos^2\varphi + \sigma_y\sin^2\varphi - \sigma_z)\sin^2\psi \\ &\quad + [(1 + \nu^{hkl}) / E^{hkl}]\, \sigma_z \\ &\quad -(\nu^{hkl} / E^{hkl}) (\sigma_x + \sigma_y + \sigma_z) \end{aligned} \qquad \textbf{(Eq 13)}$$

Two data sets, φ= 0° and φ= 90°, are needed to obtain $\sigma_x$, $\sigma_y$, and $\sigma_z$. The slopes and intercepts of a linear function of $d_{jy}^{hkl}$ vs. $\sin^2\psi$ at φ= 0° and φ= 90° are given by:

$$\begin{aligned} &M\varphi{=}0° = d_0^{hkl}\ [(1 + \nu^{hkl}) / E^{hkl}]\, (\sigma_x - \sigma_z); \\ &M\varphi{=}90° = d_0^{hkl}\ [(1 + \nu^{hkl}) / E^{hkl}]\, (\sigma_y - \sigma_z); \\ &I = d_0^{hkl}\ \{[(1 + \nu^{khl}) / E^{hkl}]\, \sigma_z \\ &\qquad -(\nu^{hkl} / E^{hkl}) (\sigma_x + \sigma_y + \sigma_z)\} \end{aligned} \qquad \textbf{(Eq 14)}$$

Stresses $\sigma_x$, $\sigma_y$, and $\sigma_z$ can be determined from the sum of the slopes and the intercept in Eq 14.

***Triaxial Stress State With Shear Stress.*** A coating with a three-dimensional (triaxial) stress state, including shear stresses, is fully described by Eq 8. The shear stresses, $t_{xz}$ and $t_{yz}$, have a $\sin^2\psi$ dependence. The $d_{jy}^{hkl}$ vs. $\sin^2\psi$ distribution is no longer linear and has two branches of an ellipse for ψ> 0 and ψ< 0. This effect is termed "ψ splitting," which is an indication of the presence of shear stress.

To obtain these stress-tensor components, three data sets (φ = 0°, φ= 45°, and φ= 90°) are obtained for both -ψ and +ψ. The average strain $a_1$ and the deviation $a_2$ from the strains of "ψ splitting" are determined to be (Ref 9, 11, 12):

$$\begin{aligned} a_1 &= ( e_{jy}^{hkl} + e_{jy}^{hkl} - ) / 2 = [( d_{jy}^{hkl} + d_{jy}^{hkl} ) / 2\, d_0^{hkl} ]\ \text{-}1 \\ &= [(1 + \nu^{hkl}) / E^{hkl}]\ (\sigma_x\cos^2\varphi + t_{xy}\sin^2\varphi \\ &\quad + \sigma_y\sin^2\varphi - \sigma_z)\ \sin^2\psi + [(1 + \nu^{hkl}) / E^{hkl}]\, \sigma_z \\ &\quad - (\nu^{hkl} / E^{hkl}) (\sigma_x + \sigma_y + \sigma_z), \end{aligned} \qquad \textbf{(Eq 15)}$$

$$\begin{aligned} a_2 &= ( e_{jy}^{hkl} + - e_{jy}^{hkl} - ) / 2 = ( d_{jy}^{hkl} - d_{jy}^{hkl} ) / 2\, d_0^{hkl} \\ &= [(1 + \nu^{hkl}) / E^{hkl}]\, ( t_{xz}\cos\varphi + t_{yz}\sin\varphi)\ \sin^2\psi \end{aligned} \qquad \textbf{(Eq 16)}$$

The stress-tensor components can be calculated from the slopes of linear plots of $a_1$ vs. $\sin^2\psi$ and $a_2$ vs. $\sin^2\psi$. For $a_1$ vs. $\sin^2\psi$, $(\sigma_x - \sigma_z)$ is obtained at φ= 0°, $(\sigma_y - \sigma_z)$ at φ= 90°, and $t_{xy}$ at φ= 45°, whereas $\sigma_z$ is evaluated from the intercept if $d_0^{hkl}$ is known. Similarly, $t_{xz}$ and $t_{yz}$ are obtained when φ= 0° and φ= 90 °, respectively, from the slope of $a_2$ vs. $\sin^2\psi$.

**Stress Measurement.** Modern diffractometers are fully automated and equipped with computer software for performing numerically intensive analyses. Diffractometers are capable of measuring residual stresses efficiently and economically. Typically, the measurement can be completed in several hours. The following examples illustrate some stress measurements using Cu Kα radiation on cathodic arc PVD titanium nitride coatings on a substrate with various stress states.

***Biaxial.*** An approximately 10 μm (400 μin.) thick coating of highly (111) oriented titanium nitride was deposited on AISI 304 stainless steel at 500 °C (930 °F). The x-ray diffraction $\sin^2\psi$ technique was applied to determine the residual stress in the (333)/(511) reflection of the coating. Figure 4 shows the linear distribution of $d_{jy}^{hkl}$ vs. $\sin^2\psi$, indicating typical biaxial stress in the coating. As shown, the slope $M = -1.1933 \times 10^{-3}$ nm ($4.698 \times 10^{-11}$ in.) and the intercept $I = d_{jy}^{hkl} = 0 =$ 0.082123 nm (0.003233 μin.). Young's modulus and Poisson's ratio for titanium nitride in (333)/(511) are 364 GPa ($52.8 \times 10^6$ psi) and 0.245, respectively (Ref 13). The calculated residual stress for titanium coating is -4248 MPa (-615 ksi) in compression. For highly (111) oriented titanium nitride film, (511) contribution is negligible. This is addressed in Ref 13. The (422) reflection has $2\theta < 130°$, which is not desirable.

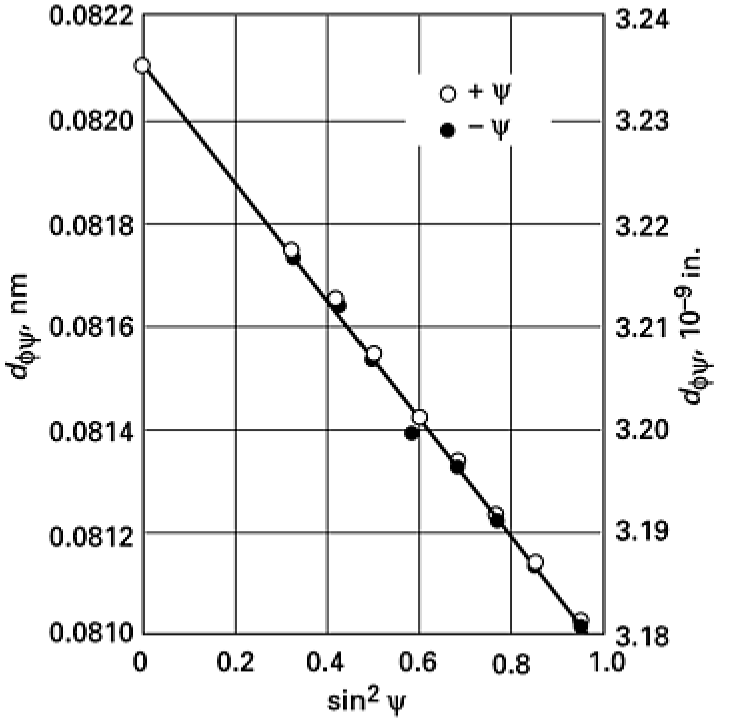

**Fig. 4 Linear distribution of $d_{jy}^{hkl}$ as a function of $\sin^2\psi$ of titanium nitride coating from (333)/(511) reflection**

***Triaxial Without Shear Stress.*** To exemplify a triaxial stress distribution, without shear stresses, triaxial stress analysis was applied to a titanium nitride coating deposited on Inconel 718 substrate at 550 °C (1020 °F). The $d_{jy}^{hkl}$ vs. $\sin^2\psi$ distributions were obtained from (333)/(511) for φ= 0° and φ= 90° (Fig. 5). The slopes *Mφ=0* and *Mφ=90°* are -0.96782 and $-1.01415 \times 10^{-3}$ nm (-3.8103 and $-3.9927 \times 10^{-11}$ in.), respectively, and the intercept $I$ is 0.082083 nm (0.003231 μin.). The strain-free interplanar spacing for (333)/(511) is 0.08160 nm (0.003213 μin.). Based on Eq 14, the stress tensor ($\sigma_{ij}$) from this analysis, in units of MPa, is:

$$s_{ij} = \begin{pmatrix} s_x & t_{xy} & t_{xz} \\ t_{yx} & s_y & t_{yz} \\ t_{zx} & t_{zy} & s_z \end{pmatrix} = \begin{pmatrix} -2653 \pm 151 & 0 & 0 \\ 0 & -2819 \pm 150 & 0 \\ 0 & 0 & 815 \pm 140 \end{pmatrix}$$

The result shows that the planar stresses are equal biaxial within experimental error and that the stress perpendicular to the coating surface is in tension.

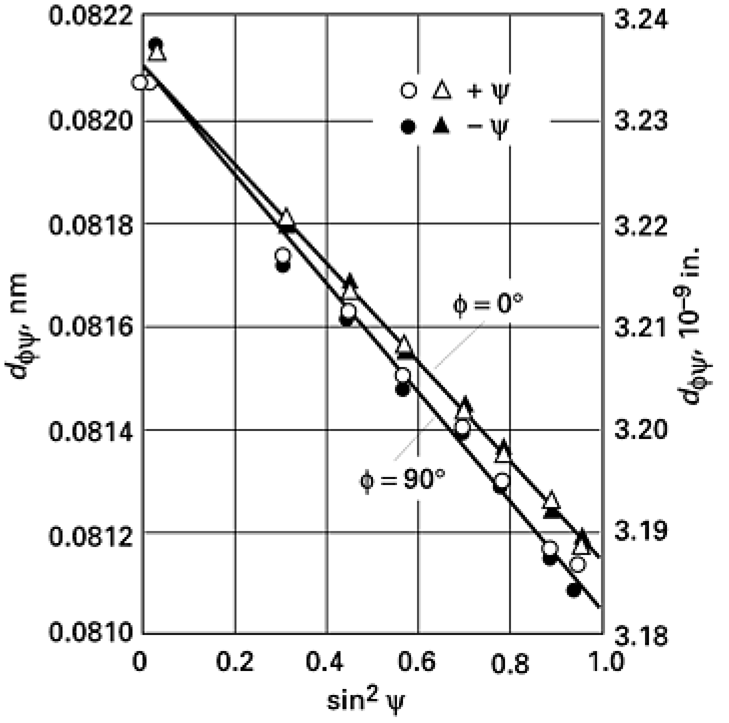

**Fig. 5 Linear distribution of $d_{jy}^{hkl}$ as a function of $\sin^2\psi$ of titanium nitride coating from (333)/(511) reflection at $\varphi = 0°$ and $\varphi = 90°$**

***Triaxial With Shear Stress.*** A triaxial stress distribution, including shear stresses $t_{xy}$, $t_{yz}$, and $t_{xz}$, was studied in a cathodic arc PVD titanium nitride coating on AM-355 stainless steel. The $d_{fy}^{hkl}$ vs. $\sin^2\psi$ distributions were obtained from (333)/(511) at $\varphi = 0°$, $\varphi = 45°$, and $\varphi = 90°$ using Cu Kα radiation. Figure 6 shows the typical ellipse distribution of $d_{jy}^{hkl}$ vs. $\sin^2\psi$ at $\varphi = 0°$. Based on analysis discussed at the beginning of this section, the stress tensor in the titanium nitride coating, in units of MPa, is:

$$s_{ij} = \begin{pmatrix} -2899 \pm 148 & 1 \pm 181 & 110 \pm 32 \\ 1 \pm 181 & -2776 \pm 148 & -34 \pm 34 \\ 110 \pm 32 & -34 \pm 34 & 833 \pm 148 \end{pmatrix}$$

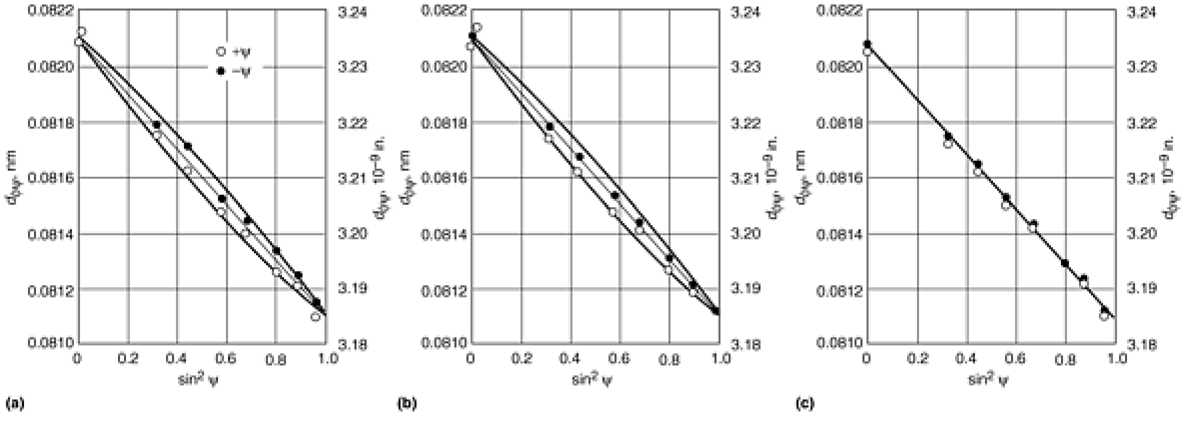

**Fig. 6 Typical ellipse distribution of $d_{jy}^{hkl}$ as a function of $\sin^2\psi$ of titanium nitride coating from (333)/(511) reflection at varying angles. (a) $\varphi = 0°$. (b) $\varphi = 45°$. (c) $\varphi = 90°$**

**Practical Considerations.** First, a ψ-diffractometer is preferable for conducting stress measurements. The Ω-and ψ-diffractometers are defined on the basis of the sample axis for ψ tilt perpendicular or parallel to the plane of the incident and detected x-ray beam, respectively. A ψ-diffractometer gives symmetric irradiated areas in -ψ and +ψ tilted angles at a given (*hkl*) reflection line and a greater range of $\sin^2\psi$ (from 0 to 0.95 for a ψ-diffractometer and 0 to 0.5 for an Ω-diffractometer).

Second, the diffractometer should be mechanically aligned and calibrated using a stress-free standard sample (NIST SRM 660 lanthanum hexaboride powder or SRM 640 silicon powder) to obtain the peak position of the (*hkl*) reflection line within ±0.01° at Bragg angles 2θ in the range of $\psi > 0$ and $\psi < 0$.

Third, an appropriate x-ray wavelength should be selected to achieve the desired sampling volume (penetration depth) for a particular set of (*hkl*)planes. The penetration depth, which is defined as the distance from the surface to the depth with 63% or 1/*e* of the intensity of the reflection line, is calculated for Ω- and ψ-diffractometers, respectively:

$$t\ \Omega = (\sin^2\theta - \sin^2\psi) / [2\mu(\sin\theta \cos\psi)]$$

$$t\ \psi = (\sin\theta \cos\psi) / 2\mu$$

where μ is the linear absorption coefficient, which can be obtained from Ref 14 for various materials and radiations.

Fourth, to achieve high accuracy in residual stress, the measurement should only be carried out on an (*hkl*) reflection line with Bragg angles 2θ > 130° and with sufficient intensity for peak position determination.

Fifth, an appropriately sized collimator should be selected. It should have an irradiated area large enough to ensure that a statistically relevant number of grains or subgrains in the coating are included in the measurement. The angular resolution is essential in stress measurement. If the spot mode of x-ray beam cannot sample a sufficient number of grains, one should use another method.

Sixth, appropriate methods (Ref 9, 10, 15, 16, 17), such as modified Lorentzian, Gaussian, Cauchy, Pearson VII, parabola, center of gravity, gravity line, and cross correlation should be applied to determine the peak positions of the reflection line (*hkl*).

Seventh, a sufficient number of measurements in the -ψ and +ψ directions should be conducted to obtain an accurately linear distribution or ψ-splitting of $d_{jy}^{hkl}$ vs. $\sin^2\psi$. The significance of this distribution should be verified by repeating measurements at different φangles. If a nonlinear relation other than ψ-splitting is obtained in the $d_{jy}^{hkl}$ vs. $\sin^2\psi$ distribution, then the coating being measured is inhomogeneous and, therefore, the x-ray diffraction $\sin^2\psi$ method is no longer applicable.

Eighth, the x-ray elastic constants of the coating for an (*hkl*) plane, $S_1^{hkl} = -\nu^{hkl}/E^{hkl}$ and $S_2^{hkl}/2 = (1 + \nu^{hkl})/E^{hkl}$, can be calculated from single-crystal compliance, according to an appropriate model (Ref 11, 12), or measured experimentally in uniaxial tension or bending tests with a series of loads (Ref 13, 18, 19). X-ray elastic constants and applied loads ($\sigma_a$) obey these equations:

$$\begin{aligned} S_2^{hkl} / 2 &= (1 + \nu^{hkl}) / E^{hkl} \\ &= (1 / d_0^{hkl})[\partial / \partial \sigma_a(\partial d_{jy}^{hkl} / \partial \sin^2\psi)] \\ S_1^{hkl} &= -\nu^{hkl} / E^{hkl} = [1 / (2 d_0^{hkl})](\partial d_{jy}^{hkl} = 0 / \partial \sigma_a) \end{aligned}$$

Ninth, a stress-free interplanar spacing, $d_0^{hkl}$, for a coating may not be readily available in practice. For biaxial stress analysis, the lattice spacing measured at $\psi = 0$, $d_{jy}^{hkl} = 0$, can be substituted for $d_0^{hkl}$. In this case, the contribution to the total error is less than 0.1%. For a triaxial stress analysis, the difference between $d_{jy}^{hkl} = 0$ and $d_0^{hkl}$ is included in the calculation. Consequently, a small error in $d_0^{hkl}$ can lead to a relative large error in the measured stress. To obtain acceptable stress results, $d_0^{hkl}$ must be within 0.01% of its true value. The stress-free interplanar spacing $d_0^{hkl}$ in the strain-free direction ψ* is given by (Ref 20):

$$\sin^2\psi^* = [-S_1^{hkl} / (S_2^{hkl} / 2)] \{1 + [(\sigma_y - \sigma_z) / (\sigma_x - \sigma_z)] + [3 + (S_2^{hkl} / 2 S_1^{hkl}) \sigma_z] / (\sigma_x - \sigma_z)\}; \varphi=0$$

$$\sin^2\psi^* = [-S_1^{hkl} / (S_2^{hkl} / 2)] \{1 + [(\sigma_y - \sigma_z) / (\sigma_x - \sigma_z)]\} \text{ when } | \sigma_x + \sigma_y - 2\sigma_z | \ ? \ 2 | \sigma_z |$$

$$d_0^{hkl} = d_{jy}^{hkl} = 0 / [1 + S_1^{hkl} (\sigma_x + \sigma_y + \sigma_z) + (S_2^{hkl} / 2)\sigma_z]$$

**Significance and Use.** The advantage of the x-ray diffraction method is its capability for measuring residual stress directly and nondestructively on a product component. Portable diffractometers are commercially available and can be used for on-site measurement. The method can apply to a coating with a thickness ranging from 0.5 to 350 μm ($2 \times 10^{-5}$ to $1.4 \times 10^{-2}$ in.). However, it is difficult to measure residual stresses in extremely thin coatings and, in some cases, highly textured coatings. Furthermore, x-ray diffraction is inapplicable to amorphous coatings, and a large scatter in stress measurement is often encountered in coatings with large grain size.

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## Hole-Drilling Method

**Basic Principles.** The hole-drilling method for measuring residual stresses involves drilling a shallow hole in the test specimen to a depth approximately equal to the hole diameter. Typical hole diameters range from 0.8 to 5.0 mm (0.030 to 0.200 in.). The creation of the hole redistributes the stresses in the material surrounding the hole. A specially designed three-element strain-gage rosette, such as that shown in Fig. 7(a), measures the associated partial strain relief. The in-plane residual stresses that originally existed at the hole location can then be calculated from the measured strain reliefs using the method described in ASTM E 837-92 (Ref 21). The ASTM standard also gives details of practical drilling procedures.

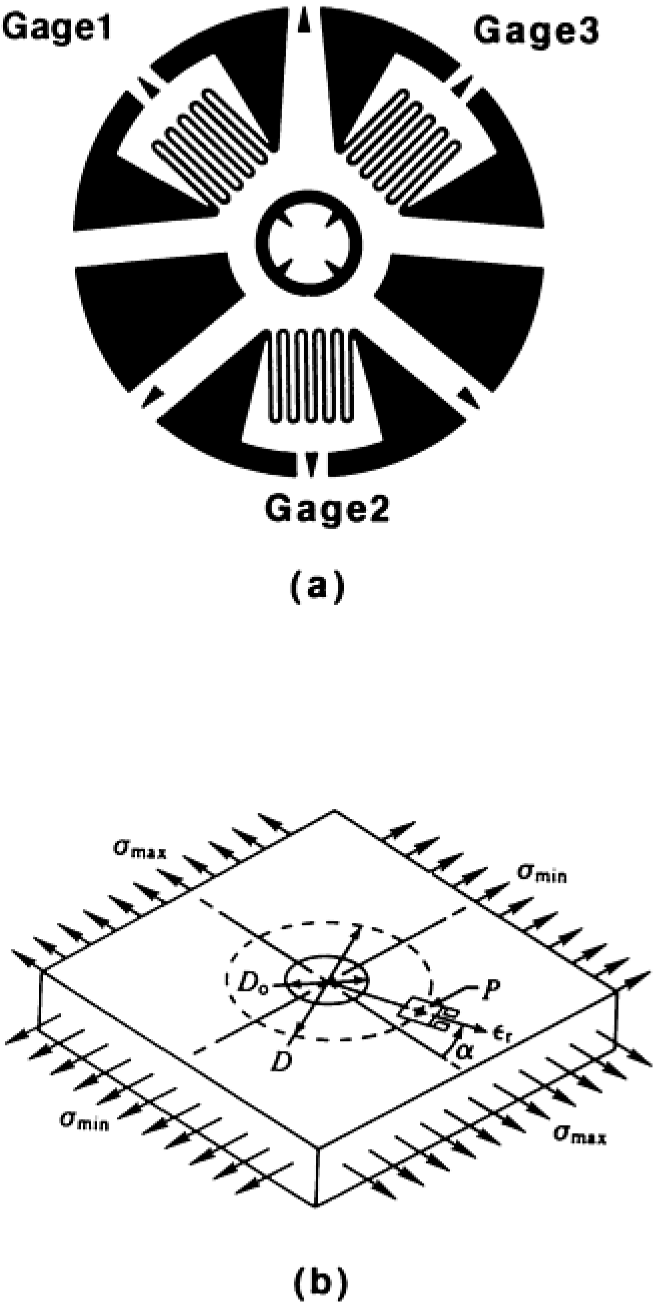

**Fig. 7 (a) Typical three-element strain-gage rosette. (b) In-plane strain components caused by release of residual stress through introduction of a hole. Source: Ref 21**

The partial strain relief measured by one of the three strain gages in the rosette in Fig. 7(b) is related to the principal in-plane residual stresses by:

$$\varepsilon_r = (\sigma_{max} + \sigma_{min})A + (\sigma_{max} - \sigma_{min})B \cos 2\alpha \qquad \textbf{(Eq 17)}$$

where $\sigma_{max}$ and $\sigma_{min}$ are maximum and minimum principal residual stresses, and $\alpha$ is the angle from the gage axis to the maximum principal stress direction. $A$ and $B$ are calibration constants, the values of which depend on the specimen material properties, the rosette geometry, the hole diameter, and the hole depth. ASTM E 837-92 tabulates the calibration constants for the standard rosette pattern shown in Fig. 7.

Equation 17 can be inverted to determine the principal residual stresses from the measured strain reliefs. The result is:

$$s_{\max}, s_{\min} = [(e_3 - e_1)/4A] \pm \{[(e_3 - e_1)^2 + (e_3 + e_1 - 2e_2)^2]^{1/2}/4B\}$$
$$b = \tfrac{1}{2}\arctan[(e_3 + e_1 - 2e_2)/(e_3 + e_1)]$$

**(Eq 18)**

where β is the angle measured clockwise from the location of gage 1 to the direction of $\sigma_{\max}$. The above equations are valid for a homogeneous isotropic material that is wide, when compared with the hole diameter, and thick, when compared with the hole depth. The equations also apply to a through-the-thickness hole in a material in the form of a thin sheet, provided that the sheet thickness is uniform near the hole. The associated calibration constants have slightly different values than those of the thick-material case. Table 2, reproduced from ASTM E 837-92, lists the dimensionless calibration coefficients for both the thin-sheet and thick-material cases. *A* and *B* can be determined from the dimensionless coefficients using:

$$A = -(1 + \nu)\,\bar{a}/2E$$
$$B = -\bar{b}/2E$$

**(Eq 19)**

**Table 2 Numerical values of dimensionless calibration coefficients $\bar{a}$ and $\bar{b}$**

| $D_0/D$ | **Through-the-thickness hole[(a)]** | | **Blind hole[(b)], depth = 0.4 *D*** | |
|---|---|---|---|---|
| | $\bar{a}$ | $\bar{b}$ | $\bar{a}$ | $\bar{b}$ |
| 0.30 | 0.089 | 0.278 | 0.111 | 0.288 |
| 0.31 | 0.095 | 0.295 | 0.118 | 0.305 |
| 0.32 | 0.101 | 0.312 | 0.126 | 0.322 |
| 0.33 | 0.108 | 0.329 | 0.134 | 0.340 |
| 0.34 | 0.114 | 0.347 | 0.142 | 0.358 |
| 0.35 | 0.121 | 0.364 | 0.150 | 0.376 |
| 0.36 | 0.128 | 0.382 | 0.158 | 0.394 |
| 0.37 | 0.135 | 0.400 | 0.166 | 0.412 |
| 0.38 | 0.143 | 0.418 | 0.174 | 0.430 |
| 0.39 | 0.150 | 0.436 | 0.182 | 0.448 |
| 0.40 | 0.158 | 0.454 | 0.190 | 0.466 |
| 0.41 | 0.166 | 0.472 | 0.199 | 0.484 |

|  |  |  |  |  |
|---|---|---|---|---|
| 0.42 | 0.174 | 0.490 | 0.208 | 0.503 |
| 0.43 | 0.183 | 0.508 | 0.217 | 0.521 |
| 0.44 | 0.191 | 0.526 | 0.226 | 0.540 |
| 0.45 | 0.200 | 0.544 | 0.236 | 0.558 |
| 0.46 | 0.209 | 0.562 | 0.246 | 0.576 |
| 0.47 | 0.218 | 0.579 | 0.255 | 0.594 |
| 0.48 | 0.228 | 0.596 | 0.265 | 0.612 |
| 0.49 | 0.237 | 0.613 | 0.275 | 0.630 |
| 0.50 | 0.247 | 0.629 | 0.285 | 0.648 |

Source: ASTM E 837-92

(a) In a thin sheet.

(b) In a thick material.

Residual stress measurements in coated materials create an additional complication because the combination of coating and substrate is no longer a homogeneous material. The calibration coefficients provided in ASTM E 837-92 no longer accurately apply. However, the above two equations are still valid for coated materials, if the coating has a uniform thickness. If the substrate is less than several times greater than the hole depth, then it is also necessary for the substrate thickness to be uniform.

The calibration coefficients *A* and *B* for hole drilling in a coated material differ from the standard values given in ASTM E 837-92. The actual values depend on the elastic properties of the coating and the substrate, the coating thickness, and the hole diameter and depth. These coefficients can be determined by either experimental calibrations (Ref 22) using known externally applied stresses or finite-element calculations (Ref 23).

Approximate values of *A* and *B* for thick coatings can be estimated from the values given in ASTM E 837-92. For this purpose, a "thick" coating is one that is at least 0.25 times the mean radius of the strain-gage rosette. For the smallest commercially available hole-drilling rosette, the mean radius is about 1.25 mm (0.050 in.). Therefore, the minimum acceptable coating thickness is about 0.3 mm (0.012 in.).

An approximate estimation of *A* and *B* for a coated material is based on the observation that the hole-drilling method is most sensitive to the stresses closest to the specimen surface. Almost all of the measured strain relief is due to the stresses in the material within a depth of about 0.25 times the mean radius of the hole-drilling rosette. Thus, a specimen coated to at least this depth is likely to behave similarly to a homogeneous thick specimen consisting only of coating material. Thus, the *A* and *B* calibration coefficients for a "thick" coating are approximately equal to the ASTM tabulated values for a homogeneous material with the elastic properties of the coating.

The *A* and *B* coefficients for coatings that are thinner than 0.25 times the mean radius of the hole-drilling rosette will deviate significantly from the ASTM tabulated values. The coefficients must be determined on an individual basis, either by experimental or computational means. The use of the hole-drilling method with such "thin" coatings is not generally recommended because the sensitivity of the resulting strain measurements is rather low. As a result, small absolute errors in the strain measurements can cause large relative errors in the computed residual stresses.

**Stress Measurement.** The following example illustrates a hole-drilling measurement on a detonation gun type of tungsten carbide-cobalt (WC-Co) coating deposited on an AISI 1018 steel substrate. The coating was approximately 0.75 mm (0.03 in.) thick and had a macroscopically homogeneous structure. The elastic properties of the coating were $E_c$ = 172 GPa (25 × $10^6$ psi) and $u_c$ = 0.3.

A 062-RE hole-drilling strain-gage rosette (5.13 mm, or 0.202 in., strain-gage mean diameter) was attached to the coated specimen. A 2.44 mm (0.096 in.) diameter hole was cut in the WC-Co coating by abrasive-jet drilling using 27 μm (1080 μin.) alumina particles. Drilling proceeded in four approximately equal depth increments, up to a final depth of 0.356 mm (0.014 in.). The strain measurements listed in Table 3 were made after each hole-depth increment. Using the *A* and *B* calibration coefficients from ASTM E 837-92, adjusted for the elastic properties of the coating material, the principal residual stresses in the coating were found to be -260 MPa (-38 ksi) and -286 MPa (-41 ksi), respectively. As might be anticipated, the residual stresses in the coating are approximately isotropic.

**Table 3 Hole-drilling residual stress measurements on a detonation gun WC-Co coating**

| **Depth** | | **Strains, με** | | | **Average stress** | | | | | | | | | | | | **α** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | **$\sigma_x$** | | **$\sigma_y$** | | **$t_{xy}$** | | **$\sigma_{max}$** | | **$\sigma_{min}$** | | **$t_{max}$** | | |
| **mm** | **in.** | **$\varepsilon_1$** | **$\varepsilon_2$** | **$\varepsilon_3$** | **MPa** | **ksi** | **MPa** | **ksi** | **MPa** | **ksi** | **MPa** | **ksi** | **MPa** | **ksi** | **MPa** | **ksi** | |
| 0.00 | 0.000 | 0 | 0 | 0 | -271 | -39.3 | -275 | -39.9 | -13 | -1.9 | -260 | -37.7 | -286 | -41.5 | 13 | 1.9 | 41° |
| 0.10 | 0.004 | 56 | 52 | 52 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... |
| 0.20 | 0.008 | 116 | 107 | 109 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... |
| 0.28 | 0.011 | 163 | 155 | 168 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... |
| 0.36 | 0.014 | 210 | 200 | 218 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... |

Note: Rosette type, EA-XX-062RE; Young's modulus, 172.0 GPa (25 × $10^6$ psi); Poisson's ratio, 0.3; hole diameter, 2.440 mm

**Practical considerations** for the use of the hole-drilling method are:

- A high-speed drilling technique using carbide drills is recommended for producing a hole in a ductile coating. Abrasive-jet drilling is recommended for a brittle, hard coating (Ref 24).
- The use of specially made hole-drilling strain-gage rosettes is essential. The application of the strain-gage should follow the procedure recommended by the manufacturer.
- A smooth coating surface less than 0.41 μm $R_a$ (16 μin. $R_a$) is desirable for secure strain-gage adhesion. An abrading or grinding process that does not induce significant residual surface stress should be used for surface preparation.
- The selection of an appropriately sized strain gage should be based on coating thickness, as well as on

the depth and diameter of the hole to be drilled. The diameter of the drilled hole, $D_0$, should be related to the diameter of the gage circle, $D$, where $0.3 < (D/D_0) < 0.5$.

- A depth microscope with a resolution better than 12.7 μm (0.0005 in.) should be used to measure the depth of the drilled hole at each depth increment.
- The center of the drilled hole should coincide with the center of the strain-gage circle within $\pm 0.015\, D_0$. A measurement microscope should be used to align the drill holder or abrasive-jet nozzle with the center of the rosette.
- Precautions should be taken to ensure that the walls of the drilled hole are square to the coating surface on which the rosette is cemented. It is important to protect the strain gage from abrasive-particle erosion or mechanical damage during the drilling operation.
- Values for the Young's modulus and Poisson's ratio of the coating should be independently measured in order to determine the residual stress from strain relaxations.

**Significance and Use.** The hole-drilling strain-gage method is a semidestructive technique for measuring residual stress on a coating with a thickness of at least 0.1 mm (0.004 in.). The method, which is quite versatile, can apply to test samples as well as to actual components with complex geometries. Furthermore, it can be used for on-site measurements.

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### Method Comparison

The mechanical-deflection method is capable of measuring the average stress throughout the coating thickness, but requires the stress to be uniform over large distances in the in-plane directions. In contrast, the x-ray diffraction and hole-drilling methods can make a much more localized measurement in-plane, but they have a significantly more limited depth capability. A good agreement in stress measurements between the deflection and x-ray diffraction methods has been demonstrated (Ref 13). With the extrapolation of blind-hole measurements to the near surface, the stress measurement is in good agreement with that measured by x-ray diffraction (Ref 25). A user can select the most suitable method based on economics, environment, coating microstructures, and the geometry of the component to be measured.

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## Testing of Stability and Thermal Properties of Thermal Barrier Coatings

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### Introduction

THERMAL BARRIER COATINGS (TBCs) are applied to metallic components of advanced heat engines to reduce the metal temperature, increase the environmental resistance and life of the component, and in some cases reduce noxious exhaust emissions. This thin coating usually consists of a metallic bond coat applied to the metal component, followed by a layer of magnesia- or yttria-stabilized zirconia (YSZ). If the TBC is on nickel- or cobalt-base superalloy components intended for high-temperature operation, it is advisable to heat treat the TBC to achieve bond coat densification and diffusion bonding to the substrate. The selection of the TBC system involves many considerations, principally knowledge of the intended service conditions, temperature reduction expectations, component life estimates, cost, and in some cases the external surface finish requirements. It is implicit that a successful TBC will also survive the rigors of service without spalling or eroding. This article discusses the various tests applied to the TBC system, and to the zirconia layer separately, to establish thermal design properties and thermomechanical and environmental stability.

## Acknowledgements

The authors wish to thank Danny L. Appleby and Dr. Glenn C. Whichard of Praxair Surface Technologies, Inc. for providing the data for Fig. 5 and providing the samples and doing the x-ray analysis for Fig. 7, respectively. We also appreciate the suggestions of the reviewers of this article: Catherine Cotell (Naval Research Laboratory), Robert Miller (National Aeronautics and Space Administration, Lewis Research Center), Albert Sue (Praxair Surface Technologies), Gary McGuire (MCNC), and Michael Barber (Allison Engine Co.).

## Thermomechanical Stability

The TBC system is expected to survive the thermal shock of rapid cycle heating and cooling, as experienced in gas turbine or diesel engines, without spallation. Spallation is the result of the thermal stress pattern created when the thermal cycle repeatedly exceeds the stress for crack growth within the zirconia layer. This results in a time-dependent extension of pre-existing cracks within the plane of the coating until critical link-up and spallation. In many tests, the location of the spall line is in the zirconia layer, but near the bond coat interface. In the finite element modeling studies of Chang et al. (Ref 1), the near-interface area in the zirconia layer was shown to be the high-stress zone in simulated thermal cycling. In the thermal spray process, the crack nuclei are probably the interfaces between splats in the coating.

Two strategies to improve the resistance to in-plane crack growth in thermally sprayed zirconias are to use a low-density coating, with the pores acting to blunt growing cracks, or to increase the cohesive strength between splats, which requires high-density coating conditions. In the first case, 12 to 15% porosity is useful, and in the latter case, it is critical to generate macrocracks vertical to the plane of the coating, spaced about 0.2 to 1 mm apart, to relieve short-range stress (Ref 2). In physical vapor deposition coating, the zirconia deposition conditions are adjusted to grow columnar grains, which similarly reduce the in-plane modulus and limit the accumulation of coating stress during a thermal cycle.

**Thermal Fatigue Testing.** Laboratory testing has been used, particularly in the coating development stage, to cycle thermally a TBC specimen followed by post-test microscopic examination for spallation-type cracks. The thermal cycle for evaluation of thermal shock resistance employs rapid heating and cooling rates, using direct impingement flames or heating jets on the oxide face of the specimen, with little hold time at the maximum temperature. This test principally challenges the oxide layer, because the bond coat remains at relatively low temperatures due to the insulating nature of the zirconia layer and the short time at high temperatures.

Figure 1 illustrates a cycle that simulates the thermal shock of first-stage gas turbine outer airseals with a zirconia layer 1.27 mm (0.050 in.) thick. Detail of the flame impingement on the button sample is shown in Fig. 2. The test sample is a 25 mm (1 in.) diameter button, 3.2 mm (0.125 in.) thick, made from the substrate alloy of interest. After the button is coated with the TBC system, the edges are ground and polished to produce a square edge to allow examination of the coating layers.

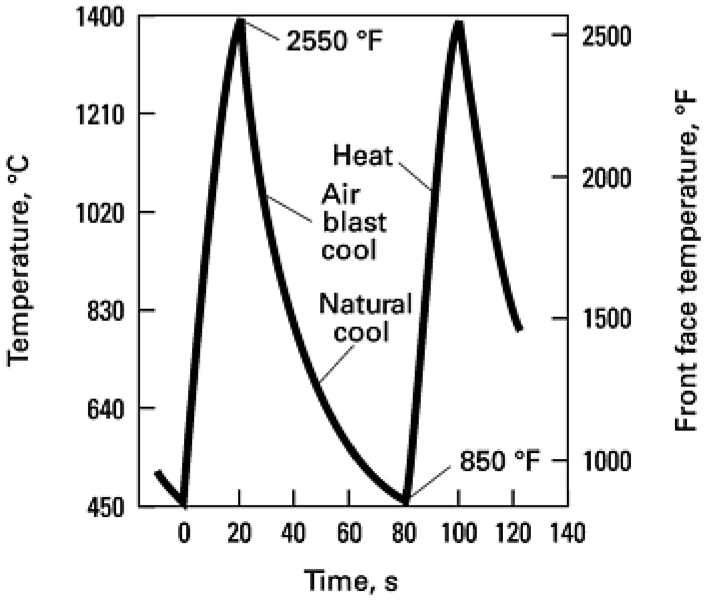

**Fig. 1 Schematic illustration of oxide surface temperature cycle used for thermal fatigue testing of $ZrO_2$-coated test buttons 1.27 mm (0.050 in.) thick, simulating a first-stage gas turbine outer airseal application**

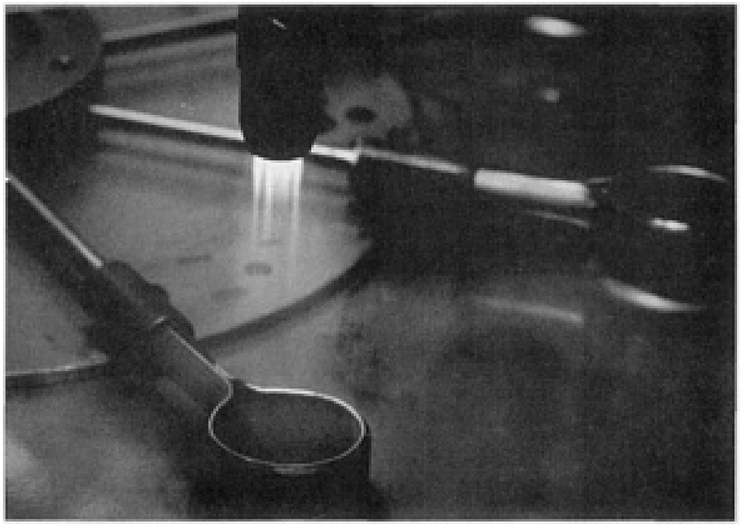

**Fig. 2 Flame impingement on the button sample in a thermal fatigue test rig**

The test rig consists of an oxygen-propane or propylene burner, a fixture arm to hold the button sample, a stepping motor system to advance quickly between stations and to hold for prescribed times in the heating and cooling positions, and a means to record at least the front oxide face temperature during the heating cycle. Two-color infrared optical pyrometers are widely used for the latter task, with the output connected to a chart recorder or computer. One word of caution concerning the temperature measured. If the zirconia coating is not an ideal gray body, that is, the emissivity is not the same at the two wavelengths used by the pyrometer, the reading may be in error. This issue is under study at several test facilities, and it could affect burner rig tests as well. If the samples being tested are all the same material, such as plasma-sprayed 8% YSZ coatings of common thickness, the measured temperatures should be relatively correct.

In one test configuration, the heating cycle is 20 s, followed by a 20 s air blast and two 20 s periods of natural convection cooling. The burner-to-specimen standoff, burner size, and gas flows are set to heat the oxide face of a standard specimen rapidly to 1400 °C (2550 °F) in the first 20 s. The air blast then drops the front face temperature to about 815 °C (1500 °F), and it finally reaches about 454 °C (850 °F) after 40 s of natural cooling. After the cycle is repeated 2000 times, the edge of the coated button is examined at 10× to 30× for evidence of separation-type cracking in the zirconia layer. The specimen edge should also be inspected before the test, with few to no starting cracks expected.

The post-test cracking of good TBC systems having zirconia thicknesses of about 1.27 mm (0.050 in.) should be less than 15% of the circumference, and typically much less. If a tested specimen is mounted in cross section and serially polished, it will be seen that the crack is indeed at the edge of the coating and extends inward toward the center of the button. The cracks will continue to extend around the circumference and grow inward until eventual spallation, for the case of a TBC with poor thermal fatigue resistance. In good TBC systems, additional sets of 2000 cycles will show little crack growth, if any, and typically at a lower rate than in the first test period.

It has been found that the edge-cracking rate is a function of the zirconia coating density (Ref 2), as shown in Fig. 3. In addition, use of the conventional tensile bond-cap test (ASTM C 633-79) has shown that the higher-density coatings have increasing cohesive strength within the zirconia (Ref 2). The result of Fig. 3 must be further qualified. The coatings of density above about 90% of theoretical density (below 10% porosity) also had intentional long macrocracks throughout the coating running perpendicular to the coating plane. Without these macrocracks, the higher-density zirconia coatings will spall quickly, perhaps even on the first thermal cycle.

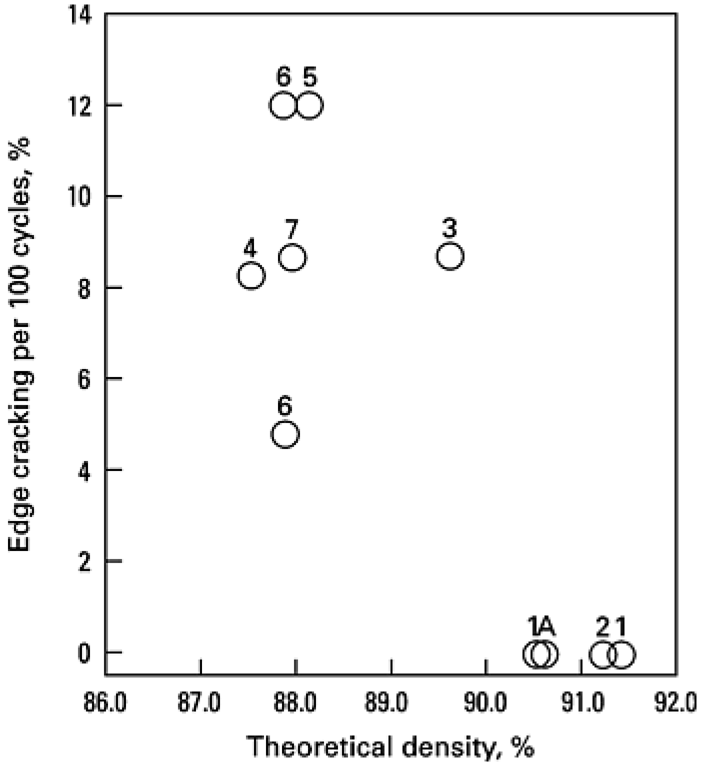

**Fig. 3 Thermal fatigue edge-cracking rate for thick $ZrO_2$ coatings as a function of coating density. Thermal fatigue test with peak temperature of 1400 °C (2550 °F) and 1.1 to 1.3 mm (0.4 to 0.5 in.) thick oxide. Specimen numbers allow correlation to Fig. 4. Source: Ref 2**

If the back metal side of the button specimen also has temperature instrumentation, the differential front-to-back temperature drop, $\Delta T$, can be measured at the peak of the heating cycle. Figure 4 shows that $\Delta T$ is also related to coating density, with lower-density coatings having greater thermal insulation.

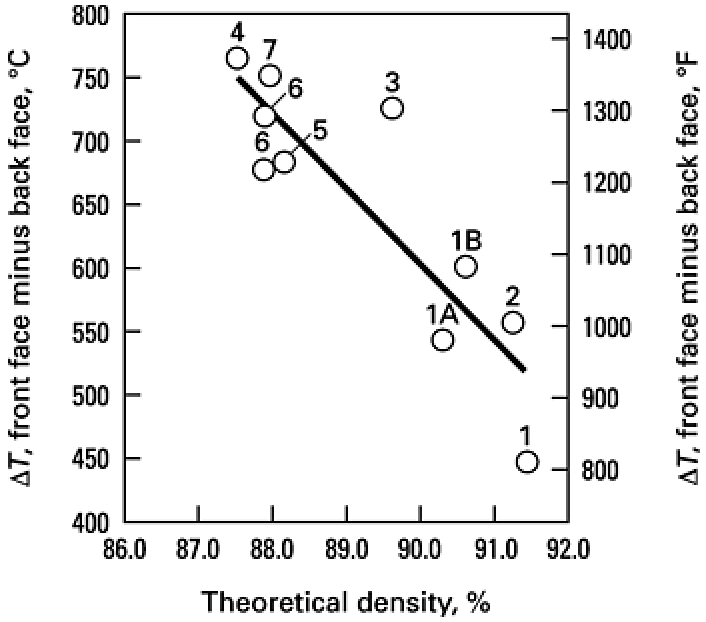

**Fig. 4 Temperature drop across thick $ZrO_2$ coatings on an IN 718 substrate (thickness, 3.2 mm) as a function of $ZrO_2$ coating density. Thermal fatigue test with peak temperature of 1400 °C (2550 °F) and 1.1 to 1.3 mm (0.4 to 0.5 in.) thick oxide. Specimen numbers allow correlation to Fig. 3. Source: Ref 2**

The same rapid heating test rig can be used to evaluate thin TBCs. On aircraft turbine components such as first-stage blades or vanes, the zirconia thickness required may be from 0.13 to 0.30 mm (0.005 to 0.012 in.), and on combustion chambers, 0.30 to 0.38 mm (0.012 to 0.015 in.). If the front face oxide peak temperature is set at 1400 °C (2550 °F) on a standard YSZ sample of 90 to 91% theoretical density and 1.27 mm (0.050 in.) thickness, specimens with thinner zirconia layers will reach lower temperatures in the same test cycle, while those with thicker layers will reach higher temperatures. Figure 5 shows this dependence on oxide layer thickness when other conditions are constant. For this reason, the burner parameters should be set using a standard sample to ensure a constant heat flux for all tests. One way to do this is to have a rotary carousel of samples, including one standard sample, that provides a check on the test conditions every time it cycles through the heating station. The parameter $\Delta T$ will also increase with zirconia thickness, as one would expect. Furthermore, the edge-cracking rate will depend on coating thickness for constant coating density and structure. For example, a dense macrocracked TBC specimen 0.30 to 0.38 mm (0.012 to 0.015 in.) thick can easily sustain 20,000 or more of the above cycles without edge cracking.

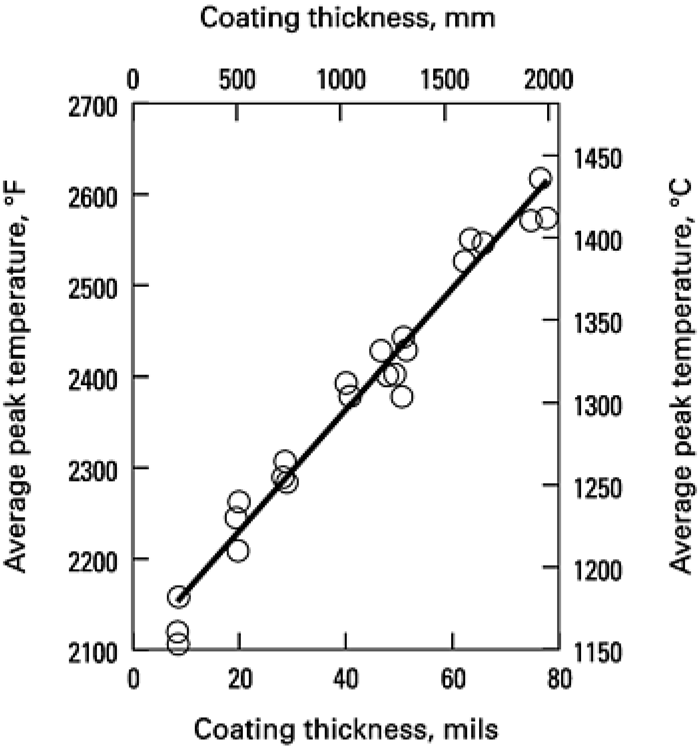

**Fig. 5 Peak temperature of zirconia surface for $ZrO_2$ coatings as a function of coating thickness, in standard thermal cycle test of Fig. 1 (20 s cycle to 1400 °C, or 2550 °F). All samples were run at the same relative heat flux (1330 °C, or 2423 °F, on a nominal coating 1270 μm, or 50 mils, thick).**

A similar thermal fatigue test cycle can be established for testing TBCs for the diesel environment. In this case, the heat flux across the TBC is expected to be greater than in gas turbines, but the peak temperature is expected to be lower. In one test configuration, the burners were moved closer to the oxide face of the coated button, the heating cycle was reduced to 8 s, and the peak oxide temperature was held to 982 °C (1800 °F).

Another testing approach, used by aircraft gas turbine manufacturers and the National Aeronautics and Space Administration, is to coat solid 1.2 cm (0.5 in.) diameter burner bars and expose a rapidly rotating carousel of bars to a high-velocity fuel-oxygen burner. This test has the advantage of allowing use of commercial engine fuel, with controlled doping of known impurities such as sulfur or vanadium if desired. Substrate-side air cooling is sometimes introduced by using hollow bars, to make the test a better simulation of actual coated hardware conditions where back-side cooling is typical.

Although the button tests establish the capability of the basic coating candidate, the button and burner bar coating conditions are usually ideal. Only on real components will practical issues such as the effect of component geometry on the coating structure be faced. One further stage of testing might be considered: putting actual coated components in large thermal cycling chambers. Even so, the laboratory screening tests described above should be followed by actual engine tests of components with TBCs.

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## Environmental Stability

A TBC must also resist environmental degradation. This may occur as oxidation of the bond coat, phase transformation stress deterioration of the zirconia layer, or chemical destabilization of the oxide layer. The severity of these effects depends on the oxidation resistance of the bond coat, the initial crystalline phase mixture of the zirconia coating, the service temperature, and the environmental impurities present.

**Bond Coat Oxidation.** To test the oxidation resistance of the bond coat and its effect on the spallation of the TBC, a thermal cycle needs to combine extended soak time at high temperatures with periodic heating and cooling cycling to induce thermal stress. One such cycle used to test TBCs for aircraft gas turbine applications is a simple tube furnace that operates at a constant temperature of 1121 °C (2050 °F), with the sample set pneumatically moved in and out of the hot zone. The TBC samples rest on an alumina firebrick boat, with dense alumina pushrods made from thermocouple insulator ceramics, for an all-oxide hot-zone support system. The samples heat to furnace temperature in about 5 min, soak for 50 min, and then are quickly pulled out for a 5 min cooling period. At the end of every 25 cycles, the samples are held out and visually examined at room temperature. After 200 cycles, the samples are inspected for spallation or edge cracking, then are mounted in plastic for evaluation in polished cross section. There the extent of bond coat oxidation and interface cracking can be measured. The test temperature is as much as 110 °C (200 °F) higher than expected for the component in service and is thus an accelerated test for oxidation of the bond coat. To make this comparison test valid, care should be taken that the furnace temperature profile is uniform and covers the full zone occupied by the TBC samples.

A cycle for testing coatings for diesel applications can be similarly designed by setting the soak temperature about 110 °C (200 °F) higher than the measured steady-state temperature of the substrate metal of the component in question. In the case of coatings for steel or cast iron substrates, the bond coat is typically not heat treated, which may allow internal oxidation of the Ni-Cr or Fe-Cr-Al-Y alloys used for thermally sprayed layers. Thus, a cycle soak temperature of 650 to 982 °C (1200 to 1800 °F) may still challenge inadequate coating systems.

**Zirconium Oxide Phase Stability.** Pure zirconium oxide is an allotropic material and has a cubic structure from its freezing point at 2680 °C (4856 °F) down to 2370 °C (4298 °F), where it transforms to a tetragonal structure of similar cell size. Because of this small difference in crystalline cell volume, thermal cycling across the cubic-tetragonal transition temperature does not impose severe internal stresses. Following further cooling to below 1170 °C (2138 °F), zirconia transforms to the monoclinic structure, which has about a 4% larger crystalline cell volume than the tetragonal structure (Ref 3). Large internal stresses are generated as the transformation front sweeps through the material, which can lead to crack initiation. Commercially useful zirconia is alloyed with yttria, which has a cubic-plus-tetragonal two-phase field in its phase diagram (Fig. 6) and inhibits the low-temperature tetragonal-to-monoclinic transformation (Ref 3, 5, 6).

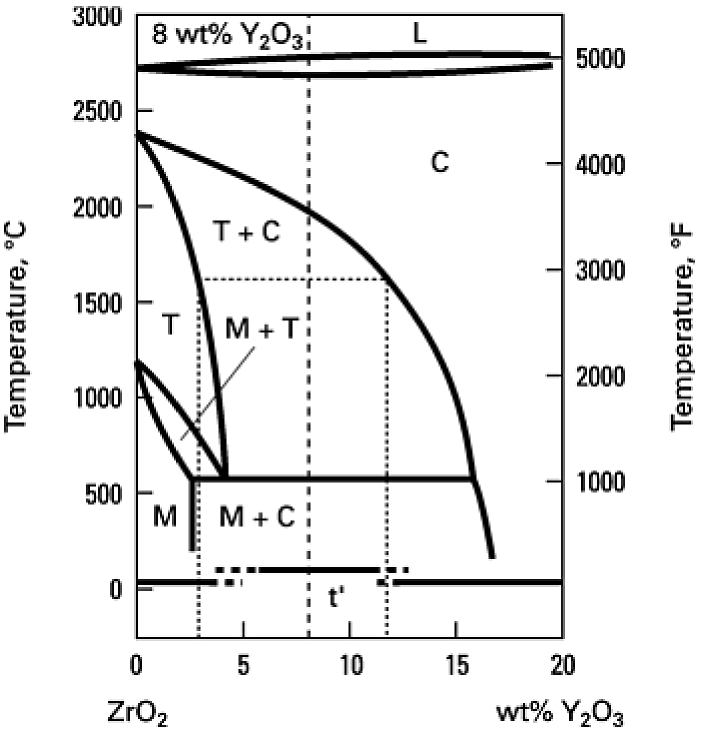

**Fig. 6 Phase diagram of the $ZrO_2$-rich region of the $ZrO_2$-$Y_2O_3$ system. M, monoclinic phase; C, cubic phase; T, tetragonal phase; L, liquid; t, nontransformable tetragonal. Source: Ref 4**

In thermally sprayed yttria-stabilized coatings, the feedstock is powder, which may be fabricated by a variety of methods (Ref 7). Partially stabilized zirconia, with about 6.5 to 9 wt% Y, mostly avoids the monoclinic phase and the fully stabilized cubic-only phase, which is known to have less thermal shock resistance than the dual-phase cubic-plus-tetragonal structure (Ref 8). A powder feedstock may have the correct average yttria content, but it may not be homogeneous at the crystalline grain level. An inhomogeneous powder may have some local volumes that have no yttria and others with yttria concentrations far higher than the bulk analysis. The x-ray diffraction pattern of such a powder thus shows the monoclinic phase characteristic of the nearly pure zirconia grains, along with tetragonal and cubic phases from the volume of the material that was sufficiently combined with yttria. When an inhomogeneous powder is plasma sprayed to form a coating, the particle melting in the arc improves the degree of homogeneity. However, this may not be sufficient to fully homogenize the material, depending on the state of the starting powder and the chosen spray parameters.

Figure 7 shows the x-ray diffraction patterns of an inhomogeneous powder and a sprayed coating. In this example, the spray conditions did eliminate nearly all of the starting monoclinic phase. The following table gives the phase distribution for the two materials in Fig. 7, based on the areas under the diffraction peaks:

| **Material** | **Phase, mol%** | | |
|---|---|---|---|
| | **Monoclinic** | **Tetragonal** | **Cubic** |
| Starting powder | 6 | 76 | 18 |

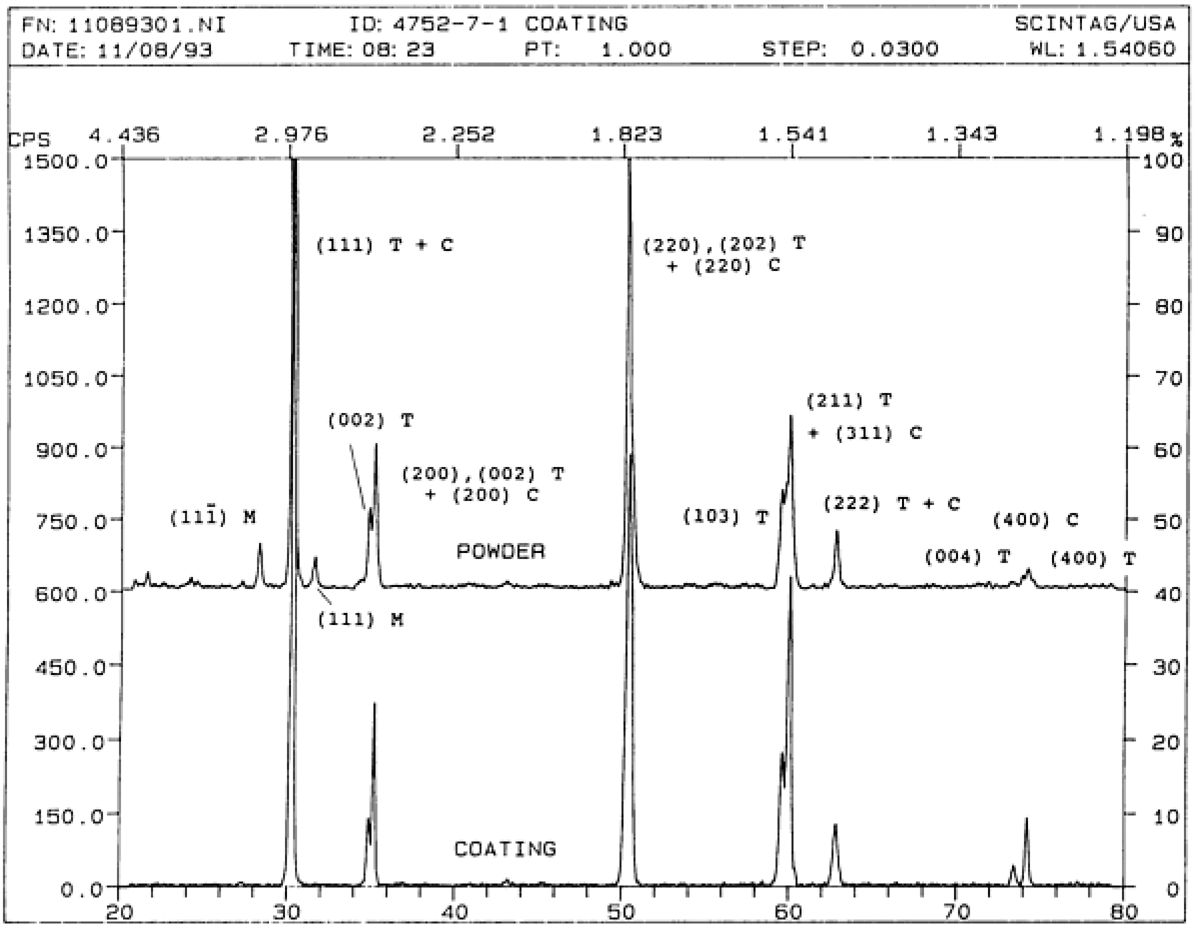

**Fig. 7 X-ray diffraction patterns of yttria-stabilized zirconia powder showing some monoclinic phase, and of a coating made from that powder. M, monoclinic phase; C, cubic phase; T, tetragonal phase; T + C, overlapping tetragonal and cubic reflection**

The values in the table were obtained with the Miller algorithm (Ref 6):

$$\frac{M}{T+C} = 0.82\frac{I_{(11\bar{1})M} + I_{(111)M}}{I_{(111)T+C}} \qquad \textbf{(Eq 1)}$$

$$\frac{C}{T} = 0.82\frac{I_{(400)C}}{I_{(400)T} + I_{(004)T}} \qquad \textbf{(Eq 2)}$$

$$M+T+C = 1.00 \qquad \textbf{(Eq 3)}$$

where M, T, and C denote the mole percentages of the monoclinic, tetragonal, and cubic phases, respectively, and $I_{(hkl)}$ is the integrated intensity for the (hkl) diffraction peak. For the high-angle (400) peaks, a deconvolution routine was used first to separate the three overlapping peaks.

Not all TBCs need to be made from homogeneous 6 to 9 wt% YSZ. The importance of the degree of homogeneity and the allowable amount of monoclinic phase in the starting powder depend on the maximum temperature to be experienced by the TBC. Consider the zirconia-yttria phase diagram in Fig. 6 in the following argument. Assume that a coating made from inhomogeneous 8% YSZ powder has some fraction of grains of very low yttria content. These grains will behave as if they were a separate entity and experience the phase transitions characteristic of nearly pure zirconia. At room temperature these grains should exist in the monoclinic structure. The other grains may be partially stabilized with yttria and exist mainly as the nontransformable tetragonal phase, and possibly some cubic-phase material. These higher-yttria-content nontransformable tetragonal grains exist as a nonequilibrium phase because of the rapid quench from the liquid state upon deposition at the substrate. They have high thermal fatigue resistance because they will not transform to the monoclinic phase and experience the large volume change. On the other hand, the nearly pure zirconia grains having the monoclinic structure may be safe from transformation stresses as long as they remain below the temperature of the M + T two-phase field, which can be as high as about 1100 °C (2000 °F).

Therefore, coated components that have a maximum exposure of only 760 °C (1400 °F) should be stable against deleterious phase transformation, even though they may have a zirconia coating composed of both stabilized and unstabilized grains. As the operating temperature of the component increases, the need for a homogeneous coating increases. Applications at temperatures above about 1100 °C (2000 °F) should require fully homogeneous coatings. For applications at 760 to 1100 °C, thermal cycle testing is needed to determine whether the powder and coating process selected are adequate. If monoclinic-phase material exists in the coating and is tested with flame impingement on the oxide face to temperatures that cycle through the transformation temperature, the surface layer will begin to flake away small particles. Because of the insulating effect of zirconia, the lower layers of the coating would be at a lower temperature and thus remain intact. If the same nonhomogeneously stabilized coating is exposed to a uniform temperature test, the whole zirconia layer could develop cracks, leading to early spallation if the whole layer is cycled through the phase-transformation temperature.

Although the use of fully homogeneously stabilized coatings may seem warranted for all applications, regardless of operating temperature, economic considerations argue against this. Fully homogeneous powders, which are more costly, must either be fused and crushed or sintered from pure zirconia and yttria components at high temperatures. If the exposure temperature of the TBC does not demand monoclinic-phase-free material, a less costly powder will still meet the thermal barrier performance required. The key is to know the relation between operating temperature limits and the phase content of the coating.

**Chemical Effects on Phase Stability.** As discussed above, powders that are inhomogeneous in regard to yttria concentration could lead to coatings with phase-transformation-induced cracking if used at high temperatures. It has also been found that fully homogeneous yttria-stabilized coatings used in high-temperature environments containing vanadium and/or sulfur can experience surface degradation. In this case, the impurities can form yttrium vanadate and yttrium sulfide by leaching yttrium from the coating (Ref 5, 9). This leads to a surface layer that is progressively depleted in yttria content, and eventually to a material that is in the fully monoclinic structure when cooled and has a large volume change and disruptive stresses when thermally cycled. This surface transformation can also be detected by x-ray diffraction, which will give the evidence needed to understand the failure mechanism.

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## Thermal Property Measurements

**Coefficient of Thermal Expansion.** The coefficient of thermal expansion (CTE) of the TBC in the in-plane direction should match as closely as possible the CTE of the bond coat. The expansion in the through-thickness direction is not of great interest, which is fortunate because this measurement is relatively difficult to perform. The in-plane expansion on a freestanding sample can be determined using a conventional pushrod dilatometer (ASTM C 228). In the case of a differential pushrod dilatometer, the differential expansion between the sample and a known standard reference material is measured as a function of temperature. The expansion of the sample is computed from this differential expansion and the expansion of the standard. The measurements are made under computer control, and linear expansion is calculated at preselected temperature intervals. The expansion can be monitored with the visual display during the measurement process. Seven standard reference materials for expansion are available from the National Institute of Standards (NIST, formerly the National Bureau of Standards), including materials with low, moderate, and large expansion. For purposes of calibration and checkout, one NIST standard is measured against another NIST standard.

**Specific Heat.** Measurements of the specific heat of TBCs can be easily performed using differential scanning calorimetry (ASTM E 1269). Reference and sample holders are equipped with heaters and temperature sensors that detect temperature fluctuations of the sample holder with respect to the reference holder as both are heated. A high-gain, closed-loop electronic system provides differential electrical power rate that can be read out directly in millicalories per second and that is equivalent to the rate of energy absorption or evolution of the sample. The specific heat is calculated by comparing this rate with the rate measured during the heating of a known mass of sapphire. The experiments are performed under computer control, and specific heat is automatically calculated at equal temperature intervals.

The procedure is to measure the differential power required to heat the empty pan at the same rate as the reference empty pan (blank amplitude). The data are collected and stored in the computer. The sapphire standard (whose mass and specific heat are known) is then placed in the empty pan, and the differential power required to heat this pan at the same rate as the reference empty pan is measured to obtain the standard amplitude. Next, the sample is substituted for the sapphire standard and the sample amplitude is determined. The computer then calculates the specific heat. The results for $ZrO_2$-8wt%$Y_2O_3$ coatings are very close to those predicted from the rule of mixtures, as calculated using values for the pure oxides (Ref 10).

**Thermal Transport Properties.** Thermal conductivity can be calculated from:

$$\lambda = q/A\,(dT/dx) \qquad \textbf{(Eq 4)}$$

where $\lambda$ is the thermal conductivity, $q$ is the heat flux, $A$ is the cross-sectional area conducting the flux $q$, and $dT/dx$ is the temperature gradient. Alternatively, conductivity can be determined from:

$$\lambda = \alpha C_p \rho \qquad \textbf{(Eq 5)}$$

where $\alpha$ is the thermal diffusivity, $C_p$ is the specific heat, and $\rho$ is the density. It should be noted that thermal conductivity cannot be measured directly. Equation 4 involves steady-state determinations, and Eq 5 involves transient determinations. Relatively large errors have been documented for steady-state determinations, even under good conditions (Ref 11). Because specific heat and density (expansion) measurements are straightforward, and because diffusivity measurements involve only length and time, transient techniques are more attractive, especially for the small samples associated with coatings in the through-thickness direction. In addition, the diffusivity technique is much faster and costs less.

A particularly useful diffusivity technique (Ref 12) is the laser flash method, ASTM E 1461-92. It is shown schematically in Fig. 8. The sample, normally the size of a nickel, is held at the desired measurement (e.g., room temperature, 100 °C, 200 °C, etc.). The front surface receives a pulse of energy from the laser, which soon raises the back face temperature a degree or two. The rear face temperature response is normalized and compared with the theoretical model based on Carslaw and Jaeger's solution to one-dimensional heat flow (Ref 13). Using that model, diffusivity values can be obtained at any percent rise of the curve. For example, at 50% rise, the diffusivity is calculated from:

$$\alpha = 0.1338\, l^2/t_{0.5} \qquad \textbf{(Eq 6)}$$

where $l$ is the sample thickness and $t_{0.5}$ is the elapsed time needed for the rear-face temperature to reach one-half of its maximum rise (Fig. 8).

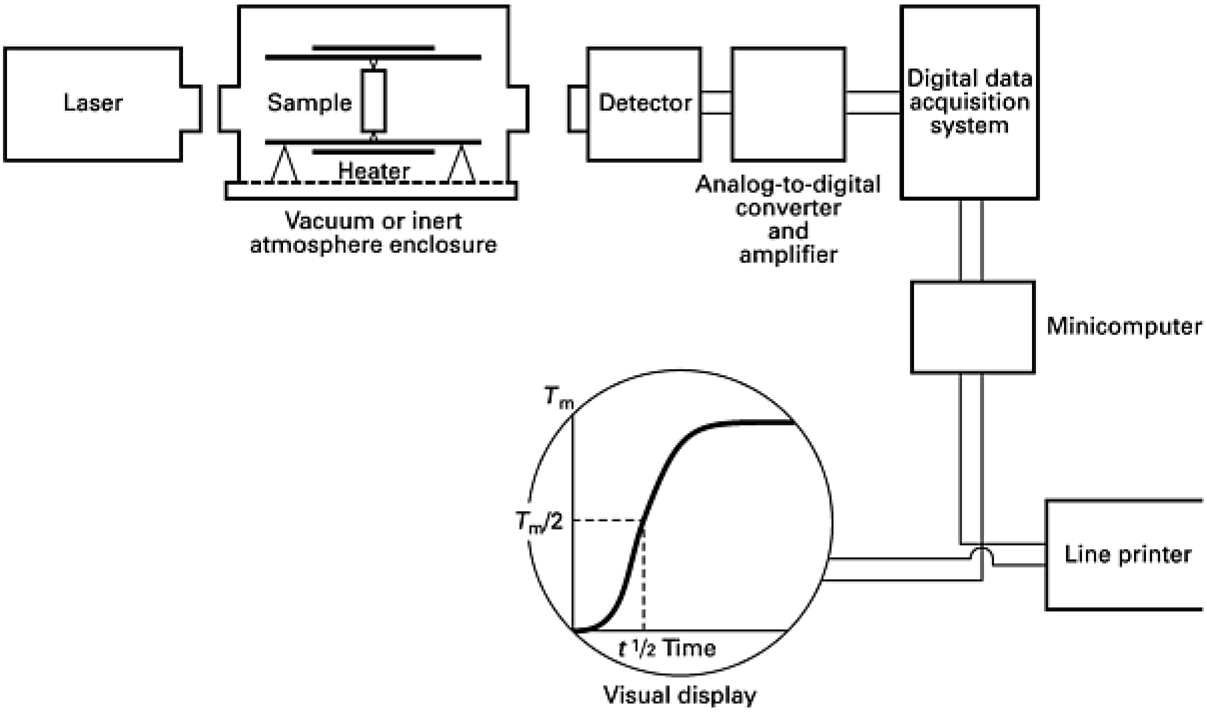

**Fig. 8 Schematic diagram of laser-flash method for thermal diffusivity measurement. $T_m$, maximum temperature measured by the liquid nitrogen-cooled infrared detector**

It is possible to measure freestanding coatings, but it is also possible to measure the coatings on the substrate. In the latter case, the effects of any interfacial resistance are included in the calculated diffusivity/conductivity of the coating. Because TBCs may be translucent, part of the laser beam could penetrate significantly into the sample, violating an assumed boundary condition. Thus, for freestanding coatings, it is necessary to put a very thin opaque layer on at least one surface. In the case of TBCs on substrates, this is not a problem because the substrate side faces the laser.

Thermal conductivity values in the literature have rarely been corrected for thermal expansion, because the expansion correction has been within the accuracies of steady-state determinations of conductivity. This general practice is usually followed when computing thermal conductivity from transient measurements: density and diffusivity values are not corrected for expansion. If one does correct density for expansion by dividing by $(L_0 + \Delta L)^3$, one must also correct the diffusivity values by multiplying by $(L_0 + \Delta L)^2$, where $L_0$ is the length at the reference (room) temperature and $\Delta L$ is the length change at any temperature from that at the reference temperature. Thus the total correction is a factor of $(L_0 + \Delta L)^{-1}$. For TBCs at operating temperature, this correction is less than 2%.

Thermal diffusivity and conductivity values may increase after thermal cycling (Ref 10, 14) or upon heat treatment to progressively higher temperatures (Fig. 9). These effects may be due to closing of horizontal microcracks. In addition, the conductivity/diffusivity of the TBCs can be thickness dependent due to the somewhat cone-shape structure. It should also be noted that the in-plane conductivity values of TBCs are different from the through-thickness values because of the lamellar nature of thermally sprayed coatings and the columnar structure of zirconia deposited by physical vapor deposition. In general, the in-plane values are relatively unimportant for TBC applications.

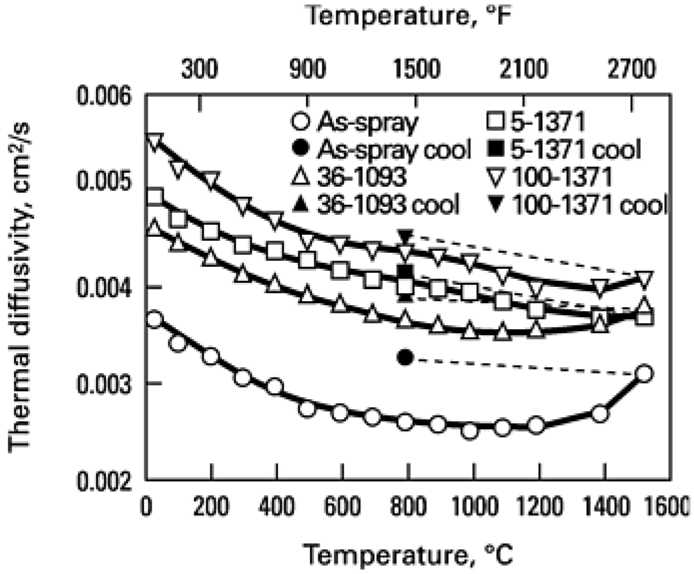

**Fig. 9 Thermal diffusivity of plasma-sprayed ceramic coatings subjected to selected heat treatments**

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# Microstructural Characterization of Coatings and Thin Films

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## Introduction

BOTH METALLURGY AND MATERIALS SCIENCE are concerned with the relationship between structure and the macroscopic properties of materials. Structure can be important at different levels. For example, on the atomic scale, structure dictates the strength of grain boundaries. On a larger scale, extending over many grain diameters, structure influences more complex phenomena, such as contact at surfaces or optical properties. For coatings, structure-property relationships are further complicated by the fact that coating microstructures are generally highly anisotropic and contain concentrations of defects that can vary from grain to grain for some coatings (e.g., plasma-sprayed coatings). Clearly, the ability to characterize coating microstructures is important in understanding the properties and behavior of coatings in many applications.

This article describes the structure of coatings produced by plasma spraying, vapor deposition, and electrodeposition processes. It also introduces the main techniques that can be used for microstructure assessment. Although examples are given for a limited range of deposition technologies, they are widely applicable to coatings produced by other processes.

## Microstructure of Coatings

The microstructure of a coating is critically dependent on the deposition technology used to produce it (Ref 1). In some technologies, such as physical vapor deposition (PVD), the structure of the coating can be controlled to a certain extent by the choice of deposition parameters. In other technologies, such as weld surfacing or diffusion treatment, it is the thermal history of the component surface that dictates microstructure. Good process control is needed to ensure the production of a layer with the correct microstructure and the required properties for the application. A number of microstructural factors are important in dictating the properties of the coating:

- Phase composition
- Size and shape of grains
- Size and distribution of porosity
- Defects (vacancies, dislocations, etc.)
- Presence of cracks and pin holes
- Anisotropy
- Stress and strain

In most cases, the first three factors are the most important. However, the others can be critically important for certain applications. Stresses and strains occur when the microstructural units of the coating (e.g., columnar grains in PVD coatings or splats in plasma-sprayed materials) are moved with respect to their equilibrium positions by externally applied forces, which can be due to mechanical or thermal loading or the mismatch of properties with the substrate. Stresses can lead to bending of the coating, distortion of the microstructural units, and generation of defects within microstructural units where they contact (e.g., dislocation loops are created by compressive stresses forcing columnar grains together in PVD films). Strains usually manifest themselves as changes to the lattice parameter of the material. There are two types: macrostrains (changes that affect the whole coating, produced by thermal expansion mismatch) and microstrains (highly localized distortions of the structure around defects). Described below is the evolution of microstructure in several important deposition technologies.

**In the thermal spraying process,** the powder form of a coating material is injected into a flame, where it melts and is ejected against the component surface to build up the coating. Thermal spraying is actually a generic term for a number of processes that all produce coatings with similar microstructures, ranging from flame spraying and high-velocity combustion processes to plasma spraying. The structure and properties of the coatings depend on the stability of the particles within the flame and the choice of process parameters. Ideally, the powder particles are completely melted, but not vaporized, in transit between the injection point and the substrate surface. The molten particles then strike the substrate surface, where they flatten and freeze. Succeeding particles acquire the same lenticular shape over material that has already been deposited, so that the coatings develop an anisotropic lamellar structure parallel to the interface (Fig. 1). The extent of flattening depends on factors such as degree of melting, viscosity of the liquid, and wetting of the surface. Coatings may contain voids that are due to outgassing, shrinkage, or topographical effects (e.g., shadowing). Metal coatings processed in air will also probably contain oxide inclusions.

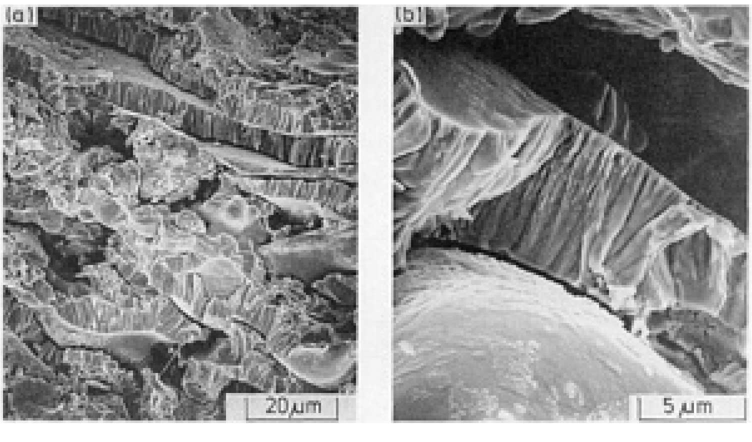

**Fig. 1 Scanning electron micrographs of fracture cross sections of air plasma-sprayed tungsten coatings. (a)**

**Lamellar structure. (b) Presence of columnar structure within the splats**

Cooling rates can be very high (as much as $10^6$ K/s) for plasma-sprayed particles. This produces a very fine microstructure within the lenticular splats (Ref 2), as shown in Fig. 1(b). The rapid solidification can form amorphous deposits from some ferrous alloys (Ref 3), whereas metastable or nonstoichiometric phases can be observed in some ceramics. For instance, alumina coatings contain an increasing proportion of the λ phase as the energy of the spraying process increases or the particle size decreases (Ref 4).

**Vapor Deposition Processes.** The structure of coatings deposited from the vapor phase is controlled as much by the nucleation of the coatings as by the way in which they subsequently grow. One feature common to vapor-deposited coatings is that solid material is distributed in an array of fairly closely packed columns that run perpendicular to the substrate. It is this anisotropy in structure that controls many of the properties of the films.

A number of factors can influence the nucleation of vapor deposited coatings. The surface structure of the substrate is critically important, including grain size, defect density, texture, roughness, and surface composition, and it is often necessary to pretreat materials prior to coating to enhance nucleation. Surface contaminants introduced in the coating process can promote or inhibit nucleation, as can ion bombardment in PVD processes. In many cases a chemical or physical activation step is required to get the best surface structure for coating (e.g., a chemical etch is required to remove surface magnesium from aluminum alloys). This needs to be followed by careful control of the early stages of coating to ensure that reliable structures are produced.

***Structure Zone Models.*** An essential feature of the structure of these thin films is that they are formed from a flux of atoms that approaches the substrate from a limited range of directions. This generates the columnar microstructure, but can lead to problems, because there are many boundaries running perpendicular to the interface that can act as planes of weakness (e.g., as short-circuit diffusion paths).

Movchan and Demchishin (Ref 5) were the first to classify thin-film microstructures. They identified three distinct structure zones as a function of the homologous temperature $T/T_m$, where $T$ represents the substrate surface temperature and $T_m$ represents the coating melting point. A low-temperature zone 1 structure ($T/T_m$ < 0.25-0.3) corresponds to low adatom mobility and consists of tapered columns with domed tops. In a zone 2 structure ($T/T_m$ = 0.3-0.5), surface diffusion becomes increasingly important, and the structure consists of straight columns with a smooth surface topography. With increasing temperature ($T/T_m$ > 0.5), bulk diffusion becomes a dominant process. The zone 3 microstructure therefore consists of equiaxed grains, as are observed in recrystallized metals. For sputtered coatings, Thornton (Ref 6) later suggested that the presence of a sputtering gas could modify the model, and a further region was identified between zone 1 and zone 2. This region consists of poorly defined fibrous grains and is named zone T.

At the temperatures used in the chemical vapor deposition (CVD) process, surface diffusion of adatoms is actuated and structures of the zone 2 type are produced, in the case of most coating materials. However, the structure of the coating is often controlled by the nucleation density. In the early stages of coating, a very high density of small nuclei is established, which becomes constant after a time, that is, no new nuclei are formed, but newly deposited adatoms move to the existing nuclei and are trapped there. For longer deposition times, the nuclei grow until they eventually coalesce to form the film. In the case of some CVD coatings (e.g., diamond on silicon), the nuclei grow in both height and width, and the coalescence process may result in pores at the interface. Because porosity at the interface decreases adhesion, it is necessary to maximize the density of nuclei formed in order to obtain optimal adhesion. Porosity also remains at the triple points created as the nuclei grow together. These nuclei provide the seeds for the columnar units that compose the coating. Maximizing the nucleation density also reduces the size and extent of this through-thickness porosity.

Because the typical deposition temperatures in PVD processes is very low, many coatings are deposited with a zone 1 microstructure. Instead of increasing the deposition temperature, the occurrence of this microstructure can be overcome by bombarding the growing films with particles having sufficient energy so that the resulting momentum transfer will cause the coating atoms to fill the voided boundaries. Messier (Ref 7) has suggested a modification to the structure zone models that accounts for the evolution of morphology with increasing film thickness, as well as the effect of both thermal and bombardment-induced mobility. The model draws attention to the fact that ion bombardment promotes a dense structure of the zone T type, but it also indicates that the atomic rearrangement can have either thermal or ion-bombardment-induced origins.

Increasing the energy (or the flux) of ion bombardment, by applying a substrate bias, for example, has a significant effect on the structure of PVD films (Ref 8, 9). The coating on an unbiased substrate shows an open columnar structure (zone 1, Fig. 2a), whereas the film on a biased substrate appears more dense, because the individual columns are less well defined (zone T, Fig. 2b). The two coatings will have different properties that are due primarily to changes in the packing density of the columns.

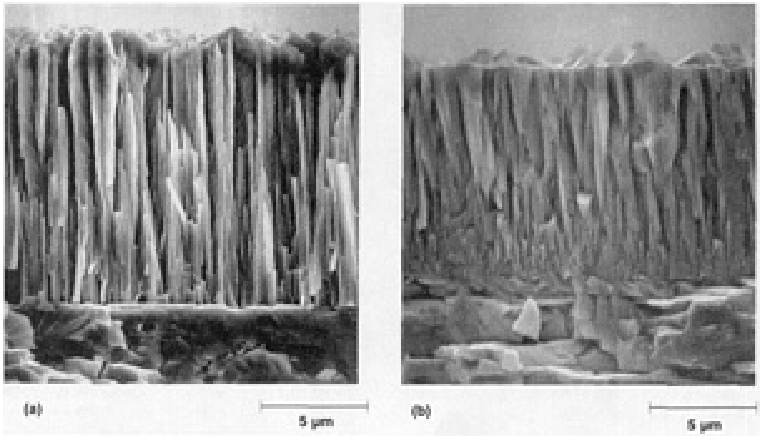

**Fig. 2 Scanning electron micrographs of fracture cross sections of sputtered tungsten films on a tungsten substrate. (a) Unbiased (zone 1 structure). (b) -100V bias (zone T structure)**

The deposition of predominantly covalent coatings, such as silicon carbide or diamond-like carbon, causes a further complication. Because of bonding directionality, it becomes very difficult to incorporate adatoms into their correct crystallographic location at low deposition temperatures. For this reason, amorphous coatings are produced with smooth, featureless, fracture cross sections. At a critical deposition temperature, some crystallization occurs, and structures of the zone T or zone 2 type can be produced. However, identifiable zone 1 structures are not usually observed.

Zone 1, zone T, and zone 2 microstructures are all associated with the development of texture in PVD films. For titanium nitride coatings, for example, a {111} orientation is commonly reported, although both {200} and {220} orientations have also been observed (Ref 10, 11, 12). The development of texture occurs in three stages:

- Nucleation, where crystallites are nucleated on the substrate from the vapor phase, the distribution and orientation of which depend on the substrate surface structure and deposition parameters
- Competitive growth, where certain favorably oriented nuclei will grow into the vapor phase faster than others, but which may not constitute the majority of the nuclei population
- Steady growth, which occurs once a preferred orientation has achieved dominance

The detailed deposition conditions in any PVD process can change any or all of the above stages and will also affect the morphology of the coating. At the interface region, a very fine grain size is established initially, but with increasing thickness, the columnar structure becomes established and the grain size increases. During the competitive growth phase, intercolumnar voids will open up because of shadowing processes. These voids will be increasingly closed up once the steady-state growth conditions are achieved. Clearly, if porous coatings are to be avoided, it is advisable to know in which thickness range these changes are taking place, as well as how to minimize their effects.

**Electrodeposition** was one of the earliest plating processes developed for depositing one metal onto another. The method is now widely used for both decorative and engineering purposes. The process involves the reduction of metallic ions at the surface of the substrate, which acts as the cathode of an electrolytic cell. The electrodeposit structure is controlled by the composition of the electrolyte, by the plating conditions, and, in particular, by the presence of growth-inhibiting substances and by the substrate itself (Ref 13). In solution, the metal ions (surrounded by their solvation sheath) migrate toward the deposit, where they lose their sheath and accept electrons to become atoms. The atoms are adsorbed onto the surface and migrate until they encounter a site where they can be incorporated into the existing structure. Impurities or bath additions (inhibitors) may block such sites and can thereby control the structure of the deposit. Under growth-inhibiting conditions (i.e., when the current density is high and the bath temperature is low, so that atoms cannot readily diffuse), the deposit is finely grained and there is essentially continuous nucleation. Under other conditions, extended three-dimensional crystallite networks can grow.

The growth rate perpendicular to the surface is not the same for all grains, because the adsorption of inhibiting substances is anisotropic. As the deposit thickness increases, the slower-growing grains can become covered, and a texture will develop in the film. Slight misorientations between the grains lead to the need for misfit dislocations at boundaries. This is the reason for the high dislocation densities associated with coatings deposited under inhibited conditions. The microstructure of hard electrodeposits used for tribological applications (such as hard chromium) is equiaxed, and extremely finely grained, and it contains some oxide inclusions and microcracks, which give the coating some porosity (Fig. 3). Tensile residual stresses can be produced in the coating during plating and can lead to a network of larger cracks on the material. Similar structures are observed for autocatalytic coatings, such as electroless nickel, where phosphorus-containing reducing agents are present in the plating solution and get incorporated in the coating. Both electrolytic and autocatalytic coatings can be modified to incorporate fine particles (typically, 0.5-5 μm, or 20-200 μin. in size) into the growing film. They can be hard particles, such as silicon carbide, as well as solid lubricants, such as polytetrafluoroethylene. A nonuniform distribution of codeposited substances can lead to crevices or a banded structure (Ref 13).

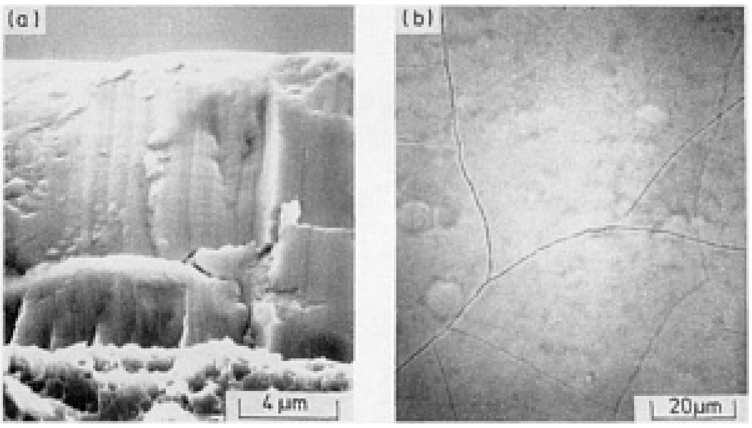

**Fig. 3 Scanning electron micrographs of an electrodeposited chromium film. (a) Fracture cross section. (b) Plan view showing the presence of cracks within the coating**

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## Microstructure / Property Relationships

In the preceding section, it was shown that although the same coating materials can be deposited by a number of different processes, the tructure of the coatings produced will be very different. Whereas a very fine equiaxed grain structure is produced by electrodeposition, a columnar structure is produced by vapor-deposition processes (grain boundaries perpendicular to the interface), and a splat structure is produced by plasma spraying (splat boundaries parallel to the interface). Thus, it should be intuitive that the coatings will not have the same properties, and this is what is observed in practice. Considerable attention should be paid to the microstructure of the coating if performance is to be understood. There are numerous techniques that can provide relevant information.

Structure/property relationships have been determined empirically for many deposition processes for a restricted range of coating materials (e.g., Ref 13, 14). However, theoretical modeling of coating properties based on microstructure is not well advanced. A characterization of the structures and properties of commercially available coatings produced by different deposition technologies is often necessary to aid in coating selection and specification. Because some control of coating structure is possible for most deposition technologies, optimizing the microstructure of the coating for a given application is also a possibility. Structural characterization is a necessary step in achieving this rather ambitious goal.

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## Experimental Techniques for Microstructural Characterization

It is not possible to determine all the structural features of a material using any one analysis technique. Therefore, many techniques that can be used to provide information about specific microstructural features have been developed. It is important to know what factors are important in any application before undertaking a program of structural analysis.

For coatings, many of the techniques are applicable, but somewhat more care must be taken in preparing representative samples, because the volume of material to be investigated is relatively small. Table 1 identifies the most important microstructural features and defines what techniques can be used to assess them. However, other, more unusual techniques can also provide the same information.

**Table 1 Techniques for microstructural analysis**

| Coating property | Technique |
|---|---|
| Phase composition | X-ray or electron diffraction |
| Phase distribution | Metallographic sections, SEM, TEM, optical microscopy |
| Grain size | X-ray diffraction, SEM, TEM (plus image analysis) |
| Grain shape | SEM, TEM (plus image analysis) |
| Preferred orientation | X-ray diffraction, TEM |
| Surface morphology | SEM |

|  |  |
|---|---|
| Porosity | TEM, mercury intrusion porosimetry, metallographic section (plus image analysis) |

Note: SEM, scanning electron microscopy; TEM, transmission electron microscopy

Brief descriptions of some of the most frequently used techniques are described below, as are some of the factors that need to be considered when applying them to coated systems.

**Metallography.** Most standard metallographic preparation techniques can be applied to coatings, and polished cross sections are commonly used to determine coating thickness and uniformity. Samples are generally cut from a coated component using a low-deformation saw and are mounted in a resin medium prior to polishing. Components should be rigidly clamped and sectioned so that the abrasive wheel enters from the coating side. For most coating-substrate combinations, a hot mounting medium is preferred, but for temperature-sensitive or porous coatings, better results are obtained when a cold-setting resin is used. The section should then be ground back until a flat surface is produced. When dealing with coated samples, it is often observed that some chipping of the coating occurs next to the saw cut. It is therefore essential to grind the section well back to remove any damage prior to polishing. For thin, hard coatings, a large grit size should be avoided during grinding, because it can result in coating detachment (Ref 15). The preferred direction of grinding is from the substrate into the coating because this maintains the best edge sharpness.

After grinding, the section can be prepared using metallographic polishing techniques similar to those used for bulk materials. However, for porous plasma-sprayed coatings, better results can be achieved using more advanced metallographic techniques, as described in Ref 16. The twofold aim of the polishing process is to remove the damage introduced during grinding and to produce the high surface finish needed for metallography. For thin coatings, it is particularly important to use an edge-retaining mount, because edge rounding of the sample can occur during polishing in cases of differential polishing of the coating and the substrate or of sample tilting. For very thin or fragile coatings, the sample can be encapsulated with a thick protective layer prior to sectioning and mounting in order to prevent damage of the coating during preparation. Porous coatings, such as air plasma-sprayed coatings, are best mounted by vacuum infiltration, because the resin can then penetrate the porosity in the coating and will prevent collapse of the coating around the porosity during polishing (Ref 16).

For measuring the thickness and uniformity of the coating, a simple polished cross section may be sufficient. However, particular care must be taken to ensure that the coating has not been damaged during preparation. The importance of grinding back from the cut surface cannot be emphasized enough. Similarly, the porosity revealed in the coating may be an artifact of the preparation process, because grain pullout often occurs in the final stages of polishing materials that have weak boundaries, such as air plasma-sprayed metals. Although there is no simple technique for avoiding these problems, the measurement of thickness or porosity by other techniques can give some indication of whether the measurements obtained from metallography are consistent. A material-specific preparation technique can then be developed for the coating material and process combination of interest.

When dealing with very thin coatings, more detail can be revealed by using a taper section. A taper angle of 5.7°, for example, will give a 10× magnification in the plane of the section. In this case, the sample is mounted in the resin with one edge supported by a spacer, the height of which is chosen to give the required tilt angle, and then prepared in the same way as a cross section (Ref 15). Figure 4 shows a taper section of a PVD titanium nitride coating on stainless steel with a 400 nm (16 μin.) titanium interlayer that is not visible in the polished cross section, but which can be easily resolved in the taper section. Because of nonuniform polishing, the initially planar interface has become irregular in the taper section. This is almost impossible to avoid in practice.

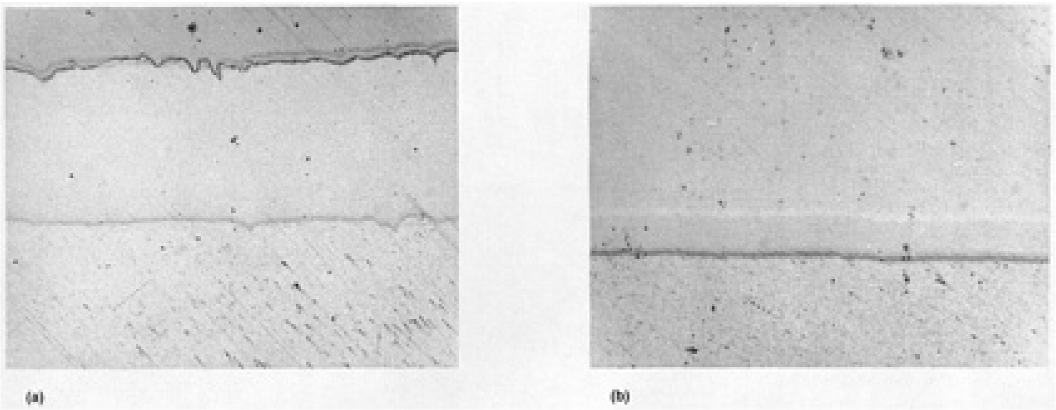


**Fig. 4 Micrographs of a PVD titanium nitride coating on stainless steel. (a) Cross section. (b) Taper section showing the presence of a 400 nm (16 μin.) titanium interlayer**

The grain structure of the substrate and coating and, sometimes, even the presence of the coating itself can be revealed by etching with an appropriate reagent, as is done for bulk materials. Because it is often difficult to choose an etch that will attack both coating and substrate, a multistage etching process may be needed. It is important to determine whether an etch used for the coating will badly attack the substrate, because that could lead to the observation that there is interfacial porosity, when this is really just an artifact of etch selection. Figure 5 shows the structure of a PVD Fe-Cr-Al-Y coating on stainless steel after 100 h of oxidation at 1000 °C (1830 °F). The structures of both coating and substrate have been revealed by electrolytic etching in $CrO_3/H_2O$. Image analysis can be used to determine grain size and shape, along with porosity, in a quantitative manner (Ref 16).

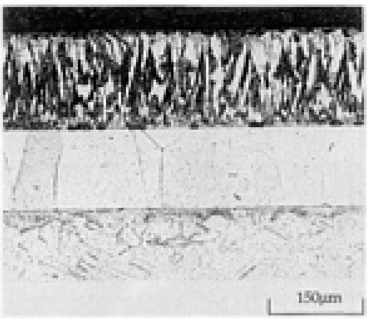


**Fig. 5 Polished cross section of a Fe-Cr-Al-Y coating on austenitic stainless steel after 100 h at 1000 °C (1830 °F), electrolytically etched in $CrO_3/H_2O$ to reveal grain structure of coating and substrate**

**X-ray Diffraction.** In most cases, diffraction analysis is used to identify the structure of a deposited film from a list of known possibilities, rather than to identify the structure of a completely unknown or new substance. The analysis is thus essentially limited to the comparison of an experimentally observed diffraction pattern with patterns of substances, the structures of which are already known. This is made considerably easier if the composition of the coating can be determined, because the number of possible structures is then limited. In a typical x-ray diffraction experiment, a monochromatic beam of x-rays, wavelength $\lambda$, hits the coated surface from which it is diffracted. The intensity of the diffracted beam is recorded as a function of the diffraction angle, $\theta$. The intensity of the beam will be nonzero only at those diffraction angles at which the Bragg condition is satisfied (Ref 17):

$$\lambda = 2d_{hkl}\sin\theta \qquad \textbf{(Eq 1)}$$

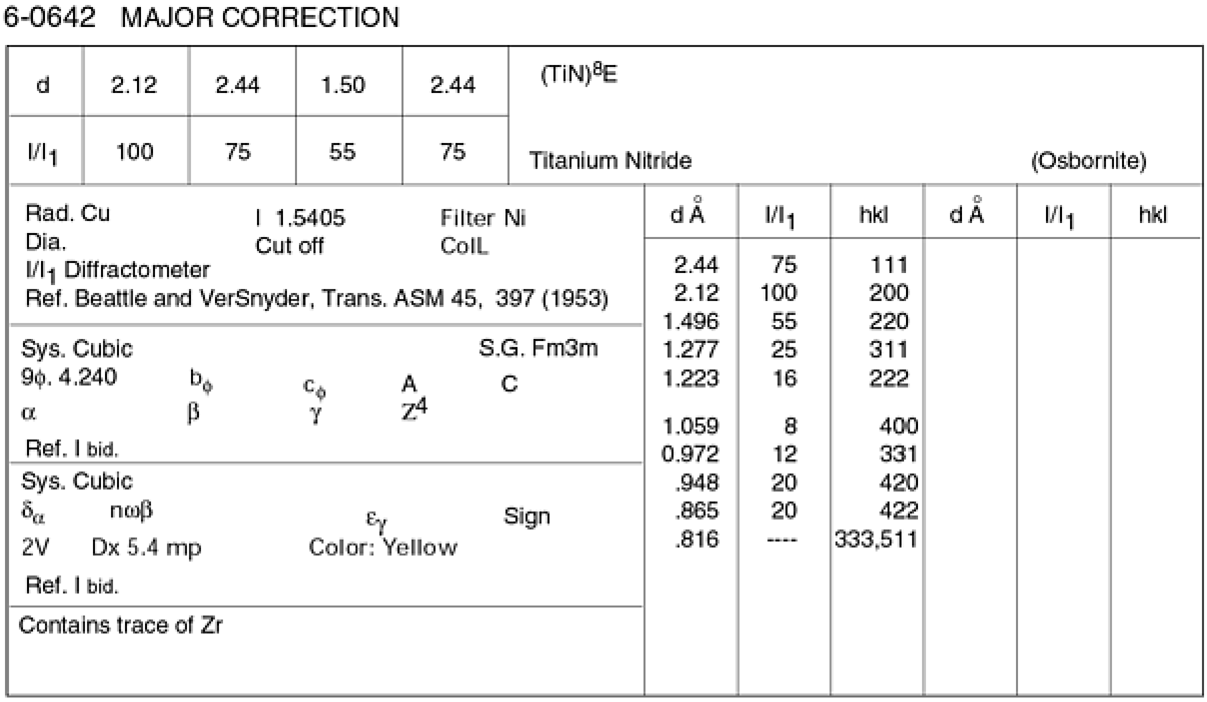
where $d_{hkl}$ is the spacing of the lattice planes with Miller indices *hkl*. All elements or compounds consist of atomic arrays with a unique combination of geometry and spacing. The smallest repeatable unit that completely defines the structure is called the unit cell, and the spacing of these unit cells is defined by one or more lattice parameters (depending on crystal structure). The position of the diffraction maxima gives information about the size and shape of the unit cell, whereas the width of the maxima can be used to evaluate the size, orientation, and strain in grains of polycrystalline materials.

The intensity of the diffracted beam depends on several factors:

- Structure of the material
- Volume of irradiated material
- Diffraction geometry
- Sample alignment

For a more detailed discussion of the x-ray diffraction technique, readers are referred to Ref 17.

Once an experimental diffraction pattern has been obtained, the position and intensities of the peaks can be easily measured. It is then possible to calculate the intensities and positions for all candidate structures and compare these to the measurements to determine the structure of the film. However, a much easier way is to rely on powder diffraction standards (Ref 18), which represent a collection of experimentally determined relative intensity values for a large number of substances. These are available in book, microfilm, or card form, and can also be retrieved from disks or data bases. A typical card, for example, contains information on the structure of the material as well as the relative density data (Fig. 6). Information is available for both stoichiometric and nonstoichiometric compounds.



6-0642 MAJOR CORRECTION

| d | 2.12 | 2.44 | 1.50 | 2.44 | $(TiN)^8E$ |
|---|---|---|---|---|---|
| $I/I_1$ | 100 | 75 | 55 | 75 | Titanium Nitride (Osbornite) |

Rad. Cu   I 1.5405   Filter Ni
Dia.   Cut off   CoIL
$I/I_1$ Diffractometer
Ref. Beattle and VerSnyder, Trans. ASM 45, 397 (1953)

Sys. Cubic   S.G. Fm3m
9ϕ. 4.240   $b_\phi$   $c_\phi$   A   C
α   β   γ   $Z^4$
Ref. I bid.

Sys. Cubic
$\delta_\alpha$   nωβ   $\varepsilon_\gamma$   Sign
2V   Dx 5.4 mp   Color: Yellow
Ref. I bid.

Contains trace of Zr

| d Å | $I/I_1$ | hkl | d Å | $I/I_1$ | hkl |
|---|---|---|---|---|---|
| 2.44 | 75 | 111 | | | |
| 2.12 | 100 | 200 | | | |
| 1.496 | 55 | 220 | | | |
| 1.277 | 25 | 311 | | | |
| 1.223 | 16 | 222 | | | |
| 1.059 | 8 | 400 | | | |
| 0.972 | 12 | 331 | | | |
| .948 | 20 | 420 | | | |
| .865 | 20 | 422 | | | |
| .816 | ---- | 333,511 | | | |

**Fig. 6 Powder diffraction standard card for stoichiometric titanium nitride**

The data on peak positions for titanium nitride (from Fig. 6) are represented as vertical lines in Fig. 7, which also shows an experimental diffraction pattern obtained for a titanium nitride film produced by sputter ion plating. It is clear that the observed peaks line up with the standard peak positions, but the measured pattern is slightly shifted to higher angles because of the presence of residual stress within the coating. The intensities, however, differ considerably from the values of the card shown in Fig. 6 because of the preferred orientation of the film. To fully assess the preferred orientation, it is necessary to compare the intensity of the measured line with that of the standard. A texture coefficient, *T**, can be defined as:

$$T^{*}(h'k'l') = \frac{I_{h'i'l'} / I^{0}_{h'k'l'}}{l/n \sum_{0}^{n} (I_{hkl} / I^{0}_{hkl}} \qquad \textbf{(Eq 2)}$$

In this equation, *h*' *k*' *l*' are the Miller indices of the plane of interest, *I* is the measured intensity, and $I^0$ is the intensity of the standard, which is randomly oriented. A value of unity corresponds to a random texture, and values greater than this show an increasing level of preferred orientation. For the data presented in Fig. 7, a {111} preferred orientation is observed, because $T^*_{\{111\}} = 4$.

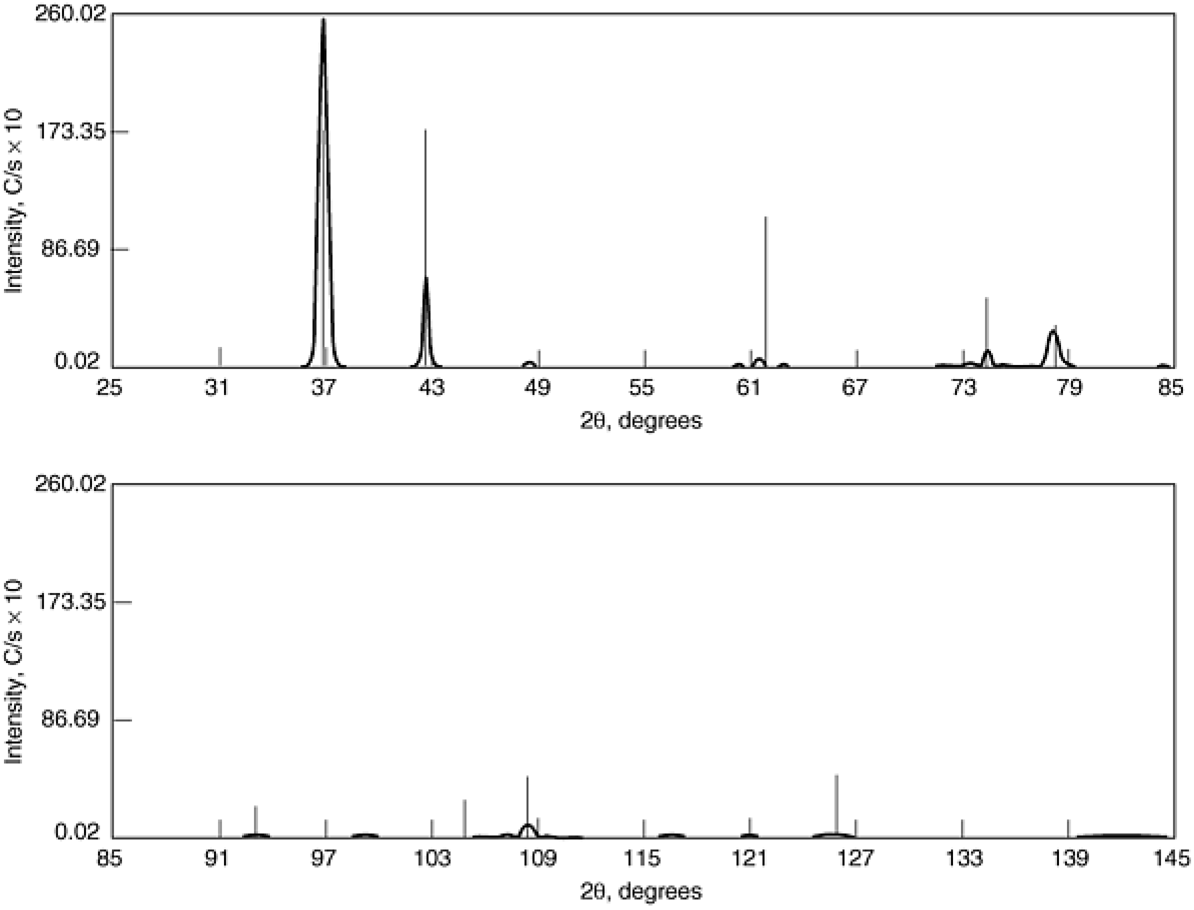


**Fig. 7 Measured x-ray diffraction pattern for sputter ion plated titanium nitride. Vertical lines represent data peak positions for titanium nitride from Fig. 6. Film shows a [111] preferred orientation. C/s, counts per second**

Once the phase composition of the coating has been identified, lattice parameter measurements can be undertaken. This is particularly important if measurements of residual stress are to be made or if there is a need to assess either the stoichiometry of a material or the composition of a solid solution. Because the accuracy of measurement increases as the Bragg angle increases, high angle reflections of sufficient intensity should be used for stress measurements. For the accurate measurement of peak position, it is necessary to fit a function to the peak profile (Ref 19). It is often assumed that a Gaussian profile provides a good description of peak shape, but, in many cases, a Pearson 7 function will provide a better fit. If the film is under stress, then measurements of the lattice parameter from a single reflection can be misleading, because of anisotropy constants. It is therefore important to use an extrapolation function, such as the Nelson-Riley or cosθ cotθ function, to improve reliability (Fig. 8). In this operation, the lattice parameter determined for a number of reflections is plotted against cosθcotθ, and a line through the points is extrapolated to θ= 0° to determine $a_0$. The deviations of some reflections from the line that are due to pseudo macrostresses can be revealed by this approach (Ref 19), which has the added advantage of minimizing alignment errors.

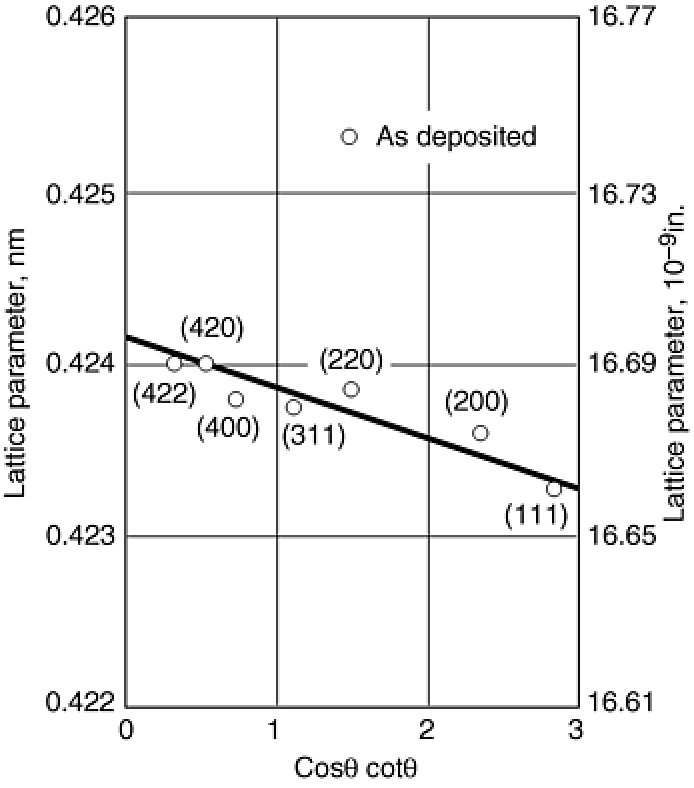


**Fig. 8 Variation of lattice parameter with cosθcotθ for sputtered titanium nitride in order to extrapolate a lattice parameter, $a_0$, corrected for measurement errors**

The width of a diffraction line is determined by the grain size and strain in a material, as well as by instrumental factors. A typical diffractometer will have an angular resolution of approximately 0.01°, which means that line broadening can be observed if the grain size *D* is lower than approximately 1 μm (40 μin.). This is easily achievable by various coating techniques, and x-ray diffraction can be used to give a measure of grain size for these technologies, averaged over the penetration depth of the x-ray (Ref 20).

If βis the full width at half-maximum intensity of the diffraction peak (for the case of a Cauchy peak shape, $\alpha_2$ stripped and corrected for instrumental broadening), then (Ref 19):

$$\frac{b \cos q}{l} = \frac{1}{D} + \frac{4e \sin q}{l} \qquad \textbf{(Eq 3)}$$

where ε is the average strain in the material. Thus, by plotting βcosθ/λ against sinθ/λ, which is the so-called Hall-Williamson plot (Ref 21), it is possible to determine both *D* and ε. Figure 9 compares the Hall-Williamson plots for titanium nitride coatings produced by several deposition technologies. The broadening is dominated by strain, because the intercept is close to zero, implying a grain size greater than 1 μm (40 μin.).

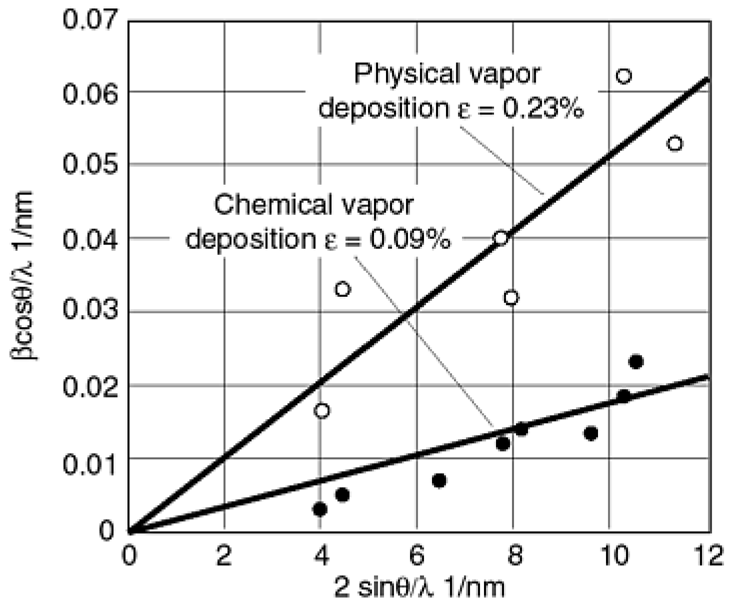


**Fig. 9 Hall-Williamson plots for physical and chemical vapor deposited titanium nitride, showing increased strain in the physical vapor deposited films**

**Electron Microscopies.** Perhaps the most useful techniques for characterizing thin films are scanning electron microscopy and transmission electron microscopy, because they can be used to investigate morphology, crystal structure, grain structure, and porosity. Both techniques depend on good sample preparation. Samples are relatively easy to produce for the former technique, but they are time-consuming and often difficult to prepare for the latter technique.

***Scanning Electron Microscope (SEM).*** Numerous signals are available for SEM imaging (Ref 22). When coupled with energy-dispersive x-ray spectroscopy (EDS), the SEM can be used to obtain a wide range of information about surface topography, composition, crystallography, and electronic properties (Table 2). For example, the SEM can be used to assess the grain size, packing density, and porosity of a coating if a fracture cross section is imaged. The chamber of many SEMs is large enough that many components can be imaged nondestructively, and the surface topography induced by surface treatment, together with damage to the coating (after deposition or after service) can be determined.

**Table 2 Scanning electron microscope imaging modes**

| **Mode** | **Detected emission** | **Best resolution** | **Information available** |
|---|---|---|---|
| Emission | Secondary electrons | 5-15 nm (0.2-0.6 μin.) | Topographic |
| Reflection | Primary electrons (back scattered) | 50-250 nm (2-10 μin.) | Topographic, atomic number |
| Leakage | Specimen current | >1 μm (>40 μin.) | Topographic, defects in some materials |
| X-ray | X-ray fluorescence | >1 μm (>40 μin.) | Chemical analysis (*Z* >5) |
| Cathodoluminescence | Luminescence | >1 μm (>40 μin.) | For some materials, quantitative chemical analysis or defect imaging |

|  |  |  |  |
|---|---|---|---|
| Crystallographic | Electron channeling | 0.05° from 1 μm (40 μin.) | Lattice parameter selected area and defect density |

In a typical SEM, an electron beam from a tip or filament is accelerated by the anode (typically, by 5 to 30 kV) and focused by two magnetic lenses to a fine spot on the sample. At the same time, the beam is scanned in the $x$ and $y$ direction. The electrons that are emitted from the sample are then either collected by a back-scattered electron detector, or, more generally, by a detector for secondary electrons. After amplification, the signal is fed to a cathode-ray tube, which is deflected in the same manner as the microscope electron beam. The magnification of the image is fixed by the $x$-$y$ deflection coils.

The primary electron beam generates a tear-drop-shape interaction volume with the specimen. Elastically reflected electrons emerge from the surface with energies close to those of the primary beam. The proportion of back-scattered electrons depends on the material. As the atomic number of the element increases, the back-scattering coefficient increases and such atomic number contrast can be used to distinguish between phases in coatings and substrates. However, back-scattered electron emission is highly directional, and strong topographic contrast is visible for rough surfaces, depending on the position of the detector.

Secondary electrons leave from the near-surface region of the sample when energies are less than approximately 50 eV and show no such directional effect, because they are collected by a positively biased detector from all points on the sample. Their emission intensity is not strongly materials dependent. The secondary electron image clearly shows topographic features, such as cracks in electroplated coatings (Fig. 3). However, it should be realized that these images should not be interpreted like reflected light micrographs, because shadows are not generally caused by topography effects.

The primary electron beam can excite core electrons in the sample, which relax by the emission of an x-ray, as is characteristic of the excited atom. Such x-rays typically escape from 0.5 μm or greater depths. X-ray analysis can be achieved by energy-dispersive or wavelength-dispersive spectroscopies (EDS or WDS, respectively). The EDS system generally uses a lithium-doped silicon detector in conjunction with a beryllium window for analysis of elements with atomic number, $Z$, greater than 9 (i.e., neon and heavier atoms), although the range can be reduced to $Z = 5$ (boron) with a windowless detector. The WDS method uses a range of crystals with different lattice parameters that can be rotated to focus x-rays from elements where $Z > 6$ into a detector. The EDS system is faster than WDS but has poorer energy resolution. Both EDS and WDS can be quantitative methods of evaluating elemental composition if care is taken in correcting for instrumental, chemical, and physical factors. This is a standard feature in most commercial analysis systems.

Fracture sections provide a very good means for assessing the structure of thin PVD coatings. Figure 2 shows fracture sections through PVD tungsten coatings deposited under unbiased conditions (zone 1), with an applied bias voltage of -150 V (zone T). The columnar structure is clearly visible for both coatings, but the columnar packing density increases with applied substrate bias (i.e., energy of ion bombardment). Because each column consists of an array of grains, a true measure of grain size is not generally possible using the SEM, but an indication of relative grain size may be possible from the column dimensions. The coatings are deposited onto a ferritic steel substrate that was cut through from the back side with a saw until it reached approximately 1 mm (0.04 in.) below the coating. The sample was then immersed in liquid nitrogen to cool below the substrate ductile-brittle transition temperature. After 10 min, the sample was removed and half placed in a vise. Then, the free end was struck with a hammer to fracture the sample in two. The coated side was struck so that the section was not put into compression during fracture, in order to avoid excessive coating damage. The cracks started in the saw cut and ran through the coating without damaging it. Similar results can be achieved for coatings on brittle substrates, such as silicon wafers, by using a diamond scribe to initiate fracture on the back of the substrate.

Insulating substrates or coatings will become charged in the electron beam, which quickly reduces image quality and occasionally damages the material. Charging can be avoided by depositing a thin carbon or gold film on the specimen surface. However, this will reduce the accuracy of any subsequent microanalysis and should only be used if necessary. Alternatively, a low accelerating voltage can be used for the primary beam, because when voltages are less than 3 kV, the sum of the secondary and back-scattered electrons generated can equal the number of primary electrons, and no charging occurs. Such low-voltage SEMs have the added advantage of better resolution, but their poorer signal-to-noise ratio means that some image processing may be necessary to obtain the best results.

Relatively poor resolution can also be encountered with magnetic coatings or substrates. For high-resolution work, it is recommended that a nonmagnetic substrate, such as silicon or stainless steel, be used wherever possible.

***Transmission electron microscope (TEM)*** studies require very thin specimens (5-500 nm, or 0.2-20 μin.), depending on the material. These specimens of foil must be prepared from the bulk of the coating or substrate. With such foils, it is possible to visualize structures on the nanometer level, and when specialized techniques are used, it is even possible to see the presence of single-atom columns and to locate dislocations in the crystal (Ref 23). Grain boundaries and interfaces can also be studied using this technique. When the crystallites range in size from micrometers to nanometers, the TEM can be used for electron diffraction studies to identify phase composition, as well (Ref 24).

The preparation of TEM samples is a skilled operation, and considerable effect is often required to develop the technique for a specific coating-substrate system. Plan-view TEM samples are by far the easiest to produce and consist of sections of the coating parallel to the interface (Fig. 10). In general, plan-view sample preparation takes place in two stages. The first is mechanical thinning, in which a parallel slice of material is cut from the coating and machined to a 3 mm (0.12 in.) disk using a punch or ultrasonic drill. The disk is then polished to approximately 0.1 to 0.2 mm (0.04 to 0.08 in.) in thickness. Finally, the center of the disk is further reduced in thickness by dimpling, that is, grinding with a spherical abrasive tool, which leaves a depression in the center that can be 20 μm (800 μin.) thick.

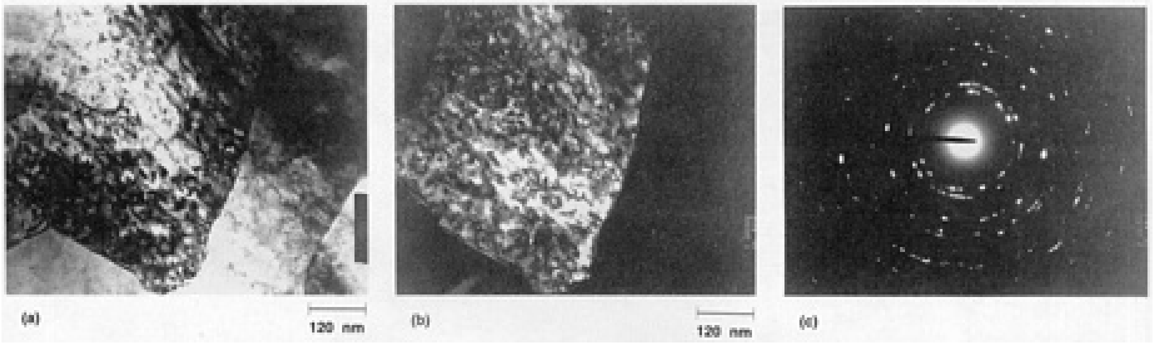


**Fig. 10 Plan-view transmission electron microscope images of sputtered titanium nitride coatings. (a) Bright-field image. (b) Dark-field image obtained by putting an aperture over two bright {200} diffraction spots. (c) Corresponding diffraction pattern**

The second stage involves final thinning to perforation, which occurs by either electropolishing, using a fine jet of etchant, or ion beam milling, using an argon ion beam of approximately 3 kV, which is directed at the surface at a low angle (5-20°). For metals and semiconductors, the electropolishing route is preferred, whereas for ceramic materials, ion beam milling is usually necessary. Depending on whether the area of interest in the coating is near the substrate interface or further out in the film, thinning of the sample will occur on the film side or the substrate side, respectively, before final perforation is achieved by thinning from both sides. Using this approach, a section can be produced from any level within the coating, but it is difficult to ascertain how far from the interface any plan-view sample lies.

Another method used to produce foils is to deposit a sufficiently thin coating onto a soluble substrate, such as aluminum (soluble in sodium hydroxide) or sodium chloride (soluble in water). After dissolution of the substrate, the film is transferred to a copper grid for imaging. However, in some cases, the film will collapse when the substrate is removed, leaving a fine powder, which can be captured on a copper grid in order to study individual grains (or columns, for PVD coatings) in more detail, but which gives no information about columnar packing.

More information can be obtained from cross-sectional TEM samples, which are considerably more difficult to produce. Usually, the sample is cut in two and joined, coating side to coating side, with a good epoxy adhesive. The assembly is then cut into thin slices and prepared in a similar manner to plan-view samples. However, the differential thinning rates of coating, substrate, and adhesive mean that it is often difficult to prevent the sample from collapsing during thinning. A number of workers have used this technique to study the interfacial regions of hard coatings in some detail (Ref 25, 26).

A TEM consists of an electron gun (typically, 100 to 400 kV for analytical configurations) and an assembly of lenses, all enclosed in a column evacuated to about $1.3 \times 10^{-3}$ Pa ($10^{-5}$ torr). The optical arrangement is similar to that of a light microscope, but additional stages of magnification are used. Condenser lenses collimate the electron beam, which passes through the specimen, and an objective lens is then used to form a first image in the object plane of the first projector lens. This image is magnified about 40 times. A small area from this image is then projected as an intermediate image, magnified about 40 times by the first projector lens. A small area of this image is then projected onto a fluorescent screen or photographic plate by another projector lens. The image is formed from the intensity distribution of the electrons leaving the bottom surface of the specimen. A total magnification ranging from 10,000 to 1,000,000 is achievable.

In addition to imaging, the TEM can be used for diffraction patterns. The diffraction pattern is formed at the back focal plane of the objective lens, and can be imaged by adjusting the projector lens excitation, which is an automatic function for most modern TEMs. The resolution of the TEM increases with electron-beam energy, and is approximately 0.19 nm (0.008 μin.) at 400 kV.

Contrast in the images is generated in two different ways. For amplitude-contrast imaging, an aperture is used to select either the primary transmitted electron beam (bright field) or one of the diffracted beams (dark field). The aperture is placed in the back focal plane of the objective lens, and the beam is focused to form an image with a further lens. Dark-field imaging is particularly useful when several phases are present. The formation of a dark-field image using a diffracted beam from one of the several phases present highlights the locations in the sample where that phase can be found. Microcracks, grain boundaries, stacking faults, and other defects can also be identified using dark-field imaging techniques (Ref 27).

For phase-contrast imaging, the primary and diffracted beams are allowed to interfere with one another. Local phase shifts of the electron waves are created by voids, defects, heavier atoms, and other phenomena. Phase contrast is the principle underlying lattice imaging (Ref 23). In addition, phase-contrast imaging under defocus conditions is used to identify voids or density variations (Ref 14, 28).

The combination of selected-area diffraction with imaging makes the TEM a very powerful tool. Phase identification and morphological characteristics can be achieved on the same areas of a sample. State-of-the-art analytical TEMs can focus the beam to a spot that is only several nanometers in diameter. The use of an x-ray detector on the column allows the analysis of chemical composition with nanometer-range spatial resolution. However, it should be realized that only a very small volume of material is sampled, because of the high magnifications used and the thin samples needed for imaging. Many microstructural variations occur on a larger scale. Therefore, x-ray diffraction is a more appropriate analytical technique for the study of large-scale structural features such as these, because it samples larger volumes of the sample.

**Porosimetry.** Porosity can be measured by the mercury intrusion porosimetry (MIP) technique, tests that use corrosive gases to decorate defects, density bottle methods, or optical or electron micrographs. These methods measure different types of porosity, namely open porosity for MIP and gas methods, closed porosity for the density bottle methods and total porosity (including sample preparation artifacts) for the microscopy measurements. No technique is particularly suitable when the porosity levels are low or the pores very small. In these cases, only electron micrographs can be used, and these sample a rather small volume of material.

MIP is very suitable for measuring the intersplat porosity for plasma-sprayed coatings. The determination of pore size distribution by MIP is based on the physical principle that mercury will not penetrate fine pores until sufficient pressure is applied to force its entry. The relationship between the applied pressure, $P$, and the pore radius into which mercury will intrude, $r$, is:

$$P\mathrm{r} = -2\gamma\cos\theta \qquad \textbf{(Eq 4)}$$

where $\gamma$ is the surface tension of mercury and $\theta$ is the contact angle between mercury and the pore wall. Varying the externally applied pressure results in changes in the intruded volume that can be related to pore-size distribution. The method assumes an ideal model in which the specimen pore structure is represented by a labyrinth of interconnected cylindrical pores of sequentially diminishing size. Most natural materials diverge from this. Completely closed pores will not be assessed, and pores accessed through a narrow neck will have their size underestimated. However, as a method of quality-control testing or to compare materials produced by different processes, this is a valuable technique. It cannot be used for materials with which mercury forms an amalgam.

The visibility of porosity can be enhanced by filling pores with a colored mount or metal. For instance, if a plasma-sprayed alumina coating is deposited onto a metal substrate, then copper can be electroplated into the pores, which will make them extremely easy to identify in polished cross sections. This minimizes the effects of grain pullout on the accuracy of porosity measurements.

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## Property / Technique Synopsis

As already noted, any single technique cannot provide all the information needed to completely categorize a coating material. For phase identification, x-ray diffraction is the primary technique used, although electron diffraction can also be used. The volume of material sampled by the x-ray technique is much larger, and a more representative picture of the complete coating phase composition is produced. However, very thin coatings or phases with very small volume fractions may be difficult to detect with x-rays, in which case electron diffraction would be preferred.

Coating thickness and surface morphology can be determined from fracture or polished cross sections using either light or scanning electron microscopy. Some estimates of grain size or porosity can also be made in these cases, if an appropriate sample preparation method is used. Etching may be necessary before polished cross sections can reveal grain or phase boundaries. For coatings that are less than 10 μm (400 μin.), scanning electron microscopy is necessary to determine the structure in cross section. For films that are considerably less than 1 μm (40 μin.) in thickness, only transmission electron microscopy is capable of giving cross-sectional images that can be used to determine grain size, phase distribution, or porosity. This is particularly true when interfacial structures are to be examined.

The importance of good specimen preparation for all structural analysis techniques cannot be overemphasized. In many cases, apparently featureless fracture or polished cross sections have been taken to indicate amorphous or single-phase coating. Subsequent etching or diffraction analysis has shown the presence of grain or phase boundaries.

It is also important to correlate the structure of coatings with their composition, which can vary through the coating thickness. The article "Surface and Interface Analysis of Coatings and Thin Films" in this Section of the Volume provides information on coating analysis.

### Surface and Interface Analysis of Coatings and Thin Films

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## Introduction

SURFACE AND INTERFACE ANALYSIS TECHNIQUES have been among the paramount characterization methods since the beginning of modern, scientifically based thin film and coatings technology in the seventies, and their use very often has led to substantial progress in new fabrication techniques and devices (Ref 1, 2). This is obvious because the structure and composition of surfaces and interfaces is decisive for many properties of thin films, such as chemical reactivity, friction and wear, film adhesion, and electronic and diffusional properties. Of course, any of the large variety of physical characterization methods is more or less surface sensitive, but this article refers mainly to the "classical" methods of surface chemical analysis, namely electron spectroscopies (Ref 3) and ion spectroscopies (Ref 4), of which the most important techniques are Auger electron spectroscopy (AES), x-ray photoelectron spectroscopy (XPS or ESCA, electron spectroscopy for chemical analysis), and secondary ion (and neutral) mass spectroscopy (SIMS and SNMS) (Ref 5, 6). Glow discharge optical emission spectroscopy (GDOES) or glow discharge mass spectroscopy (GDMS), ion scattering spectroscopy (ISS), and Rutherford backscattering spectroscopy (RBS) are becoming of increasing importance, as is total reflection x-ray fluorescence spectroscopy (TRXF) (Ref 7) in special applications. All these techniques were emerging in the late 1960s and early 1970s (Ref 5) and have been developed since then into often sophisticated instruments for local microanalysis down to the nanometer scale (Ref 3, 4, 6). A survey of the most important surface analysis techniques and their relative frequency of application is shown in Fig. 1.

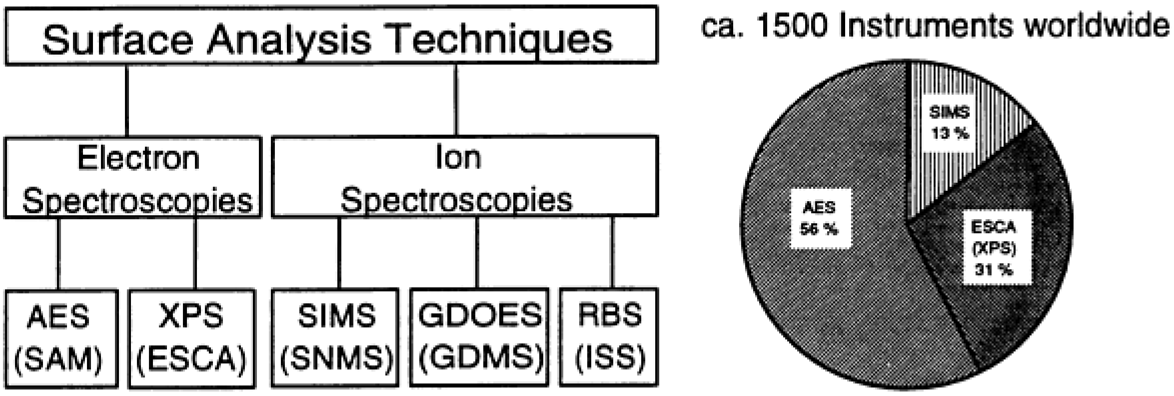

**Fig. 1 Survey of the most important surface analysis techniques. AES (SAM), Auger electron spectroscopy (scanning Auger microscopy). XPS (ESCA), x-ray photoelectron spectroscopy (electron spectroscopy for chemical analysis). SIMS (SNMS), secondary ion mass spectroscopy (secondary neutral mass spectroscopy). GDOES (GDMS), glow discharge optical emission spectroscopy (glow discharge mass spectroscopy). RBS (ISS), Rutherford backscattering spectroscopy (ion scattering spectroscopy). Source: Ref 3**

Coatings and thin films can be studied with surface analysis methods because their inherently small depth allows characterization of surface composition, interface composition, and the in-depth distribution of composition. This provides an indispensable method for the control of fabrication parameters as well as for the study of property/composition relationships. The full potential of surface analysis is further enhanced if the methods are applied in combination with other characterization methods including phase and structural identification (x-ray diffraction, transmission electron microscopy, and scanning tunneling microscopy) and stereochemistry (infrared and Raman spectroscopy). Recent trends are the development of increased spatial resolution (e.g., toward the 10 nm region and below in AES and SIMS) and improved databases and evaluation software for quantitative analysis.

With the exception of RBS, any of the above-mentioned surface analysis methods involves the use of an ion sputtering facility, which allows destructive depth profiling. Therefore, these methods can also be used for chemical analysis of the "bulk" of thin films and for the characterization of interfaces. Nondestructive depth profiling can be performed with RBS up to a few micrometers in depth, and with angle-resolved XPS up to about 5 nm thickness. Another method of interface analysis is based on brittle fracture or cleavage of the sample along internal interfaces, which exposes two surfaces to be studied by surface analysis. Following are the most important phenomena and structures that can be studied by the above-mentioned methods, the majority of which are relevant for coatings and thin films:

### Surfaces, studied directly

- Segregation
- Diffusion
- Contamination
- Adsorption
- Oxidation
- Catalysis
- Friction and wear

### Interfaces, studied by fracture and/or profiling

- Segregation
- Diffusion
- Embrittlement
- Intercrystalline corrosion
- Sintering
- Adhesion
- Composites

### Thin films, studied by depth profiling

- Interdiffusion
- Ion implantation
- Reaction layers (oxides, passivation layers, etc.)
- Evaporation layers
- Protective coatings
- Microelectronic devices

From the more than 50 different existing techniques in surface analysis (Ref 6), this article only considers the main methods that have broad applicability and for which commercially available instruments exist (AES, XPS, SIMS, SNMS, GDOES, ISS, and RBS). They are characterized by the ability to provide quantitative analysis of all elements (except hydrogen and helium in AES and XPS) and intrinsic information depth in the nanometer range or below.

The latter point is the important difference to (spatially resolved) bulk analysis methods such as x-ray analysis in the electron microprobe. It should be mentioned that high-resolution, analytical scanning transmission electron microscopy (STEM) can also be used for surface and interface analysis (see the article "Microstructure/Characterization of Coatings and Thin Films" in this Volume).

A survey of the lateral and in-depth dimensions of the analyzed volume of typical microanalytical techniques is given in Fig. 2. For surface analyzing techniques with depth resolution below 5 nm, the depth of information is an intrinsic, physical parameter determined by the mean escape depth of photoelectrons or Auger electrons or that of the sputtered particles (SIMS, SNMS). In contrast, the lateral resolution depends mainly on instrumental capabilities, such as primary beam diameter or optical imaging facility.

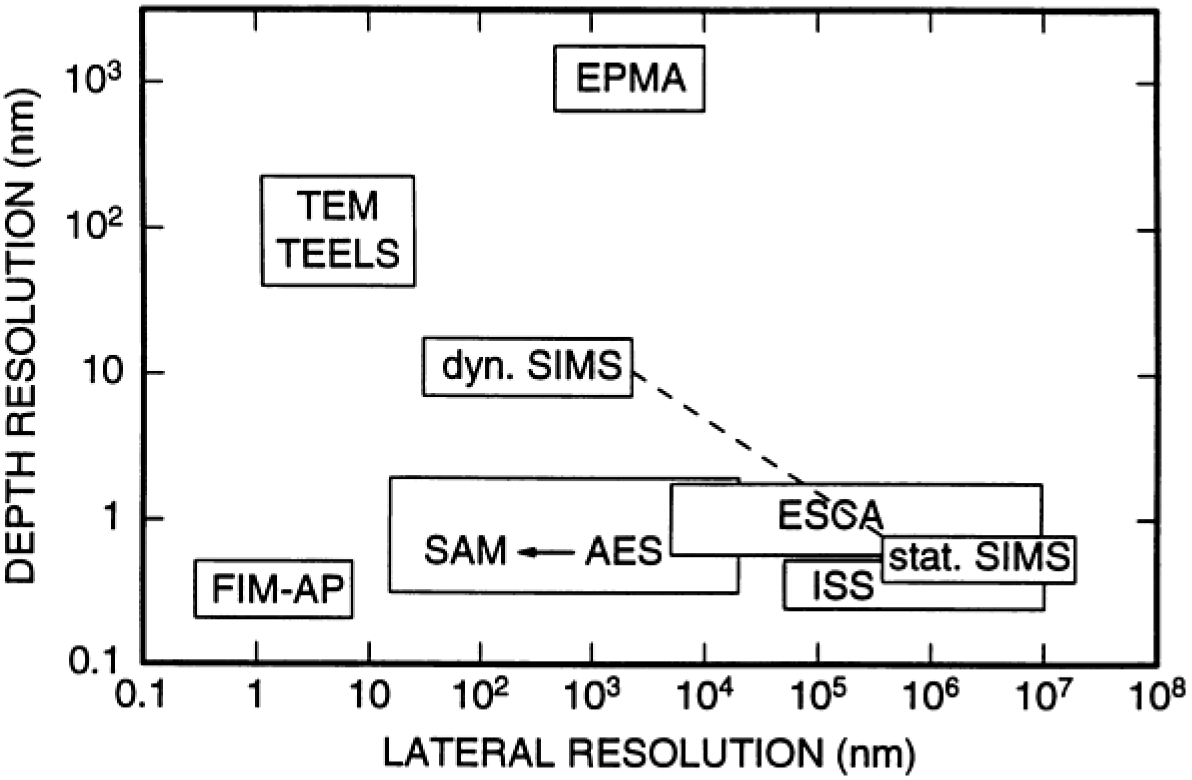

**Fig. 2 Depth of information (depth resolution) and lateral resolution of surface and microanalysis techniques. AES, Auger electron spectroscopy. EPMA, electron probe microanalysis. ESCA, electron spectroscopy for chemical analysis. FIM-AP, field ion microscopy - atom probe. ISS, ion scattering spectroscopy. SAM, scanning Auger microscopy. SIMS, secondary ion mass spectroscopy. TEELS, transmission electron energy loss spectroscopy. TEM, transmission electron microscopy.**

The principal components of an analytical surface analysis instrument are schematically shown in Fig. 3. They are: an excitation source (electrons, ions, or x-rays), an auxiliary ion gun for depth profiling, and a spectrometer (energy or mass) with particle detector, data acquisition, and processing facility. Together with the sample, the main components are in an ultrahigh vacuum chamber (UHV, $\leq 10^{-9}$ mbar). Therefore they can often be used for process control, as in modern molecular beam epitaxy or physical and chemical vapor deposition methods (Ref 7, 8) which work under UHV base pressure conditions (Ref 7). The principles of the main analysis methods are outlined in the following sections of this article. (For a quick survey and comparison of their most important features, see Table 1.)

**Table 1 Comparison of surface and thin-film analysis techniques**

| **Parameter** | **Technique** | | | | | |
|---|---|---|---|---|---|---|
| | **AES** | **XPS** | **ISS** | **RBS** | **SIMS** | **GDOES** |
| Excitation | Electrons | X-rays | Ions | Ions | Ions | Ions |
| Emission | Electrons | Electrons | Ions ($E$) | Ions ($E$) | Ions ($m/e$) | $h\nu$ (optical) |
| Typical depth of information, nm | 1 | 1 | 0.3 | 1-1000 | 0.6 | 10 |

| | | | | | | |
|---|---|---|---|---|---|---|
| Lateral resolution | 15 nm -30 µm | 5 µm -10 mm | 1 mm | 1 mm | 50 nm -10 mm | 10 mm |
| Detection limit | 0.1 at.% | 0.1 at.% | 0.1 at.% | 0.1 at.% | 1 ppb -10 ppm | 1 ppm |
| Detection of: | | | | | | |
| Elements | All except H, He | All except H, He | All except H | H only with ERD | All | All |
| Isotopes | No | No | Yes | Yes | Yes | No |
| Chemical state | Yes | Yes | No | No | Yes | No |
| Imaging/mapping | Yes | Limited | No | No | Yes | No |
| Depth profile: | | | | | | |
| Nondestructive | No | Yes (<5 nm) | No | Yes | No | No |
| Destructive | + Sputtering | + Sputtering | + Sputtering | No | Yes | Yes |
| Main usage | Element surface and thin-film analysis | Chemical state analysis | Topmost layer analysis | Nondestructive thin-film analysis | Dopant profiles | Rapid thin-film analysis |

AES, Auger electron spectroscopy; ERD, elastic recoil detection; GDOES, glow discharge optical emission spectroscopy; ISS, ion scattering spectroscopy; RBS, Rutherford backscattering spectroscopy; SIMS, secondary ion mass spectroscopy; XPS, x-ray photoelectron spectroscopy

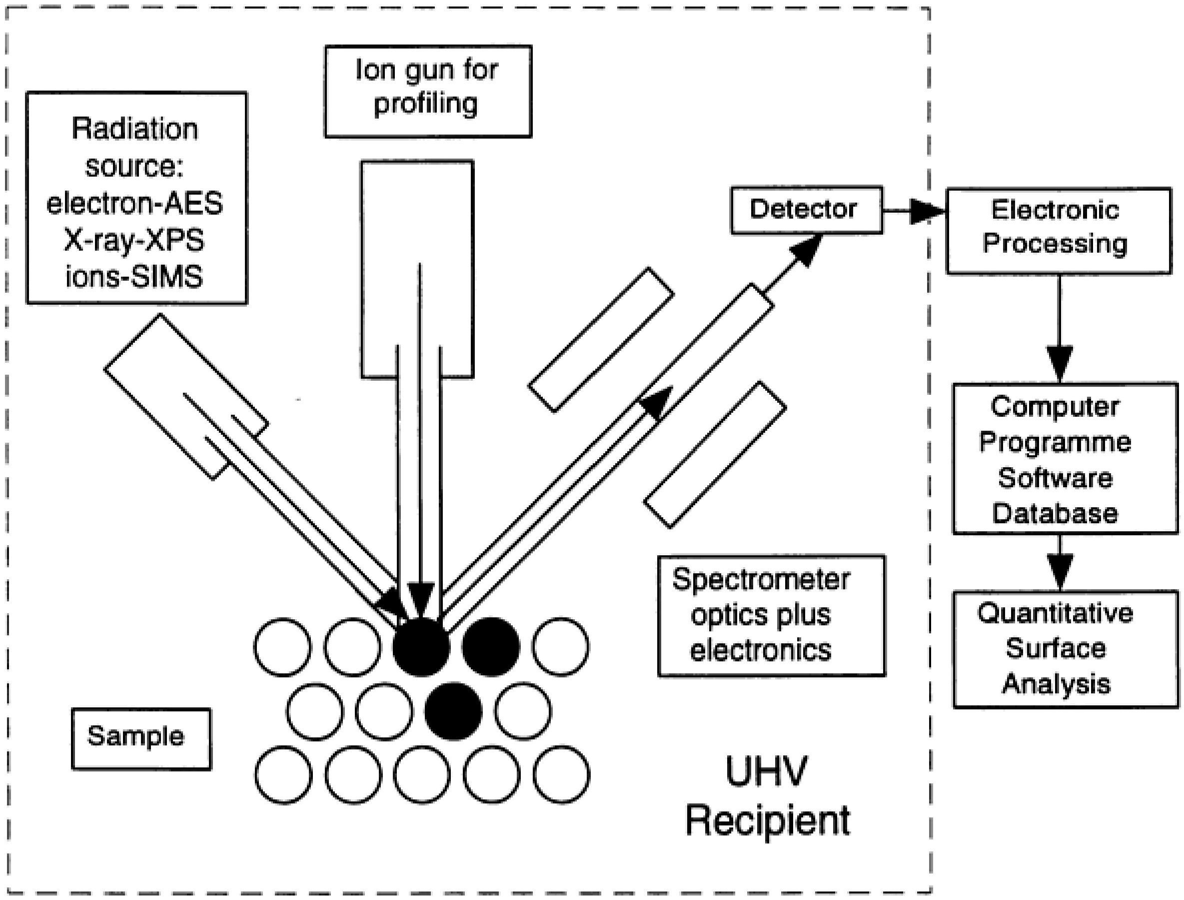

**Fig. 3 Principal components of a surface analysis instrument. AES, Auger electron spectroscopy. SIMS, secondary ion mass spectroscopy. UHV, ultrahigh vacuum chamber. XPS, x-ray photoelectron spectroscopy. Source: Ref 3**

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## Electron Spectroscopies (AES and XPS)

AES and XPS determine the energies of electrons emitted from a surface. Those with specific energies usually are photoelectrons or Auger electrons. For detailed information, the reader is referred to Ref 3, 5, and 6. Principles for basic understanding are briefly characterized in the following and illustrated by some examples.

**X-ray Photoelectron Spectroscopy.** Irradiation of the sample with x-rays of energy $h\nu$ (e.g., characteristic radiation of AlKα: $h\nu = 1486.6$ eV; or MgKα: $h\nu = 1253.6$ eV, often combined with a monochromator for narrower line width) causes emission of photoelectrons with kinetic energy $E_{kin}$ according to:

$$E_{\text{kin}} = h\nu - E_{\text{B}} - j_{\text{A}} \qquad \textbf{(Eq 1)}$$

where $E_{\text{B}}$ is the binding energy of the respective electron level and $j_{\text{A}}$ is the work function of the electron energy analyzer (Fig. 3). Because $hu$ is the energy of the x-ray source used, the binding energy can be determined directly in most usual instruments if $j_{\text{A}}$ and the analyzed energy $E_{\text{kin}}$ are empirically calibrated with standard samples. Tables of binding energies are available (Ref 9).

The terminology of XPS follows that of atomic physics. Each electronic level is characterized by its orbital number *n* (= 1, 2, 3, 4 . . .), the orbital momentum *m* (= *s, p, d, f*), and the total spin quantum number *I* (= 1/2, 3/2, 5/2 . . .).

***Chemical Effects and Compound Analysis.*** In general, chemical bonding changes the electron binding energy of valence band and core levels, which for core levels is recognized in XPS by a distinct "chemical shift" of the elemental peak with respect to the pure element (Ref 3). An example is shown in Fig. 4 for the 2*p* 3/2 and 2*p* 1/2 doublet of the Ti-2*p* XPS spectrum of a native oxide layer on a titanium nitride (TiN) coating (Ref 10). If the characteristic binding energies are known from measurements of standard samples or, often less precisely, from data banks (e.g., the National Institute of Standards and Technology the XPS database in Ref 9), the relative amount of a compound can be directly determined by peak fitting of peaks at the respective energies and subsequent determination of the Ti-2*p* 3/2, 1/2 respective peak areas. This was done for the Ti-2*p* 3/2, 1/2 doublet in Fig. 4, which is decomposed into two doublets, one for $TiO_2$ and the other for TiN. Comparison of the peak areas in this case gives $X\ TiO_2/X_{TiN} = 0.49$. With the emission angle $\theta = 45°$ and an electron attenuation length of $\lambda_0 = 1.2$ nm, this value corresponds to a 1.8 nm thick $TiO_2$ layer on TiN.

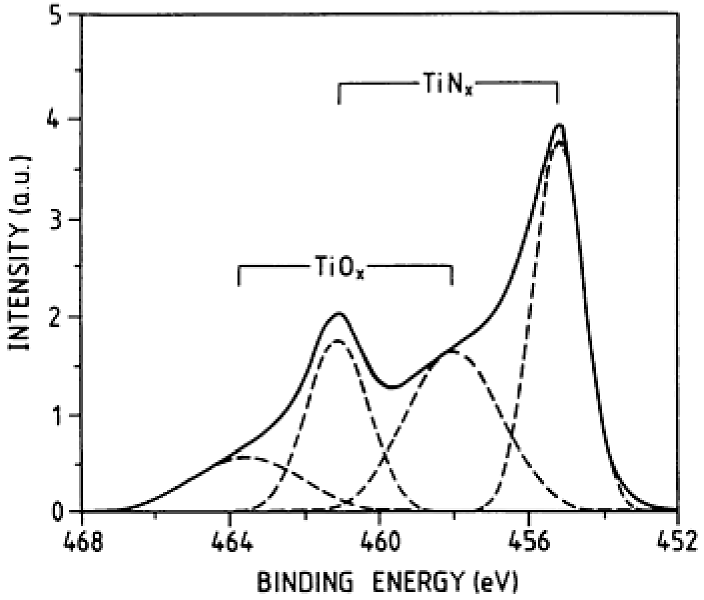

**Fig. 4 X-ray photoelectron spectroscopy of the Ti-2*p* 1/2, 3/2 doublet in TiN and $TiO_2$ obtained with a thin oxide layer on TiN. Source: Ref 10**

Usually, the chemical shift of compounds such as nitrides and oxides is of the order of a few electron volts (see Fig. 4) (Ref 3, 9). In many compounds, different valency states have a characteristic shift of the core level. For example, the Ta-4*f* doublet in $Ta_2O_5$ shows a shift of the binding energy of 5 eV from $Ta^0$ to $Ta^{5+}$, whereas for TaO a shift of 2 eV (corresponding to $Ta^{2+}$) is obtained (Ref 11).

**Auger Electron Spectroscopy.** The most important method for chemical microanalyses of a surface is electron-beam-excited AES, which is based on the Auger effect (Ref 3, 5, 6). It is a radiationless transition, competing with x-ray fluorescence when an atom is ionized (e.g., by electron impact) in an inner shell (e.g., *K*-shell). The generated electron vacancy can be filled by an electron from an outer shell (e.g., *L*-shell), and the energy gain of this transition causes the emission of another electron from the outer shell. According to the net energy of the described Auger transition involving $K$, $L_1$, $L_2$ levels, the kinetic energy of the emitted Auger electron is given by:

$$E_{\text{kin}}\,(KL_1L_2) = E_{\text{K}} - E\text{L}_1 - E\text{L}_2 - \Delta E - \varphi_{\text{A}} \qquad \textbf{(Eq 2)}$$

where $E_{\text{K}}$, $E\text{L}_1$, and $E\text{L}_2$ are the respective electron binding energies, $\Delta E$ is a small correction term for the relaxation of the twofold ionized state, and $\varphi_{\text{A}}$ is the work function of the analyzer.

Equation 2 gives a characteristic kinetic energy--independent of the excitation energy--for any specific Auger transition of an element and therefore is the basis of qualitative analysis. Because three electron levels are involved, hydrogen and helium cannot be detected. For elements with higher atomic number, transitions such as *LMM*-, *MNN*-, and so on are used for Auger analysis. In general, the derivative spectrum $d[N(E) \cdot E]/dE$ is recorded as shown in Fig. 5 for TiN (Ref 10).

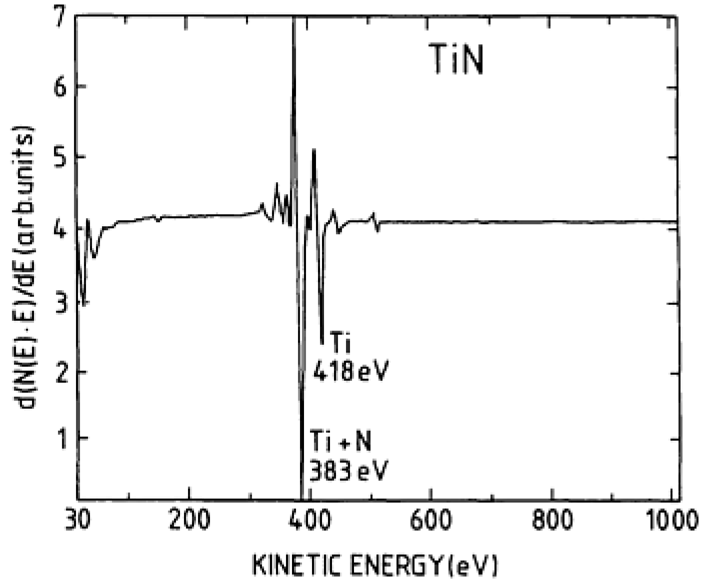

**Fig. 5 Auger electron spectroscopy of a TiN coating in the derivative mode. At 383 eV, one of the major titanium peaks overlaps with the nitrogen (381 eV) peak. Source: Ref 10**

***Chemical Effects and Compound Analysis.*** Because of the three electron levels involved in AES, the chemical bonding effect is much more complex than in XPS and is most often recognized as a peak shape change that impedes elemental quantification (Ref 3). However, the knowledge of standard spectra of the relevant factors (or principal components) allows the decomposition of a measured depth profile into quantitative contributions, as shown in Fig. 6 for $Cr_2O_3$ and CrN in an oxidized (Cr,Pd)N coating (Ref 12).

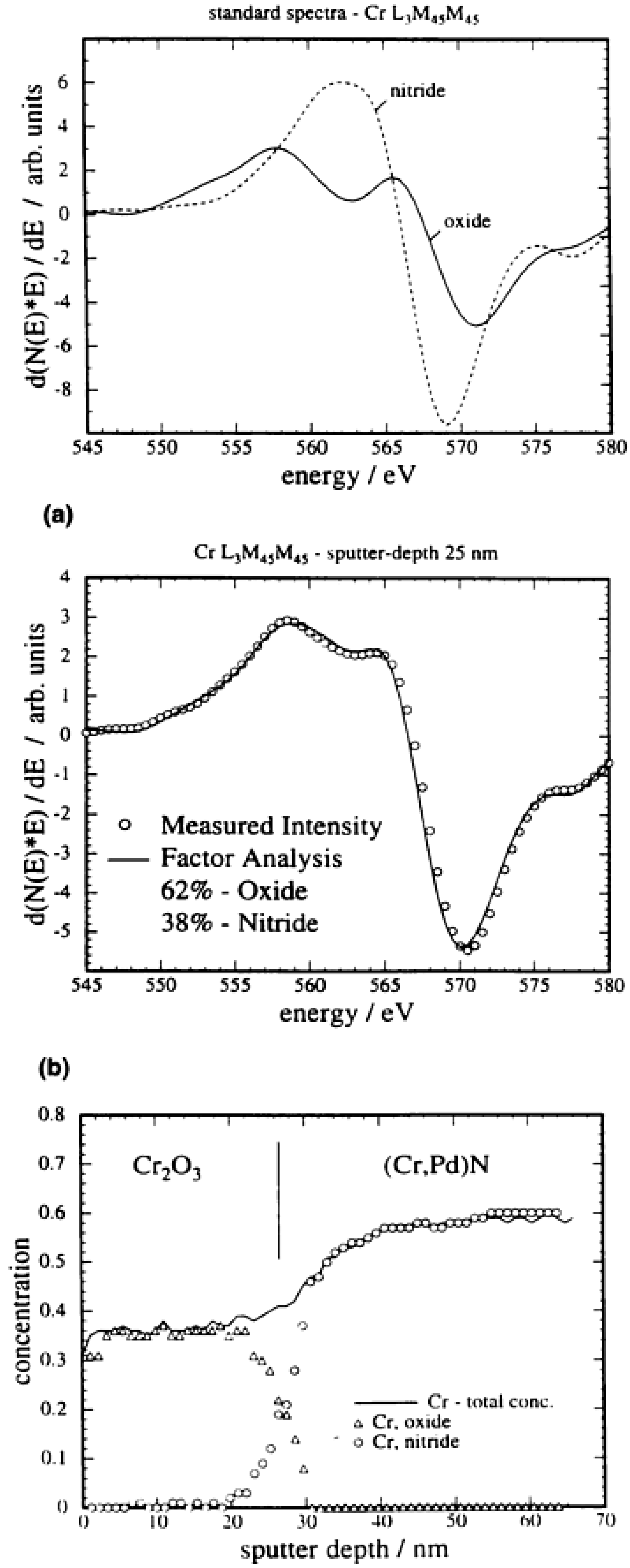

**Fig. 6 Factor analysis in Auger electron spectroscopy depth profiling of an oxidized (Cr,Pd)N coating. (a)**

**Standard spectra of the components chromium nitride and chromium oxide. (b) Comparison of measured and synthesized spectra. (c) Depth profile of the principal components. Source: Ref 12**

Applying the mathematical method of factor analysis (Ref 13) to a series of spectra, for example in a depth profile (Ref 14, 15) enables the assessment of the number of principal components and a test of the validity of the otherwise obtained standard spectra, as well as the determination of one unknown component *n* if *n*-1 components are known. For more details of this powerful method, the reader is referred to Ref 13, 14, and 15 (see also the section "Thin Film and Interface Analysis" in this article).

**Information Depth.** Whenever an Auger electron or photoelectron is generated, its characteristic energy can be analyzed outside the sample only if it leaves the surface without any inelastic scattering event by which it loses some amount of energy and contributes then only to the lower-energy background of the spectrum. The probability of inelastic scattering increases exponentially with the traveled distance and is described by the inelastic mean free path $\lambda_0$ or, more precisely, attenuation length, which additionally includes elastic scattering (Ref 16). Depending on electron energy and material, the attenuation length is typically between 0.4 and 3 nm and increases with the kinetic energy. Although physical theories for predictions of $\lambda_0$ have recently been developed (Ref 17), the semiempirical relation of Seah and Dench (Ref 18) is still useful and gives the right order of magnitude for elements as well as for many inorganic compounds for the energy range of 30 to 3000 eV:

$$l_o = \left[\frac{534}{E^2} + 0.41.(a.E)^{1/2}\right].a \qquad \textbf{(Eq 3)}$$

where $\lambda_0$ is in nanometers, *E* is the kinetic electron energy in electron volts, and *a* is the mean atomic distance in nanometers. The atomic mass number, *M*, the density, ρ, and Avogadro's number, $N_0$, determine $a = [M/(\rho \cdot N_0)]^{1/3}$. Values of $\lambda_0$ are typically between 0.4 nm ($E \approx 100$ eV) and 2 nm ($E \approx 1500$ eV), meaning that 63% of the measured intensity of Auger electrons or photoelectrons stems from a surface layer with the thickness $\lambda_0$ for emission perpendicular to the surface ($\theta = 0$). This fact is the reason for the surface-specific information of the electron spectroscopies. If the emission angle θ increases, the electron escape depth λ is smaller than $\lambda_0$ and given by $\lambda = \lambda_0 \cdot \cos\theta$(Ref 18).

**Quantification Principles of Electron Spectroscopies.** The signal intensity, given by the number of Auger electrons or photoelectrons in an elemental peak, is a measure of the number of atoms of this element in the analyzed volume and therefore of its concentration. Usually, the signal intensity is given by the area under the measured peak [$N(E)$] after background subtraction (Ref 3). Whereas background subtraction is generally used in XPS, the much larger electron background in AES causes relatively large errors. Therefore it is still customary to use the Auger peak-to-peak height in the differentiated [$d[N(E) \cdot E]/dE$] spectrum in AES to characterize the elemental signal intensity $I_i$, as shown in Fig. 5 for the Auger spectrum of TiN (Ref 10). For both AES and XPS we may write:

$$I_i = k_0 \cdot (1 + r_B) \cdot S_i \cdot X_i \cdot l_0^2 \cdot \cos\theta \qquad \textbf{(Eq 4)}$$

where $k_0$ is an instrumental constant given by the analyzed area, excitation intensity (primary current or x-ray intensity), and the total analyzer transmission; $r_B$ is the backscattering factor in AES, mainly dependent on the atomic number, and is typically between 0.1 and 1.5 (however, $r_B = 0$ for XPS); $S_i$ is the relative elemental sensitivity factor (generally defined with respect to pure silver in AES and with respect to pure carbon in XPS); $X_i$ is the mole fraction in the analyzed volume (analyzed area times $l_0^2$); $l_0^2$ is the inelastic mean free path for the peak energy of element *i* or, more precisely, the attenuation length (Ref 16, 17), and θ is the angle of emission of the detected electrons with the normal to the sample surface.

For a complete spectrum with $I_i$ the intensity of the most intense peak of every detected element *i*, $k_0$, and θ are constant. Assuming that $r_B$ (in AES) and $\lambda_i$ are approximately constant, it follows from Eq 4 that:

$$X_i = \frac{I_i / S_i}{\sum_{j=1}^{n} (I_j / S_j)} \qquad \textbf{(Eq 5)}$$

which gives the mole fraction $X_i$ for the chosen element $i$ of a total of $n$ elements. Note that Eq 5 is only a first-order approximation, because the matrix dependence of $l_0^2$, and of $r_B$ in AES, are neglected. This expected deviation can be taken into account by a correction factor $F_{AB}$ of element A in matrix B, by which every $I_A/S_A$ has to be multiplied in Eq 3 (Ref 3, 10, 19):

$$F_{AB} = \frac{(1+r_B^A).l_0^A}{(1+r_B^A).l_0^A} \qquad \textbf{(Eq 5a)}$$

where $l_0^A$ and $l_0^B$ are the electron attenuation lengths and $r_B^A$ and $r_B^B$ are the AES electron backscattering coefficients of the pure element A and of element A in matrix B, respectively. The $F_{AB}$ correction factor depends on the difference, mainly with respect to density and mean atomic number, of matrix and pure element. In favorable cases, $F_{AB}$ is of the order of a few percent; for strong differences, $F_{AB}$ can be between 0.5 and 2 (Ref 3). According to Eq 5a, these values are a measure of the error margin contained in quantification of homogeneous samples using Eq 5.

***Depth-Dependent Composition.*** Homogeneous composition in electron spectroscopies means constant composition within about 5λ from the surface, because the intensities contributing to the signal decay exponentially with depth $z$, that is, $I_i = I_i^0 \exp(-z/\lambda)$. For $z = 5\lambda$, $I_i$ is about 0.7% of $I_i^0$ of a pure element at the surface and is therefore approximately at the limit of detection for most elements. Because $\lambda_0$ is between 0.4 and 2 nm, the above condition means a required homogeneity in a range between 2 and 10 nm. This is the maximum information depth or the intrinsic sampling depth in AES and XPS.

For example, if $\lambda_0$ is 2 nm ($\lambda_0 = \lambda$ for emission perpendicular to the surface, $\theta = 0$) in an AB composition and the first monolayer $d = 0.25$ nm composed of pure A ($X_A = 1$) with the rest being pure B, then $I_A/I_A^0 = 1 - \exp(-0.25/2) = 0.12$ and $I_A/I_B^0 = \exp(-0.25/2) = 0.88$, which corresponds to $X_A = 0.12$ homogeneously distributed in a region of $\geq 10$ nm. From the measured intensity alone, both possibilities or intermediate cases are indistinguishable. If $\lambda_0$ is 0.4 nm, $X_A = 0.46$ is obtained. Figure 7 shows the relation between the ratio $\overline{X}_A (5 \cdot \lambda)/X_A(d)$, of the measured $\overline{X}_A (5 \cdot \lambda)$ and the true $X_A(d)$ homogeneously distributed within a layer of thickness $d$. It is easily recognized from Fig. 7 that because of matrix effects with respect to the elemental standard, changing λ changes the sampling depth and therefore the sensitivity factor, as outlined above (Ref 19).

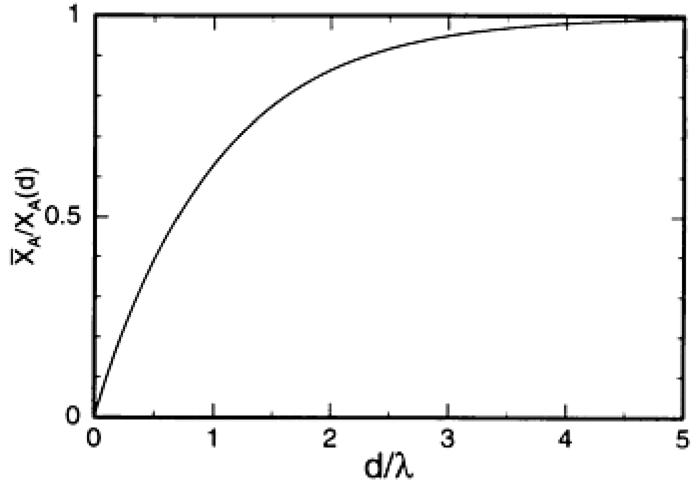

**Fig. 7 Ratio of the average concentration $\overline{X}_A$, assuming a constant $\overline{X}_A$ with depth of an A-B alloy, to the concentration $X_A(d)$ of a thin layer of thickness $d$ of A on a substrate B**

Because the relative change in λ with composition should be the same for any elemental peak, the sensitivity factor, $S_A/S_B$, which is decisive for correct quantification of homogeneous samples, should not change with changing composition (except for $r_B$ in AES, Eq 5a). Therefore, any matrix has a characteristic set of elemental sensitivity factors that can be best evaluated by the use of standards (Ref 3, 4, 19, 20).

***Microanalysis and Lateral Resolution.*** The technique of scanning a focused electron beam and simultaneous plotting the peak-to-background intensity of an elemental signal using scanning Auger microscopy (SAM) allows elemental mapping (Ref 21). A secondary electron image of an electronic thin-film device is shown in Fig. 8(a), whereas Fig. 8(b, c, d) show the silicon, aluminum, and fluorine maps. In this case, the device was etched by a fluorine-containing reactive gas. It is clearly recognized that fluorine remained only at the aluminum contact layers and not on the silicon structures (Ref 22).

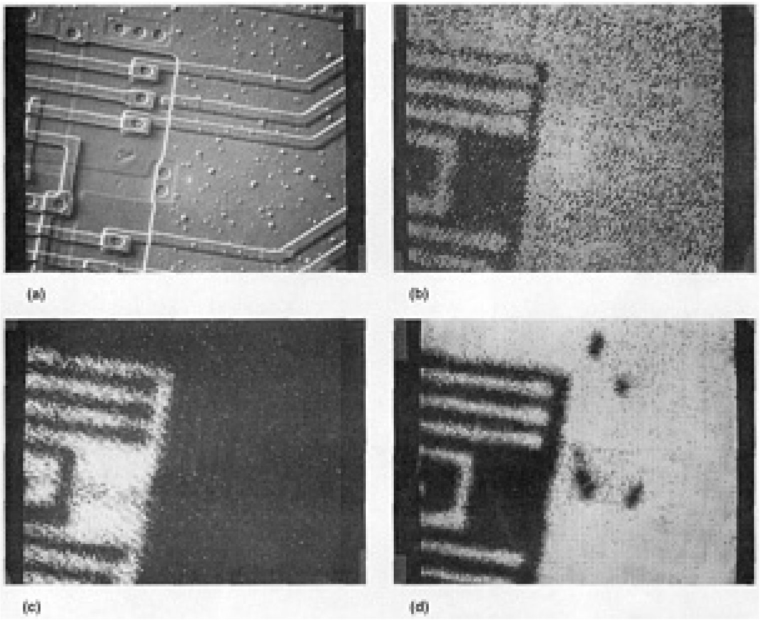

**Fig. 8 Integrated circuit after cleaning treatment with a fluorine-containing compound analyzed with Auger electron spectroscopy/scanning Auger microscopy. (a) Secondary electron image. (b) Chemical map of aluminum. (c) Chemical map of silicon. (d) Chemical map of fluorine. Note that fluorine is removed by electron-stimulated desorption from focusing spots of the electron beam. Source: Ref 22**

A lateral resolution in SAM of about 0.1 μm can be routinely obtained. Modern instruments with field emission cathodes provide primary beam diameters of 15 nm at 1 nA beam current, suitable for the analysis of microelectronics devices. Limitations in quantification and detrimental effects such as beam heating are discussed in Ref 22.

XPS offers somewhat less spatial resolution than SAM, about 70 to 5 μm. Small-spot XPS can be performed either by excitation of a restricted sample area (e.g., a focused x-ray beam by a bent monochromator crystal) or by an electron optical lens in front of the analyzer, which selects a limited area of the sample for analysis (Ref 23). Imaging XPS uses monochromatic electrons and a multichannel parallel detection device to generate an elemental image (Ref 23).

***Limitations and Special Problems.*** High-spatial-resolution AES of small particles, protrusions, or precipitates in micrometer dimensions is difficult to analyze quantitatively because of distortions by backscattered primary electrons that excite Auger electrons from the surrounding material. The achievable resolution is limited by the amount of current in a small-diameter beam that is necessary for a sufficient signal-to-noise ratio and by the temperature increase that is due to the high current density (up to $10^3$ A/cm$^2$), which may cause diffusion and even evaporation processes in thin films on substrates with low thermal conductivity (Ref 21, 22). Furthermore, electron-stimulated desorption may lead to decomposition of compounds at the surface. For both cases of sample damage, lowering the current density (e.g., by enlarging the beam diameter or scanning the electron beam over a certain area) is a remedy, but at the cost of decreasing spatial resolution. The usually much lower power density greatly reduces this problem in XPS.

Charging of insulating materials is a severe problem in both AES and XPS. However, whereas negative charging of the sample in AES is difficult to overcome in practical analysis, even though a number of special techniques can help (Ref 24, 25), XPS causes positive surface charging, which can often be successfully compensated by low-energy electron flooding with an auxiliary electron source (Ref 26).

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## Ion Spectroscopies

When ions are used as a probe, there are several possibilities for surface chemical analysis: the characteristic energy loss of scattered primary ions (ISS, RBS), the mass of secondary (sputtered) particles (SIMS, SNMS, GDMS), or their optical emission (GDOES). Primary ion energy spectroscopy is performed either at low energy (<10 keV) (Ref 27) or at high energy (>300 keV) (Ref 28). The term *low-energy ion scattering* (LEIS) is often used synonymously with ISS. The term *high-energy ion scattering* (HEIS) is akin to RBS. SIMS (Ref 29) and SNMS (Ref 30) or GDMS (Ref 31) are based on mass spectrometric detection of the sputtered species, while GDOES (Ref 32) measures optical emission lines characteristic for specific elements.

### *Energy Analysis of Scattered Primary Ions*

**Ion Scattering Spectroscopy.** The principle of ISS is the collisional elastic momentum and energy transfer of a primary ion of mass $m_1$ and energy $E_0$ (1 to 5 keV) with an atom of mass $m_2$ in the topmost layer of the sample (Ref 27). For a given scattering angle, the energy $E_1$ of the backscattered primary ion (generally $He^+$) is a unique function of the ratio $m_2/m_1$. For example, at 90° scattering angle the relation

$$E_1 = E_0 \cdot \left(1 - \frac{m_1}{m_2}\right) / \left(1 + \frac{m_1}{m_2}\right) \qquad \textbf{(Eq 6)}$$

is valid and shows how the energy scale ($E_1$) can be calibrated in a mass scale ($m_2$). The single-collision binary scattering described by Eq 6 occurs only at the surface. Therefore ISS is unique in determining the composition of only the topmost surface layer. However, the limitations in sensitivity and mass resolution at higher masses (see Eq 6), along with its difficult quantification, have confined ISS to more fundamental research.

**Rutherford backscattering spectroscopy** is one of the techniques first applied to thin-film analysis (Ref 28). The reason is that due to their high energy (>300 keV, up to several MeV), the primary ions penetrate between several 100 nm and some 10 μm of a solid until they lose their energy and are stopped. Along their way, a considerable fraction undergoes Rutherford backscattering, provided that the nuclei in the target have a higher mass than the primary ions. (These are usually $He^+$ ions, so hydrogen and helium cannot be detected by RBS.) However, forward ejection of these atoms, that is, elastic recoil detection, can be applied to detect hydrogen (Ref 33). The backscattered primary ions lose a specific amount of energy, which is determined by both the mass $m_2$ of the scattering atomic nuclei in the sample and by the well-known energy loss that occurs mainly through electronic interaction, which is proportional to the totally traveled distance $z$ and the loss rate $dE/dz$. The measured energy $E_1/(m_2, z)$ of the primary ion ($m_1$) after backscattering is given by the following two terms:

$$E_1(m_2, z) = f(m_2, E_0) - z \cdot f(m_2, E_0, dE/dz) \qquad \textbf{(Eq 7)}$$

Because of the second term, the width of the peak due to scattering at $m_2$ is a measure of the thickness of the respective material, and its intensity is proportional to the (areal) concentration. It is obvious that the achievable depth resolution depends on the energy resolution of the analyzer. Thin-film analysis with high depth resolution is enabled by modern electrostatic energy analyzers. An example is shown in Fig. 9, where the measured and calculated intensity-energy relations for a 10.4 nm thick niobium layer on sapphire is depicted (Ref 34). The notch of the measured profile is due to a native niobium oxide layer of about 2 nm thickness. The main advantages of RBS are that it is a nondestructive and quantitative method. The main disadvantages are the relatively large analyzed spot (typically 1 mm diameter), the necessity of expensive particle accelerators, and the lack of chemical information. For a summary of the typical features of RBS in comparison with other methods, see Table 1.

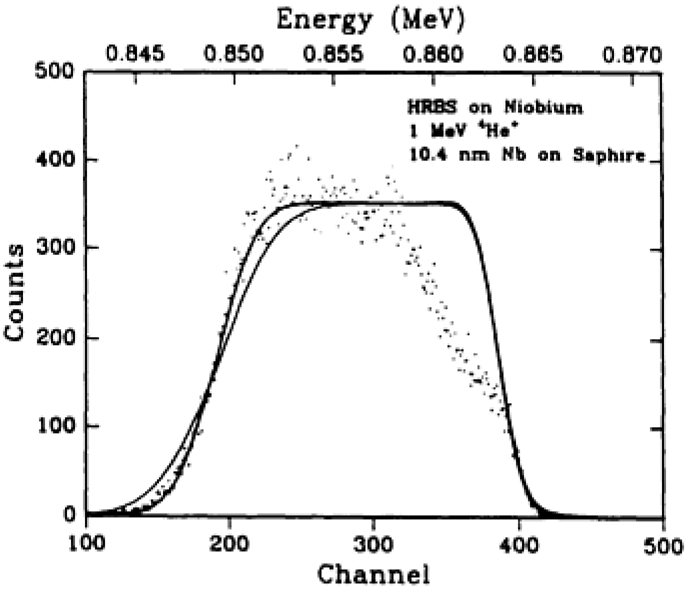

**Fig. 9 High-resolution Rutherford backscattering spectroscopy of a 10.4 nm niobium layer on sapphire (calculated solid lines) that was oxidized in air (shoulder in the experimental points distribution). 1 MeV $^4He^+$. Source: Ref 34**

## *Detection of Sputtered Particles*

**Secondary ion mass spectroscopy (SIMS)** is probably the first technique used for depth profiling (Ref 29). A primary ion beam of about 0.5 to 15 keV energy causes sputter erosion of the surface by emission of neutrals and ions. The ejected secondary ions are separated in a mass spectrometer (electric quadrupole or magnetic sector or, in time-of-flight SIMS, by flight time measurements of pulse-accelerated secondary ions). The precision of identification of atomic and molecular species depends on the mass resolution, ($m/\Delta m$), which typically is 500 to 2000 for quadrupole, up to 10,000 for magnetic sector, and up to 15,000 for time-of-flight spectrometers. The basic equation for quantitative SIMS can be written as (Ref 29):

$$I_I^{\pm} = I_0^{\pm} \cdot T_i \cdot Y_i \cdot b_i^{\pm} \cdot X_i \qquad \textbf{(Eq 8)}$$

where the measured count rate at mass $i$ of the positive or negative secondary ions, $I_I^{\pm}$, is determined by the primary ion intensity $I_0^{\pm}$, the total instrumental transmission $T_i$, the sputter yield $Y_i$ (atoms/ion), the ionization probability $b_i^{\pm}$ ($\leq 1$) of the sputtered particles ($i$), and their mole fraction $X_i$ in the sample.

The main advantages of SIMS are its:

- Ability to detect all elements, including hydrogen
- Ability to detect elements in the parts-per-billion range
- Ability to perform microanalysis and imaging in the submicrometer range
- High dynamic range of up to 8 orders of magnitude in concentration

Besides its intrinsic destructiveness, the main disadvantage of SIMS is its difficult quantification. The strong matrix dependence of the ionization probability $b_i^{\pm}$ (up to 5 orders of magnitude) is the main reason for the notorious difficulty of quantifying SIMS in a multicomponent matrix with varying composition. Because the sputter yield $Y_i$ is much less matrix dependent, ionization of practically all sputtered neutrals (i.e., $b_i^{\pm}$ approaching unity) would drastically reduce the matrix effect. Indeed, this is done in the so-called SNMS method, where the sputtered neutrals are ionized by a low voltage of plasma or an electron beam ("positonization") (Ref 30). The simplest way to achieve enhanced ionization is a direct-current glow discharge on the sample surface, which at the same time generates sputtered particles and ionizes them (GDMS method) (Ref 31).

A similar method that also uses a direct-current glow discharge is GDOES (Ref 32), where the excitation of optical emission is used as a means to analyze the sputtered species. As in GDMS, the main advantages are the high sputter rate due to the high current density and therefore the speed of thin-film depth profile analysis and high sensitivity. However, lack of spatial resolution and a generally lower depth resolution than with SIMS and SNMS are disadvantageous.

Table 1 compares the most important surface and thin-film analysis methods: AES, XPS, SIMS, and ISS, together with the generally non-UHV methods for thin-film analysis, RBS and GDOES.

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## Surface Analysis Applications

**Surface Adsorbates and Contamination.** The most obvious application of surface analysis methods is the study and control of the surface composition prior to further treatment, as in the production of thin-film structures in microelectronics (Ref 35) (see Fig. 8). Trace elements on flat, larger surfaces, for example silicon wafers, can be investigated with total reflection x-ray fluorescence spectroscopy at glancing incidence angle (Ref 7) with high sensitivity. Different chemical species can be observed. For example, the detection of residues after etching of a silicon surface with a ($CHF_3 + O_2$) plasma in semiconductor fabrication is enabled by the carbon 1*s* XPS spectrum, which allows the recognition of different peaks attributable to several compounds. Further $Ar^+$ ion etching removes the fluorine-containing compounds (Ref 35). Any kind of surface contamination can be detected. For example, friction and wear often is accompanied by transfer of materials from one part to the other, which can be monitored by surface analysis.

**Thin Film and Interface Analysis.** Analysis of internal interfaces with surface analysis methods can be principally performed in either of two ways: in-situ fracture of a sample along the interface (e.g., coating-substrate) and subsequent surface analysis of one or both parts (Ref 36, 37, 38), or by depth profiling through the interface (Ref 39, 40). A special method is angle lapping of the sample and taking a line scan across the interfacial region (Ref 3).

Coating-substrate interfaces are often prone to accumulation of impurities (e.g., by segregation or oxidation) that lead to a change in adhesive properties. These can be disclosed by a scratch test, by which a part of the interface is exposed due to peeling of the coating. For example, sulfur segregation was shown to have a detrimental effect on the adhesion of thin films, as determined by an in-situ scratch test in an AES instrument (Ref 41).

Whereas sputter depth profiling is a destructive method, nondestructive methods make use of the known energy-range relation of ions (RBS) or electrons (AES, XPS) in solids. A particularly important nondestructive method to disclose the in-depth distribution of composition is angular resolved XPS, which is, however, restricted to a probing depth of 2 to 3 times the electron attenuation length (i.e., to <5 nm for conventional XPS). By tilting the sample around an axis perpendicular to the analyzer axis and away from the latter, relatively more and more intensity from the species in the top layer is obtained as compared to deeper layers. An example is given in Fig. 10 for the determination of the thickness of an oxide layer ($Al_2O_3$) on aluminum. The peak area $I_{ox}$ of the Al-2*p* peak indicating $Al_2O_3$ (75.7 eV) increases relative to that of pure aluminum (72.3 eV, $I_{met}$) with increasing takeoff angle $\varphi$. The thickness $d$ of the $Al_2O_3$ layer is given by (Ref 42, 43, 44):

$$d = \lambda \cdot \sin\varphi \cdot \ln(1 + k \cdot I_{ox}/I_{met}) \qquad \textbf{(Eq 9)}$$

where $\lambda$ is the electron attenuation length (2.0 nm) and $k$ is a sensitivity correction factor of the order of unity. Figure 10(b) shows a plot of the ratio $I_{ox}/I_{met}$ from Fig. 10(a) as a function of the emission angle $\theta = 90° - \varphi$. Using a more general formulation of the angular dependence $I(\varphi)$ being a Laplace transform of $I(1/\lambda)$, more detailed layer profiles can be revealed, as shown by Bussing and Holloway (Ref 45) for the altered layer of sputtered Ga-As surfaces. Recently, multilayer samples were successfully studied by using grazing incidence XPS, which combines the low penetration depth of x-rays at $\varphi < 3°$ incidence angle to the surface (and its variation with $\varphi$) with all the XPS features (Ref 46).

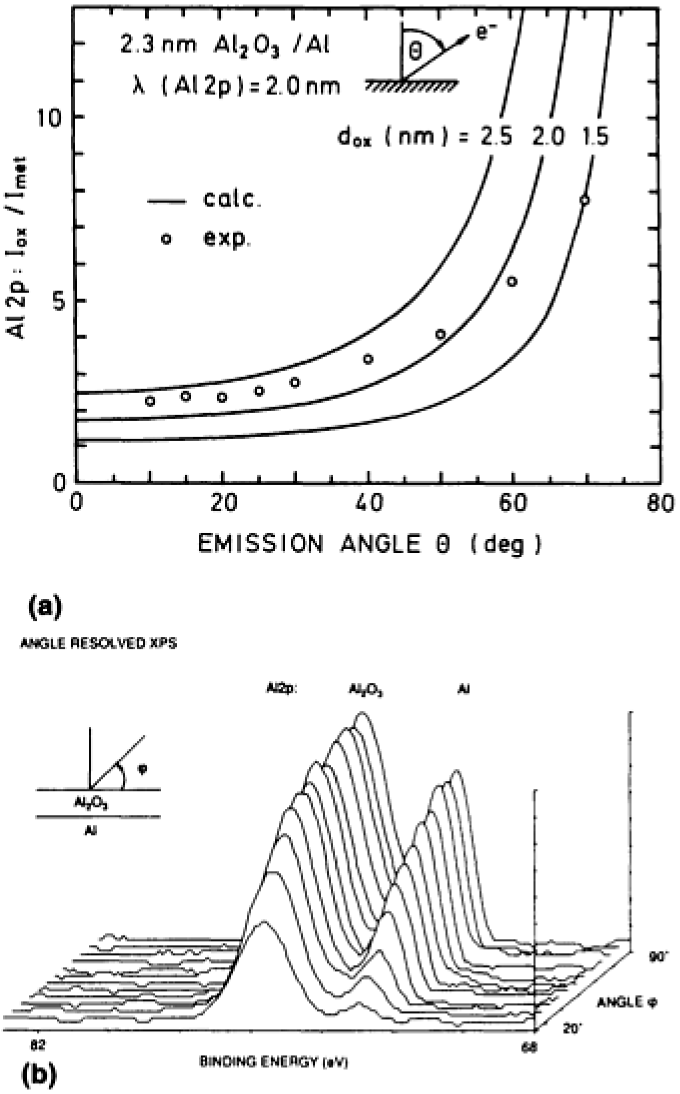


**Fig. 10 Angle-resolved x-ray photoelectron spectroscopy spectrum of a 2.3 nm thick $Al_2O_3$ layer on aluminum. (a) Al-2*p* peak as a function of the takeoff angle *j* . (b) Ratio of the peak areas of $Al_2O_3$ and aluminum as a function of the emission angle θ= 90° - *j* . Source: Ref 47**

Most common and straightforward is depth profiling by ion sputtering in combination with a surface analysis method. This technique discloses the elemental distribution as a function of the sputtered depth, including the composition of interfaces. Important is the attainment of a high depth resolution (Ref 3, 39, 47), which can be achieved by a rastered beam of $Ar^+$ ions with less than 3 keV energy, a small analyzed area, and a high angle of incidence (e.g., 70°) of the ion beam (Ref 39). Sample rotation during profiling has been shown to give optimum results with respect to high depth resolution (Ref 40, 48). With this technique, a depth resolution of $\Delta z = 6$ nm was achieved for Ni-Cr multilayer thin films (even at a sputtered depth of about 0.5 μm) employing AES and SIMS profiling in a study involving four laboratories (Ref 48).

SIMS depth profiling is particularly useful for determining dopant profiles (e.g., implantation profiles) in semiconductors or detecting impurity segregation at interfaces. The profile obtained from less than a monolayer ("delta layer") of aluminum in Ga-As is shown in Fig. 11 (Ref 49, 50), demonstrating the advantageous sensitivity and high depth resolution of SIMS. Other examples of thin-film depth analyses are given in previous sections of this article.

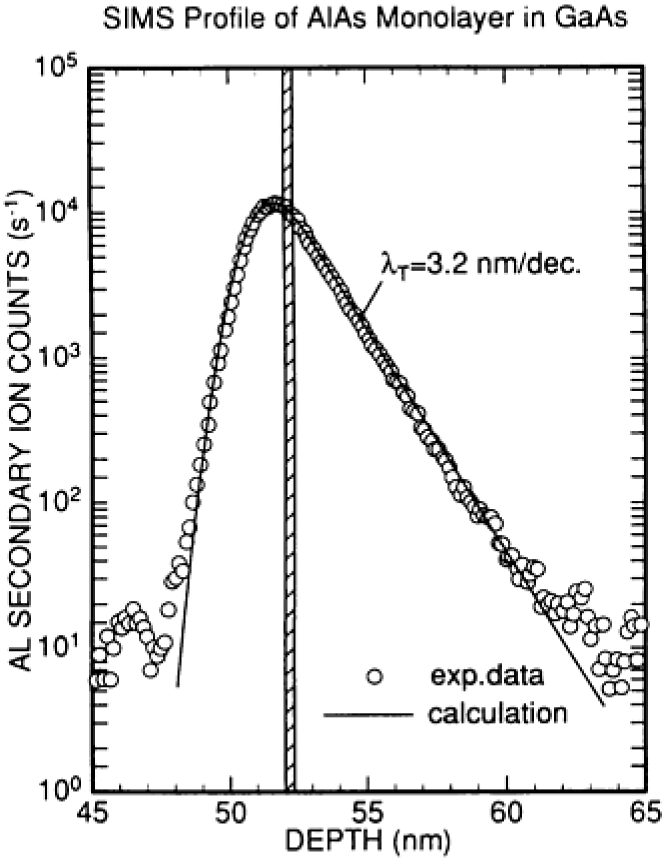
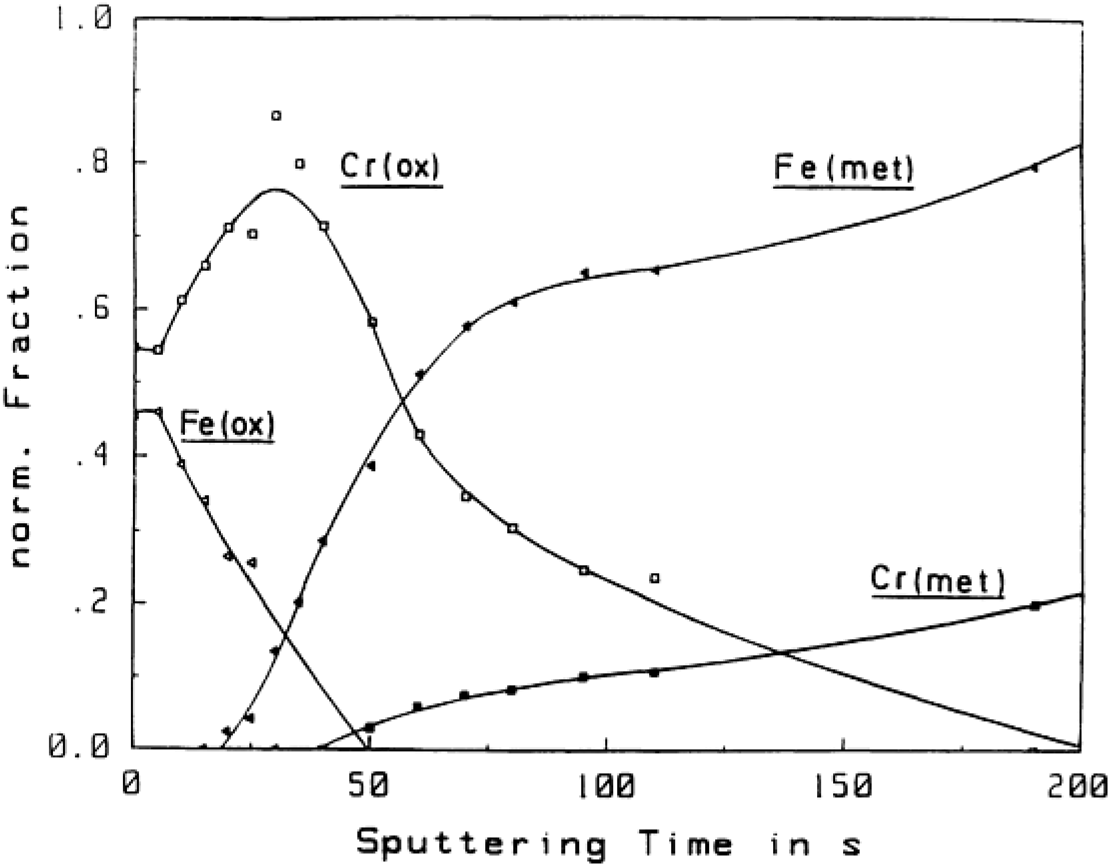
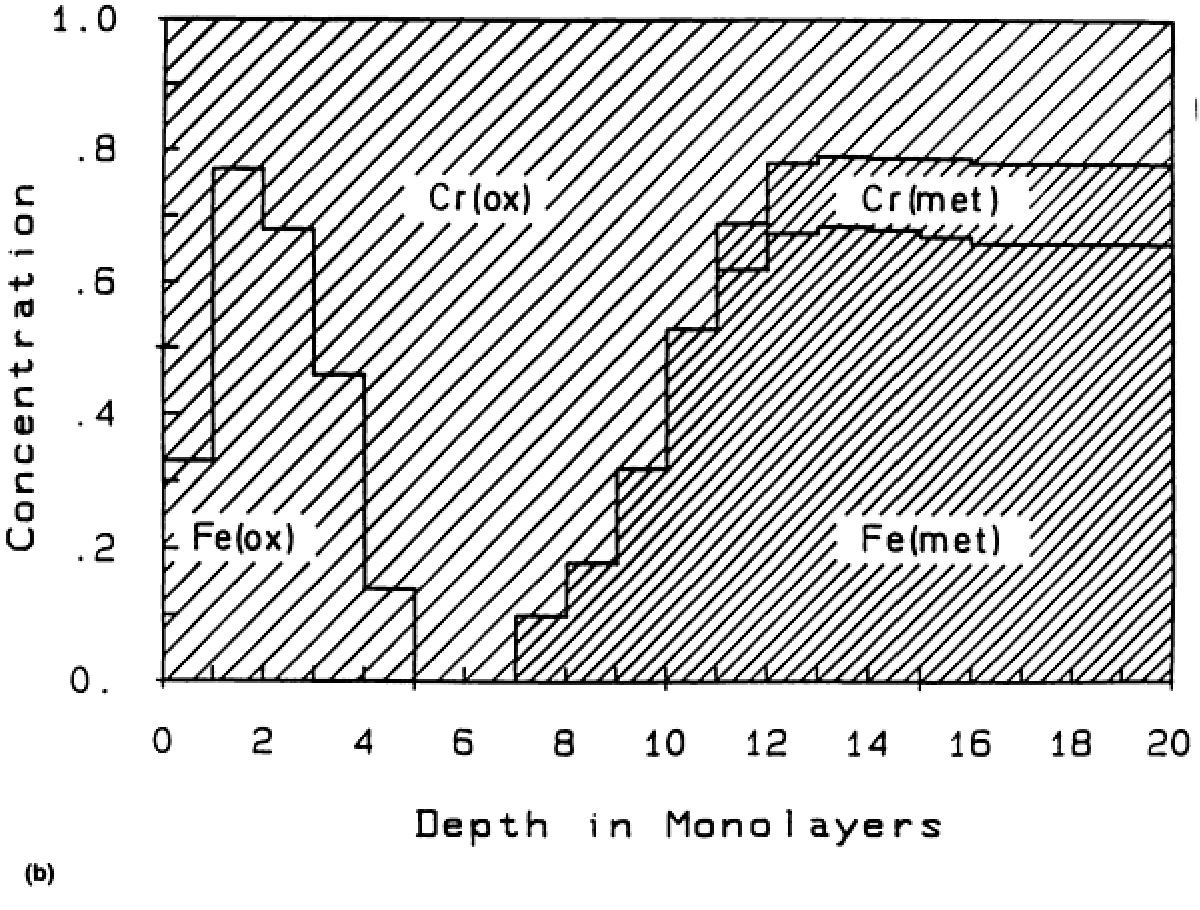


**Fig. 11 Secondary ion mass spectroscopy depth profile of an AlAs monolayer doping in GaAs. Comparison between measured points (circles) (Ref 49) and calculations (solid line). Source: Ref 50**

The result of chemical reactions at the gas-solid or liquid-solid interface often are specific layer structures, and further reaction behavior depends on their chemical composition. Passive layers on stainless steels (Ref 51) and oxide layers on different alloys and nitride coatings (Ref 52) have frequently been studied. An example of the composition of a passive layer on an Fe-Cr alloy is shown in Fig. 12. Figure 12(a) shows the AES depth profile obtained by using factor analysis and least-squares fitting of the four different standard spectra of metallic and oxidized iron and chromium (Ref 53). Figure 12(b) gives the result of a "convolution" procedure employed in order to calculate the original depth distribution (Fig. 12b) from the measured profile (Fig. 12a). Profile broadening schemes are used to account for the effects of sputtering and information depth influences on the assumed profile in Fig. 12(b) until an optimal fit with the profile in Fig. 12(a) is obtained (Ref 34, 39).



(a)



(b)

**Fig. 12 Depth profile of the chemical composition of a passive layer on an Fe-18at.%Cr alloy. (a) Normalized fractions of the standard components $Cr_{met}$, $Cr_{ox}$, $Fe_{met}$, and $Fe_{ox}$ in the Auger spectra as a function of the**

**sputtering time. (b) Concentrations of the alloy elements in metallic and oxidic states after fitting all fractions of the respective components with a sequential-layer sputtering model. Source: Ref 53**

High-resolution AES (i.e., scanning Auger microscopy) is another way to obtain the in-depth composition at interfaces by line scanning the focused electron beam (of ≤ 1 μm diameter) across the rim of the crater generated by sputter profiling (Ref 39, 54). An example of such a "crater edge profile" is shown in Fig. 13 for a TiN coating on a high-speed steel interface characterized by the iron Auger intensity (Ref 55). It is clearly seen, by comparison of the traces of the oxygen signal and the titanium signal, that oxygen varies with titanium and not with iron. This means that only titanium oxide, no iron oxide, is contained in the interface.

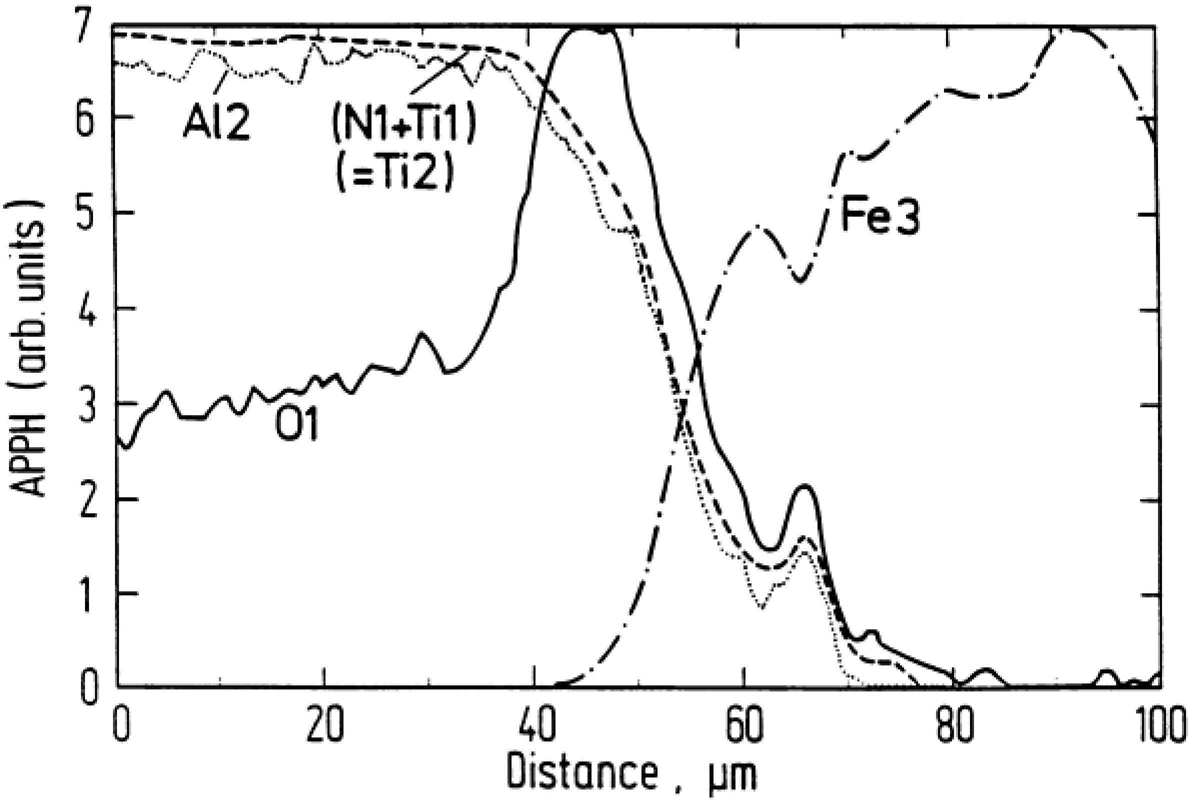
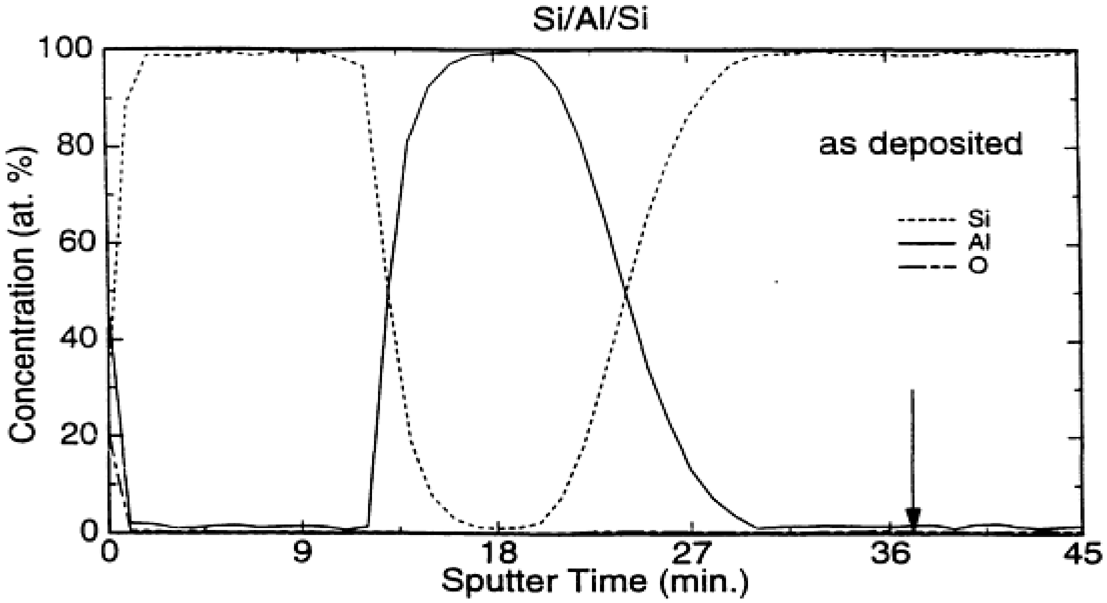


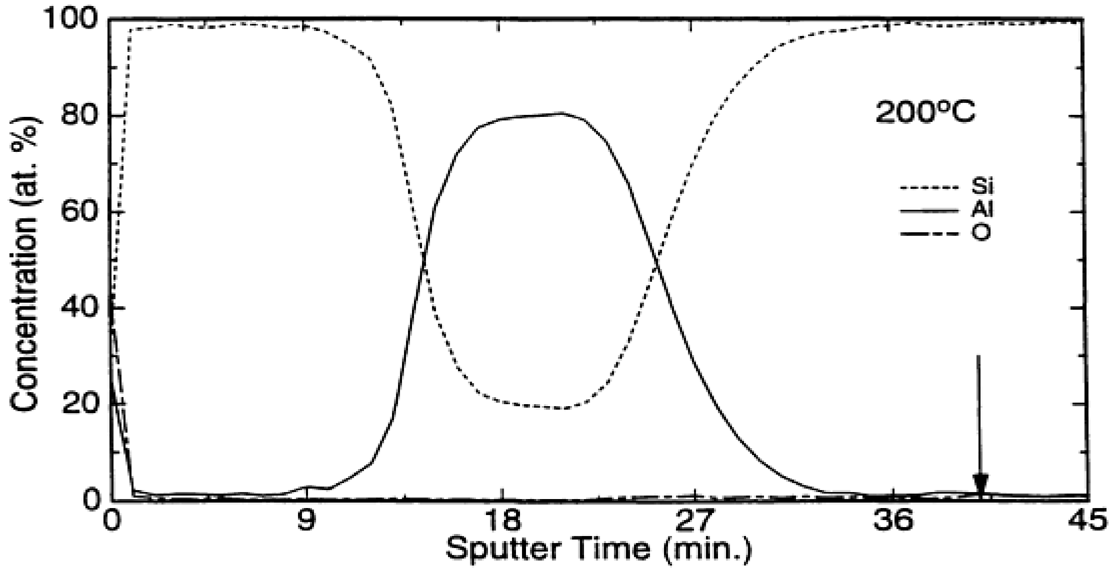
**Fig. 13 Oxide layer at the interface between an (Al,Ti)N coating and a high-speed steel substrate (Fe), disclosed by using crater edge profiling with scanning Auger microscopy. Source: Ref 54**

The chemical shift in XPS can be used to disclose different chemical bonding states at interfaces. For example, the two phases $ZrO_2$ and ZrN were found at the interface ZrN-Fe of a ZrN coating on a high-speed steel substrate (Ref 54). Another example is that different $SiO_x$ suboxides in the interface of ultrathin $SiO_2$ layers on silicon were disclosed by high-resolution XPS (Ref 56).

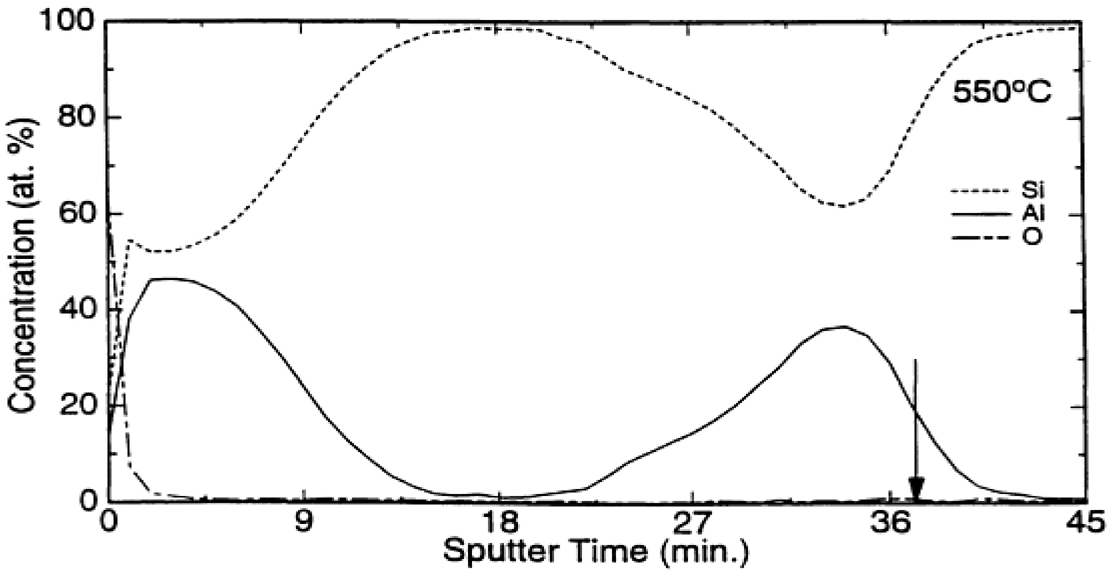
Reactions at interfaces can be directly studied by AES and XPS depth profiling. An example is shown in Fig. 14 for a thin-film structure of Si-Ni-Si (each layer about 50 nm thick) sputter deposited on a Si(111) substrate (Ref 57). Figure 14(a) shows the Auger depth profile for the as-deposited sample. Although the apparent interface width increases with depth, the small peak of oxygen at a sputtering time of about 9 min indicates the native $SiO_2$ layer of about 2 nm thickness on the silicon substrate. The shape of the profile after thermal treatment, with a linear temperature increase up to 205 °C at a heating rate of 40 °C/min, shows that mainly nickel was migrating into the adjacent silicon layers and that mainly a $Si_2Ni$ phase was formed, which was confirmed by selected area diffraction in TEM (Ref 57). Evaluating the increase of the measured interface width, $\Delta z = z\ (0.84\ I_0) - z\ (0.16 \cdot I_0)$, with increasing temperature, $T$, and time, $t$, $\Delta z(T) - \Delta z(T_0) \approx 2 \cdot (D \cdot t)^{1/2}$, allows determination of the interdiffusion constant, in this case $D = D_0 \cdot \exp(-Q/kT)$ with $D_0 = 2.5 \cdot 10^{-2}\ m^2/s$ and the activation energy $Q = 0.5$ eV (Ref 57). The error in this evaluation is mainly due to a change of the sputtering rate with composition (about +50% from pure nickel to pure silicon).


Si/Al/Si
as deposited
Si
Al
O
Concentration (at. %)
0
20
40
60
80
100
Sputter Time (min.)
0
9
18
27
36
45

(a)


200°C
Si
Al
O
Concentration (at. %)
0
20
40
60
80
100
Sputter Time (min.)
0
9
18
27
36
45

(b)


550°C
Si
Al
O
Concentration (at. %)
0
20
40
60
80
100
Sputter Time (min.)
0
9
18
27
36
45

(c)

**Fig. 14 Sandwich layer of 30 nm aluminum between two silicon layers, deposited on a silicon substrate, studied with Auger electron spectroscopy depth profiling. (a) As-deposited. (b) After heating to 200 °C. (c) After heating to 550 °C. Source: Ref 57**

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## Overview of Wear and Erosion Testing of Coatings

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### Introduction

WEAR AND EROSION TESTS have traditionally been used by materials engineers and scientists to optimize materials selection or development for a given application. Standardization, repeatability, convenience, short testing time, and simple measuring and ranking techniques are desirable in these tests. Currently, more demanding and complex methods of wear testing are being used by mechanical and reliability engineers to determine wear parameters that can project performance and establish the influence of various factors on these parameters.

Wear is closely related to friction and lubrication. The study of these three subjects is known as *tribology*. The apparatus used for one tribological test can frequently be used for another, but friction, wear, and lubrication are distinct phenomena, and test procedures and interpretations vary. For example, a lubricant test evaluates the ability of a lubricant to withstand temperature, speed, or load and still provide protection against wear. The degree or amount of wear is a measure of lubricant response. In contrast, the area of interest in a wear test, which can be conducted lubricated or dry, is the wear response of the material.

No general-purpose wear test exists that can establish a unique wear parameter or rating of a material. Consequently, a general discussion of wear testing must encompass overall methodology. This article presents a brief review of wear testing methods. Detailed information about significant wear mechanisms, tribological phenomena, and test methods appear in *Friction, Lubrication, and Wear Technology*, Volume 18 of the *ASM Handbook*, and in the article "Wear Testing" in *Mechanical Testing*, Volume 8 of the *ASM Handbook.*

## Acknowledgements

This article was adapted from R.G. Bayer, Wear Testing, *Mechanical Testing*, Vol 8, *ASM Handbook* (formerly 9th ed., *Metals Handbook*), 1985, p 601-608.

## Wear and Erosion Test Equipment

In the 1960s the American Society for Lubrication Engineers (ASLE) listed more than 200 types of wear tests and equipment in use (Ref 1), and the list has since grown. This wide variety is the result of a desire to ensure appropriate controls, make tests convenient, and simulate the wear conditions of the intended application.

The equipment described in Ref 2 includes apparatuses specifically designed for laboratory use. Although many of these test configurations are one-of-a-kind machines, others are available as commercial units.

Standards related to wear and erosion testing are listed in Ref 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, and 15. These standards do not suggest adequate test methods for wear or erosion resistance, but they relate to the testing of metals, plastics, refractory materials, and organic coatings. Reference 12 describes an abrasion tester that is essentially an air-blast erosion rig. Reference 13 describes an erosion tester that is similar but different in detail. References 14 and 15 describe air-blast erosion test rigs for coatings.

References 16, 17, 18, 19, 20, 21, 22, and 23 give design details of the three most commonly used erosion test rigs: air-blast rigs (Ref 16, 17, 18, 19 ), whirling arm rigs (Ref 20, 21, 22), and wind tunnel rigs (Ref 23). Reference 24 contains a general discussion of these erosion test methods.

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## Elements of a Wear Test

General elements of a wear test are simulation, acceleration, specimen preparation, control, measurement, and reporting. Simulation is the most critical, but no element of the application should be overlooked. Wear and wear phenomena can be influenced by load, environment, geometry, motion, the wearing mediums and counterface, and other factors.

**Simulation** ensures that the behavior experienced in the test is the same as in the application. Given the complexity of wear and the current incomplete understanding of wear and its phenomena, test development is subject to trial and error and is dependent on the capability of the developer. The ideal test exactly duplicates a wear situation. Generally, this is not practical, but any modifications in the test procedure should be carefully evaluated to obtain the most useful wear data.

General knowledge and experience can aid in assessing the differences between test and application, but correlations between test and application should also be studied. The most helpful correlation in developing a test is comparison of the worn surface and wear debris produced in the test to those produced in the application. For example, the morphology of the scar, the presence or absence of oxidized surface layers, changes in the microstructure of the material, and wear debris size, shape, and composition can be compared. If major features of the wear scar and debris are different, valid simulation is unlikely. Wear mechanisms frequently result in characteristic wear particles.

**Measurement.** Common direct measures of wear are mass or weight loss, volume loss or displacement, and scar width, depth, or other geometrical measures. Examples of indirect measures are the time required to wear through a coating, the load required to cause severe wear, and the load required to change surface reflectance. The selection of variables to measure wear is often based on convenience, the nature of the wear specimens, available techniques, and the amount of wear.

Material wear behavior can be compared by determining a wear curve or measuring wear at a single point in the test. Wear behavior frequently is complex, and a wear curve provides more information and allows evaluation of more complex behavior than single-point measurement. For example, the wear behaviors of two materials in the same test are plotted as functions of the number of sliding cycles (Fig. 1).

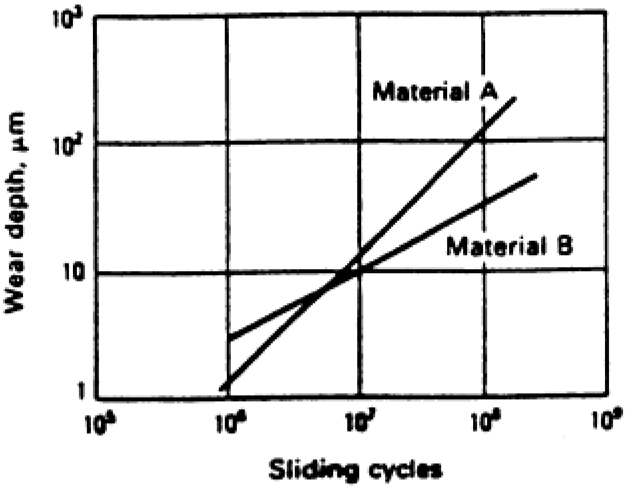

**Fig. 1 Wear behavior of two materials in the same test**

**Reporting.** Wear is a system response. When wear data are reported, a description of the wearing system must be supplied, including apparatus, geometry of contact, type of motion, load, speed, environmental condition, condition of wearing mediums, description of materials, description of lubricant and lubrication, description of wear-in period, and unusual observations, such as evidence of transfer.

## Surface Engineering of Cast Irons

**J.R. Davis, Davis & Associates**

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## Introduction

THE TERM "CAST IRON," like the term "steel," identifies a large family of ferrous alloys. Cast irons primarily are alloys of iron that contain more than 2% carbon and from 1 to 3% silicon. Wide variations in properties can be achieved by varying the balance between carbon and silicon, by alloying with various metallic or nonmetallic elements, and by varying melting, casting, and heat-treating practices.

Cast iron is produced by adding excess amounts of carbon to an austenite structure. During solidification, a portion of this carbon separates from the melt as either iron carbide or graphite. The form that the excess carbon takes is determined by the rate of cooling. If the cooling is rapid, the carbon will solidify as iron carbide. If the cooling is slow, the carbon will solidify as graphite. The type of carbon present and its shape will determine the type and, in particular, the properties of the cast iron.

Following a brief review of the classification and characteristics of cast irons, this article will review the processes used to clean iron castings as well as surface treatments used to extend casting life when resistance to corrosion, wear, and erosion is required. Additional information on the cleaning and coating processes described herein can be found in the cited articles appearing elsewhere in this Volume.

## Classification of Cast Irons

There are six basic types of cast irons and several varieties of each. The types of iron are classified as to how the excess carbon occurs in the microstructure. The correspondence between commercial and microstructural classification, as well as the final processing stage in obtaining common cast irons, is given in Table 1.

**Table 1 Classification of cast iron by commercial designation, microstructure, and fracture**

| **Commercial designation** | **Carbon-rich phase** | **Matrix**(a) | **Fracture** | **Final structure after** |
|---|---|---|---|---|
| Gray iron | Lamellar graphite | P | Gray | Solidification |
| Ductile iron | Spheroidal graphite | F,P,A | Silver-gray | Solidification or heat treatment |
| Compacted graphite iron | Compacted vermicular graphite | F,P | Gray | Solidification |
| White iron | $Fe_3C$ | P,M | White | Solidification and heat treatment(b) |
| Mottled iron | Lamellar Gr + $Fe_3C$ | P | Mottled | Solidification |
| Malleable iron | Temper graphite | F,P | Silver-gray | Heat treatment |
| Austempered ductile iron | Spheroidal graphite | At | Silver-gray | Heat treatment |

(a) F, ferrite; P, pearlite; A, austenite; M, martensite; At, austempered (bainite).

(b) White irons are not usually heat treated, except for stress relief and to continue austenite transformation.

**White iron** is essentially free of graphite, and most of the carbon content is present as separate grains of hard $Fe_3C$. White iron exhibits a white, crystalline fracture surface because fracture occurs along the iron carbide plates. White cast iron contains 2.0 to 3.6% C and 0.5 to 2.0% Si with high-alloy grades containing as much as 7% Ni, 28% Cr, and 3.5% Mo.

White cast irons have high compressive strength and good retentions of strength and hardness at elevated temperature, but they are most often used for their excellent resistance to wear and abrasion. The massive carbides in the microstructure are chiefly responsible for these properties.

**Malleable iron** contains compact nodules of graphite flakes. These are called "temper carbon" because they form during an extended annealing of white iron of a suitable composition. Malleable cast iron contains 2.2 to 2.9% C and 0.9 to 1.9% Si. Tensile strengths can range from 275 MPa (40 ksi) to 725 MPa (105 ksi).

**Gray iron,** the most commonly used cast iron, contains carbon in the form of graphite flakes. Gray iron exhibits a gray fracture surface because fracture occurs along the graphite plates (flakes). Gray irons usually contain 2.5 to 4.0% C, 1 to 3% Si, and 0.1 to 1.2% Mn. Tensile strengths range from 140 to 415 MPa (20 to 60 ksi) with higher strengths possible in high-alloy gray irons.

Gray cast iron has several unique properties that are derived from the existence of flake graphite in the microstructure. Gray iron can be machined easily at hardnesses conducive to good wear resistance. It resists galling under boundary-lubrication conditions (conditions wherein the flow of lubricant is insufficient to maintain a full fluid film). It has outstanding properties for applications involving vibrational damping or moderate thermal shock.

**Ductile iron,** also known as spheroidal graphite or nodular iron, contains spherulitic graphite in which the graphite flakes form into balls as do cabbage leaves. Ductile iron is so named because in the as-cast form it exhibits measurable ductility. Ductile iron typically contains 3 to 4% C, 1.8 to 2.8% Si, and 0.1 to 1.0% Mn. Alloying additions are sometimes made to ductile irons to improve heat and corrosion resistance. These alloyed grades may contain 1 to 6% Si, 0.7 to 2.4% Mn, 18 to 36% Ni, and up to 5.5% Cr.

The chief advantage of ductile iron over gray iron is its combination of high strength and ductility--up to 18% minimum elongation for ferritic ductile iron with a tensile strength of 415 MPa (60 ksi) as opposed to only about 0.6% elongation for a gray iron of comparable strength. Martensitic ductile irons with tensile strengths of about 830 MPa (120 ksi) exhibit at least 2% elongation.

**Austempered Ductile Iron.** If ductile iron is austenitized and quenched in a salt bath or a hot oil transformation bath at a temperature of 320 to 550 °C (610 to 1020 °F) and held at this temperature, transformation to a structure containing mainly bainite with a minor proportion of austenite takes place (Fig. 1). Irons that are transformed in this manner are referred to as austempered ductile irons. Austempering generates a range of structures, depending on the time of transformation and the temperature of the transformation bath. The properties are characterized by very high strength, some ductility and toughness, and often an ability to work harden, giving appreciably higher wear resistance than that of other ductile irons. Austempered ductile irons exhibit in excess of 5% elongation at tensile strengths exceeding 1000 MPa (145 ksi).

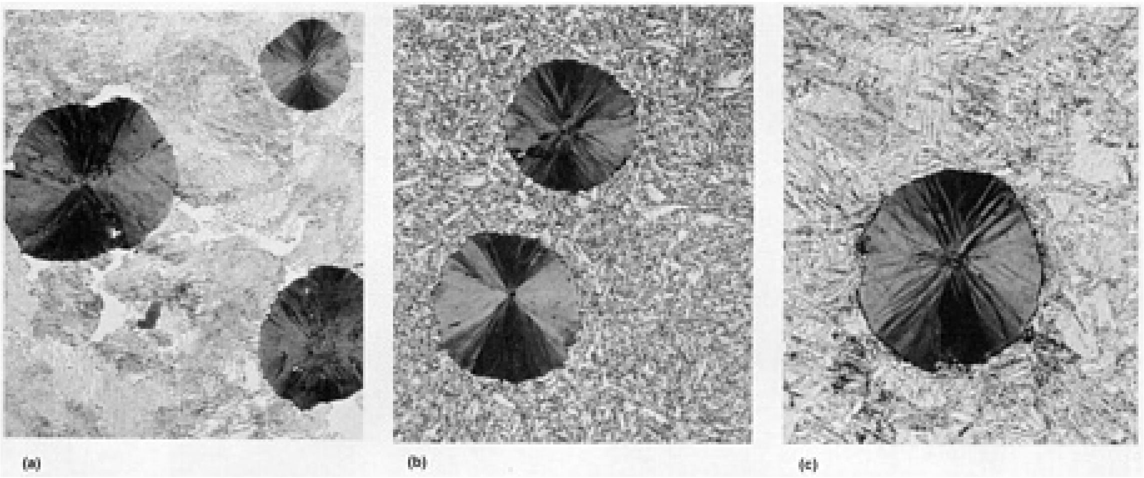

**Fig. 1 Comparison of ductile iron microstructures. (a) Microstructure of normalized ductile iron showing pearlite matrix. (b) Microstructure (tempered martensite) of hardened-and-tempered ductile iron. (c) Microstructure of austempered ductile iron showing matrix of upper bainite and retained austenite. All etched in picral. 500×**

**Compacted graphite (CG),** or vermicular graphite, irons have structures and properties that are in between those of gray irons and ductile irons. The graphite forms interconnected flakes as in a gray iron, but the flakes are shorter and thicker. The CG irons contain 2.5 to 4.0% C, 1.0 to 3.0% Si, with manganese contents varying between 0.1 and 0.6%, depending on whether a ferritic or pearlitic structure is desired.

**High-alloy iron** contains over three percent alloy content and is commercially classified separately. As indicated above, high-alloy irons may be a type of white iron, gray iron, or ductile iron. The matrix may be ferritic, pearlitic, martensitic, or austenitic, depending upon which alloying element dominates the composition. Table 2 lists approximate ranges of alloy content for various types of alloy cast irons used for abrasion-resistant, corrosion-resistant, and heat-resistant applications.

**Table 2 Ranges of alloy content for various types of alloy cast irons**

| Description | Composition, wt%(a) | | | | | | | | | Matrix structure, as-cast(c) |
|---|---|---|---|---|---|---|---|---|---|---|
| | TC(b) | Mn | P | S | Si | Ni | Cr | Mo | Cu | |
| **Abrasion-resistant white irons** | | | | | | | | | | |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Low-carbon white iron(d) | 2.2-2.8 | 0.2-0.6 | 0.15 | 0.15 | 1.0-1.6 | 1.5 | 1.0 | 0.5 | (e) | CP |
| High-carbon, low-silicon white iron | 2.8-3.6 | 0.3-2.0 | 0.30 | 0.15 | 0.3-1.0 | 2.5 | 3.0 | 1.0 | (e) | CP |
| Martensitic nickel-chromium iron | 2.5-3.7 | 1.3 | 0.30 | 0.15 | 0.8 | 2.7-5.0 | 1.1-4.0 | 1.0 | . . . | M,A |
| Martensitic nickel, high-chromium iron | 2.5-3.6 | 1.3 | 0.10 | 0.15 | 1.0-2.2 | 5-7 | 7-11 | 1.0 | . . . | M,A |
| Martensitic chromium-molybdenum iron | 2.0-3.6 | 0.5-1.5 | 0.10 | 0.06 | 1.0 | 1.5 | 11-23 | 0.5-3.5 | 1.2 | M,A |
| High-chromium iron | 2.3-3.0 | 0.5-1.5 | 0.10 | 0.06 | 1.0 | 1.5 | 23-28 | 1.5 | 1.2 | M |
| **Corrosion-resistant irons** | | | | | | | | | | |
| High-silicon iron(f) | 0.4-1.1 | 1.5 | 0.15 | 0.15 | 14-17 | . . . | 5.0 | 1.0 | 0.5 | F |
| High-chromium iron | 1.2-4.0 | 0.3-1.5 | 0.15 | 0.15 | 0.5-3.0 | 5.0 | 12-35 | 4.0 | 3.0 | M,A |
| Nickel-chromium gray iron(g) | 3.0 | 0.5-1.5 | 0.08 | 0.12 | 1.0-2.8 | 13.5-36 | 1.5-6.0 | 1.0 | 7.5 | A |
| Nickel-chromium ductile iron(h) | 3.0 | 0.7-4.5 | 0.08 | 0.12 | 1.0-3.0 | 18-36 | 1.0-5.5 | 1.0 | . . . | A |
| **Heat-resistant gray irons** | | | | | | | | | | |
| Medium-silicon iron(i) | 1.6-2.5 | 0.4-0.8 | 0.30 | 0.10 | 4.0-7.0 | . . . | . . . | . . . | . . . | F |
| Nickel-chromium iron(g) | 1.8-3.0 | 0.4-1.5 | 0.15 | 0.15 | 1.0-2.75 | 13.5-36 | 1.8-6.0 | 1.0 | 7.5 | A |
| Nickel-chromium-silicon iron(j) | 1.8-2.6 | 0.4-1.0 | 0.10 | 0.10 | 5.0-6.0 | 13-43 | 1.8-5.5 | 1.0 | 10.0 | A |
| High-aluminum iron | 1.3-2.0 | 0.4-1.0 | 0.15 | 0.15 | 1.3-6.0 | . . . | 20-25 Al | . . . | . . . | F |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| **Heat-resistant ductile irons** | | | | | | | | | | |
| Medium-silicon ductile iron | 2.8-3.8 | 0.2-0.6 | 0.08 | 0.12 | 2.5-6.0 | 1.5 | . . . | 2.0 | . . . | F |
| Nickel-chromium ductile iron(h) | 3.0 | 0.7-2.4 | 0.08 | 0.12 | 1.75-5.5 | 18-36 | 1.75-3.5 | 1.0 | . . . | A |
| **Heat-resistant white irons** | | | | | | | | | | |
| Ferritic grade | 1-2.5 | 0.3-1.5 | . . . | . . . | 0.5-2.5 | . . . | 30-35 | . . . | . . . | F |
| Austenitic grade | 1-2.0 | 0.3-1.5 | . . . | . . . | 0.5-2.5 | 10-15 | 15-30 | . . . | . . . | A |

(a) Where a single value is given rather than a range, that value is a maximum limit.

(b) Total carbon.

(c) CP, coarse pearlite; M, martensite; A, austenite; F, ferrite.

(d) Can be produced from a malleable-iron base composition.

(e) Copper can replace all or part of the nickel.

(f) Such as Duriron, Durichlor 51, Superchlor.

(g) Such as Ni-Resist austenitic iron (ASTM A 436).

(h) Such as Ni-Resist austenitic ductile iron (ASTM A 439).

(i) Such as Silal.

(j) Such as Nicrosilal

## Cleaning of Castings

Cleaning of the surface is the most important prerequisite of any coating process. Suitable levels of cleanliness and surface roughness are established by various mechanical and nonmechanical methods. Foundries deliver castings that have been shot or grit blasted (see the discussion on blast cleaning below). Supplementary nonmechanical cleaning may be needed to reach interior passages or to remove heat-treating scale or machining oil.

The choice of cleaning process depends not only on the types of soils to be removed but also on the characteristics of the coating to be applied. The cleaning process must leave the surface in a condition that is compatible with the coating process. For example, if a casting is to be treated with phosphate and then painted, the cleaning process must remove all oils and oxide scale because these inhibit good phosphating.

If castings are heat treated before they are coated, the choice of heat treatment conditions can influence the properties of the coating, particularly a metallic or conversion coating. In most cases, heat treatment should be done in an atmosphere that is not oxidizing. Oxides and silicates formed during heat treating must be removed before most coating processes.

### *Mechanical Cleaning and Finishing*

Mechanical cleaning and finishing methods most commonly employed for processing iron castings include abrasive blast cleaning (the most commonly used method for cleaning cast irons), abrasive waterjet cleaning and finishing, vibratory finishing, barrel finishing, and shot peening.

**Blast cleaning** of castings is a process in which abrasive particles are propelled at high velocity to impact the casting surface and thereby forcefully remove surface contaminants. The contaminants are usually adhering mold sand, burned-in sand, heat treat scale, and the like.

The usual methods of imparting high velocity to abrasive particles are by the use of either centrifugal wheels (Fig. 2) or compressed air nozzles. Centrifugal wheels are the most widely used method because of their ability to propel large volumes of abrasive efficiently. For example, a 56 kW (75 hp) centrifugal wheel can accelerate steel shot to 73 m/s (240 ft/s) at 55,800 kg/h (123,000 lb/h) flow. To do the same with 13 mm ($\frac{1}{2}$ in.) direct pressure venturi nozzles at 45 kg (100 lb)/min per nozzle would require approximately 20 nozzles and an air flow of 0.120 $m^3$/s/nozzle (260 $ft^3$/min/nozzle) × 20, or a total of 2.45 $m^3$/s (5200 $ft^3$/min) at 550 kPa (80 psi). Approximately 700 kW (940 hp) at the air compressor would be required to supply this amount of air, which gives a 700 kW/56 kW = 12.5 to 1 (940 hp/75 hp = 12.5 to 1) efficiency advantage for the centrifugal wheel.

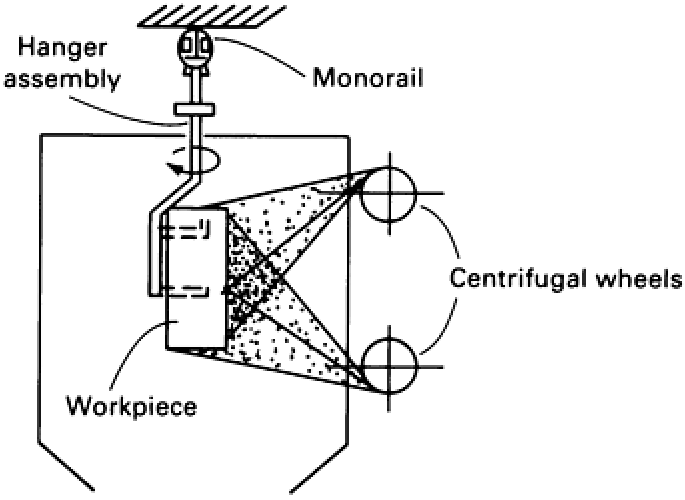

**Fig. 2 Front view of a typical rotating hanger blast cleaning assembly. The workpiece is rotated 360° as it is held in position on the monorail track to provide full coverage by the blast pattern produced by the centrifugal wheels.**

Even though the nozzle blast is not as efficient overall as the wheel blast, in some applications it may be more efficient because the blast stream can be more efficiently applied, when, for example, blasting into small holes to clean the interior areas of a casting. Other reasons for using a nozzle blast are requirements for:

- Low production
- Portability

- Suitability for very hard abrasives, such as aluminum oxide

More detailed information on the selection and design of blast cleaning equipment can be found in Ref 1 and the article "Mechanical Cleaning Systems" in this Volume.

In the past, chilled iron grit and malleable abrasives were used. Today, however, practically all the shot and grit used is high-carbon cast steel that is heat treated and drawn to give a desired tempered martensite microstructure and hardness. The hardness range of the most commonly used shot and grit is HRC 40 to 50. Harder shot and grit are also produced, with a range of HRC 55 to 65. For faster cleaning or special surface finish requirements, hard abrasive is not often used; but when it is, the wear on machine parts is high, and the abrasive breakdown rate is more rapid. This is especially true of hard grit. Table 3 lists commercially available shot and grit sizes.

**Table 3 Society of Automotive Engineers shot and grit size specifications for abrasive blast cleaning**

| | **High-limit screen** | | | **Nominal screen** | | | **Low-limit screen** | |
|---|---|---|---|---|---|---|---|---|
| | **Maximum % retained** | **Screen number and aperture (in.)** | **Maximum % retained** | **Screen number and aperture (in.)** | **Minimum % retained** | **Screen number and aperture (in.)** | **Minimum % retained** | **Screen number and aperture (in.)** |
| **Shot number** | | | | | | | | |
| S-780 | 1 | 7 (0.111) | . . . | . . . | 85 | 10 (0.0787) | 97 | 12 (0.0661) |
| S-660 | 1 | 8 (0.0937) | . . . | . . . | 85 | 12 (0.0661) | 97 | 14 (0.0555) |
| S-550 | 1 | 10 (0.0787) | . . . | . . . | 85 | 14 (0.0555) | 97 | 16 (0.0469) |
| S-460 | 1 | 10 (0.0787) | 5 | 12 (0.0661) | 85 | 16 (0.0469) | 96 | 18 (0.0394) |
| S-390 | 1 | 12 (0.0661) | 5 | 14 (0.0555) | 85 | 18 (0.0394) | 96 | 20 (0.0331) |
| S-330 | 1 | 14 (0.0555) | 5 | 16 (0.0469) | 85 | 20 (0.0331) | 96 | 25 (0.0280) |
| S-280 | 1 | 16 (0.0469) | 5 | 18 (0.0394) | 85 | 25 (0.0280) | 96 | 30 (0.0232) |
| S-230 | 1 | 18 (0.0394) | 10 | 20 (0.0331) | 85 | 30 (0.0232) | 97 | 35 (0.0197) |
| S-170 | 1 | 20 (0.0331) | 10 | 25 (0.0280) | 85 | 40 (0.0165) | 97 | 45 (0.0138) |

|  |  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|
| S-110 | All pass | 30 (0.0232) | 10 | 35 (0.0197) | 80 | 50 (0.0117) | 90 | 80 (0.0070) |
| S-70 | All pass | 40 (0.0165) | 10 | 45 (0.0138) | 80 | 80 (0.0070) | 90 | 120 (0.0049) |
| **Grit number** |  |  |  |  |  |  |  |  |
| G-10 | 1 | 7 (0.111) | . . . | . . . | 80 | 10 (0.0787) | 90 | 12 (0.0661) |
| G-12 | 1 | 8 (0.0937) | . . . | . . . | 80 | 12 (0.0661) | 90 | 14 (0.0555) |
| G-14 | 1 | 10 (0.0787) | . . . | . . . | 80 | 14 (0.0555) | 90 | 16 (0.0469) |
| G-16 | 1 | 12 (0.0661) | . . . | . . . | 75 | 16 (0.0469) | 85 | 18 (0.0394) |
| G-18 | 1 | 14 (0.0555) | . . . | . . . | 75 | 18 (0.0394) | 85 | 25 (0.0280) |
| G-25 | 1 | 16 (0.0469) | . . . | . . . | 70 | 25 (0.0280) | 80 | 40 (0.0165) |
| G-40 | 1 | 18 (0.0394) | . . . | . . . | 70 | 40 (0.0165) | 80 | 50 (0.0117) |
| G-50 | 1 | 25 (0.0280) | . . . | . . . | 65 | 50 (0.0117) | 75 | 80 (0.0070) |
| G-80 | All pass | 40 (0.0165) | . . . | . . . | 65 | 80 (0.0070) | 75 | 120 (0.0049) |
| G-120 | All pass | 50 (0.0117) | . . . | . . . | 60 | 120 (0.0049) | 70 | 200 (0.0029) |
| G-200 | All pass | 80 (0.0070) | . . . | . . . | 55 | 200 (0.0029) | 65 | 325 (0.0017) |

Making a choice between shot and grit depends on the surface contaminants or the surface texture required. Grit is used when a chiselling action is required, for example, when removing rust, or perhaps to help remove burned-in sand or provide a good bonding surface for painting, plating, or enameling. Hard grit is used to clean the surface of bathtubs prior to enameling, where a definite tooth is required on the casting surface to provide for better adhesion of the enamel. In some cleaning applications, a shot and grit mixture may be used.

**Abrasive Waterjet Cleaning.** Although most often used as a cutting or machining process, the abrasive waterjet process has been tested for its use in degating and defining castings, as well as burn-in removal from castings. High-pressure waterjets (without abrasives) have also been tested for cleaning hydraulic passageways in castings. Using this process, coherent fluid jet is formed by forcing high-pressure 200 to 400 abrasive-laden water through a tiny sapphire orifice. The accelerated jet exiting the nozzle travels at more than twice the speed of sound and impinges on the workpiece. Results from a study from a foundry producing castings used in lawn, garden, and farm equipment are given in Ref 2. Detailed information on the use of abrasive waterjets for cutting metals and nonmetals can be found in Ref 3 and 4.

**A vibratory finishing machine** is an open-topped tub or bowl mounted on springs, usually lined with polyurethane. Parts and media are loaded in a fashion similar to that of a tumbling barrel (see the discussion on barrel finishing which immediately follows). With a vibratory machine, the container can be almost completely filled. Vibratory action is created either by a vibratory motor attached to the bottom of the container, by a shaft or shafts with eccentric loads driven by a standard motor, or by a system of electromagnets operating at 50 or 60 Hz. The action of media against components takes place throughout the load, so that process cycles are substantially shorter than conventional tumbling in barrels.

Vibratory finishing is used to clean the internal passages of cast iron cylinder heads and engine blocks. The internal passages of such components are rather intricate and it is usually difficult to reach all surface areas from any externally propelled form of cleaning. High pressure water, air blast, and shot blasting all would clean the internal surface areas that were located near an external opening; however, most of the internal passageways are hidden from this method of cleaning. Therefore, the vibratory media cleaner was introduced to clean these passages (Ref 5).

The media enters the internal passageways of the castings under the vibration of the vibratory machine and literally scrubs the surface walls of the internal cavities. The in-and-out movement of the media also carries core wash and sand from the internal passages of the castings, allowing removal of the material and providing a clean casting. Additional information on vibratory finishing can be found in the article "Mechanical Cleaning Systems" in this Volume.

**Barrel Finishing.** The rotary barrel, or tumbling barrel, utilizes the sliding movement of an upper layer of workload in the tumbling barrel, as shown in Fig. 3. The barrel is normally loaded about 60% full with a mixture of parts, media, compound, and water. As the barrel rotates, the load moves upward to a turnover point; then the force of gravity overcomes the tendency of the mass to stick together, and the top layer slides toward the lower area of the barrel. The rotation of the barrel causes the abrasive medium to scour the casting surfaces. Scale, sand, and even fins can be affectively removed during tumbling. Additional information on barrel finishing can be found in the article "Mechanical Cleaning Systems" in this Volume.

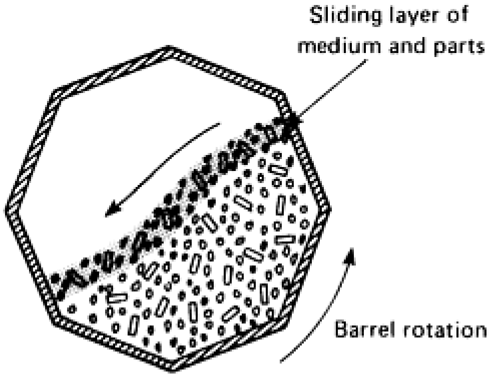

**Fig. 3 Action of media and parts within a rotating barrel**

**Shot peening** is a method of cold working in which compressive stresses are induced in the exposed surface layers of cast iron parts by the impingement of a stream of steel shot, directed at the surface at high velocity under controlled conditions. It differs from blast cleaning in primary purpose and in the extent to which it is controlled to yield accurate and reproducible results. Although shot peening cleans the surface being peened, this function is incidental. The major purpose of shot peening is to increase fatigue strength.

Both the benefits in improved fatigue strength and increased surface hardness have been shown in studies on shot peened austempered ductile iron gears (Ref 6). In cases where severe grinding operations are performed on a gear, resultant surface tensile stresses can have a negative impact on part endurance. Peening after the grinding operation can increase the endurance limit even above the original gentle grind design condition, as shown in Fig. 4.

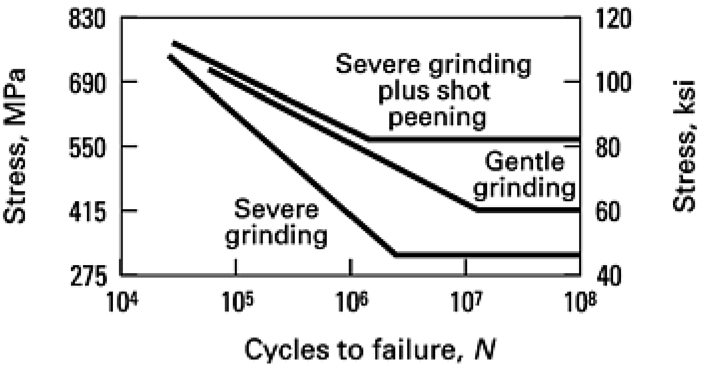

**Fig. 4 Effect of shot peening on the fatigue strength of a ground component. A part designed for a gentle grinding operation could be salvaged by shot peening after a severe grinding operation. Source: Ref 6**

When fatigue problems occur, one of the solutions is to eliminate stress risers in the part by polishing or other surface refining process. Though the stress riser in the material tends to be reduced, any subsequent scarring of the surface in application can greatly reduce any benefits of the polishing operation. Costs to produce a surface finish finer than a 125 rms will usually increase substantially.

Instead of polishing the surface, shot peening will produce a compressed stress layer below the surface of the material that will prevent crack propagation and increase fatigue strength. Not only can this be used as a salvage technique, but it can be used as a cost reducer by eliminating the need for the added polishing costs.

In cases where uniform casting texturing is required, the controls used in the peening process can impart a finish that is homogenous in appearance. In this situation, the benefits of the compressive stress to produce improved fatigue strength may not be critical, and surface texture selection will most likely determine shot size and application intensity.

To retain the fatigue strength benefits produced by peening, no more than 10% of the depth of compression can be removed by the subsequent machining operation. Shot peening should be performed after heat treating so that the compressive stresses and reduction of fatigue strength are not dissipated as heat treating temperature approaches stress relieving temperature.

### *Nonmechanical Cleaning*

Nonmechanical cleaning methods applicable to cast irons include molten salt bath cleaning, pickling, and chemical cleaning with the latter method including acid cleaning, solvent cleaning, vapor degreasing, and emulsion cleaning. Articles on each of the aforementioned processes can be found in the Section on "Surface Cleaning" in this Volume.

**Molten salt baths** are excellent for cleaning complex interior passages in castings. In one electrolytic, molten salt cleaning process, the electrode potential is changed so that the salt bath is alternately oxidizing and reducing. Scale and graphite are easily removed with reducing and oxidizing baths, respectively. Molten salt baths are fast compared to other nonmechanical methods, but castings may crack if they are still hot when salt residues are rinsed off with water.

**Pickling** of cast iron is usually done prior to hot dip coating or electroplating. When pickling is used, the castings are cleaned in solutions containing sulfuric and hydrofluoric acids. The concentration of each acid depends on whether the primary purpose is to remove sand or scale. Increased hydrofluoric acid is needed to remove embedded sand from the casting surface, whereas sulfuric or hydrochloric acids are sufficient for simple scale removal. Table 4 gives the operating conditions for pickling iron castings. Before being pickled, castings must be free of oil, grease, and other contamination. After being removed from the pickling solution, castings are rinsed thoroughly in hot water. Residual heat permits self-drying, but drying may be accelerated by the use of fans. For complex shaped castings, baking ovens may be employed.

**Table 4 Operating conditions and solution compositions for pickling cast irons**

| Operating | Sand | Scale |
|---|---|---|

| variable | removal | removal |
|---|---|---|
| Sulfuric acid, vol% | 5 | 7 |
| Hydrofluoric acid, vol% | 5 | 3 |
| Water, vol% | 90 | 90 |
| Temperature[(a)], °C (°F) | 65-85 (150-185) | 50 to over 85 (120 to over 185) |
| Average immersion time, h | 4 | 4 |

(a) 50 °C (120 °F) is for slow pickling, 65 to 85 °C (150 to 185 °F) for average pickling speed, and over 85 °C (185 °F) is for fast pickling.

**Acid cleaning** is a process in which a solution of a mineral acid, organic acid, or acid salt, in combination with a wetting agent and detergent, is used to remove oxide, shop soil, oil, grease, and other contaminants from metal surfaces, with or without the application of heat. The distinction between acid cleaning and acid pickling is a matter of degree, and some overlapping in the use of these terms occurs. Acid pickling is a more severe treatment for the removal of scale from castings, whereas acid cleaning generally refers to the use of acid solutions for final or near-final preparation of metal surfaces before plating, painting, or storage.

Mixtures of 70 wt% phosphoric acid, 5 wt% ethylene glycol monobutyl ether, and 25 wt% water are used for removing grease, oil, drawing compounds, and light rust from iron and steel. This mixture is adaptable to immersion, spray, or wiping methods and leaves a light phosphate coating (100 to 320 $mg/m^2$, or 10 to 30 $mg/ft^2$) that provides a paint base or temporary resistance to rusting if the parts are to be stored.

Acid solutions of 40 to 60 vol% hydrochloric or 6 to 8 vol% sulfuric (often containing up to 1% inhibitor) are used at room temperature for removing soil and light rust. Stronger solutions of these acids are used in electrolytic baths for final cleaning of cast irons before electroplating. Various soils, including light rust, may also be removed by combining acid cleaning and barrel finishing.

**Other Chemical Cleaning Methods.** Organic solvents that were commonly used in the past include naphtha, benzene, methanol, toluene, and carbon tetrachloride. These have been largely replaced by chlorinated solvents, such as those used for vapor degreasing. Solvents effectively remove lubricants, cutting oils, and coolants, but are ineffective against such inorganic compounds such as oxides or salts. Emulsion cleaners are solvents combined with surfactants; they disperse contaminants and solids by emulsification. Emulsion cleaners are most effective against heavy oils, greases, slushes, and solids entrained in hydrocarbon films. They are relatively ineffective against adherent solids such as oxide scale.

After wet cleaning, short-term rust prevention is accomplished by the use of an alkaline rinse. This can be followed by the application of mineral oils, solvents combined with inhibitors and film formers, emulsions of petroleum-base coatings and water, and waxes. A summary of the temporary coatings used for corrosion protection is given in Table 5.

### Table 5 Temporary coatings used for corrosion protection

| Type | Coating structure | Thickness, μm (mils) | Removal method | Uses |
|---|---|---|---|---|

|  |  |  |  |  |
|---|---|---|---|---|
| Oil | Non-drying mineral oil viscosity determines coating thickness | 5-7 (0.2-0.3) | Seldom required; solvent rinsing, emulsion spray, or vapor degreasing | Finished automotive parts; galvanized irons |
| Solvent | Petroleum-based inhibitors and film formers dissolved in petroleum solvents | 5-50 (0.2-2.0) | Seldom required; solvent rinsing or alkaline washing | External surfaces of machinery parts and tooling. Can be used outdoors |
| Emulsified | Petroleum-based coating modified to form a stable emulsion with water | 5 (0.2) | Removal seldom necessary; solvent rinsing | Same as above, but suggested for indoor use |
| Wax | Wax layer applied heated or in a volatile solvent | 38-75 (1.5-3.0) | Solvent rinsing or alkaline cleaning | Highly finished parts stored for prolonged periods |

Source: Ref 7

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## Electroplating and Electroless Plating

Cast irons are most commonly plated with chromium, nickel, copper, cadmium, and zinc. In addition, gold, lead, and rhodium are used for specialized applications. Alloy coatings, such as brass, bronze, and tin-base compositions, are used for decorative purposes. As shown in Table 6, each electroplated coating has its own characteristic properties.

**Table 6 Properties and characteristics of conventional electroplated metal coatings**

| **Metal** | **Coating hardness** | **Appearance** | **Thickness** |  | **Characteristics and uses** |
|---|---|---|---|---|---|
|  |  |  | **μm** | **mil** |  |
| Cadmium | 30-50 HV | Bright white | 3-10 | 0.15-0.5 | Pleasing appearance for indoor applications; less likely to darken than zinc; anodic to ferrous substrate |
| Chromium | 900-1100 HV | White--can be varied | 0.2-1[(a)]<br>1-300[(b)] | 0.01-0.06[(a)]<br>0.05- | Excellent resistance to wear, abrasion, and corrosion; low friction and high reflectance |

| | | | | | |
|---|---|---|---|---|---|
| | | | | 12.0(b) | |
| Cobalt | 250-300 HK | Gray | 2-25 | 0.1-1.0 | High hardness and reflectance |
| Copper | 41-220 HV | Bright pink | 4-50 | 0.2-2.0 | High electrical and thermal conductivities; used as undercoat for other electroplates |
| Lead | 5 HB | Gray | 12-200(c)<br>1300(d) | 0.5-8.0(c)<br>50(d) | Resistant to many acids and hot corrosive gases |
| Nickel | 140-500 HV | White | 2-40(a)<br>130-500(c) | 0.1-1.5(a)<br>5-20(c) | Resistant to many chemicals and corrosive atmospheres; often used in conjunction with copper and chromium; can be applied by electroless plating |
| Rhodium | 400-800 HB | Bright white | 0.03-25 | 0.001-1.0 | High electrical conductance; brilliant white appearance is tarnish and corrosion resistant |
| Tin | 5 HB | Bright white | 4-25 | 0.015-1.0 | Corrosion resistant; hygienic applications for food and dairy equipment; good solderability |
| Zinc | 40-50 HB | Matte gray | 2-13(a)<br>12-50(d) | 0.1-0.5(a)<br>0.5-2.0(d) | Easily applied; high corrosion resistance; anodic to ferrous substrate |

Source: Ref 7

(a) Decorative.

(b) Hard.

(c) Wear applications.

(d) Corrosion applications.

Iron castings are electroplated to impart corrosion resistance or to provide a pleasing appearance. Typical applications include many different types of interior hardware, machine parts such as printing cylinders, decorative trim, and casings. Iron castings are also electroplated to enhance their wear resistance; for example, hard chromium plating is applied to the wear surfaces of piston rings (see the discussion below on chromium plating). Areas not requiring a plated surface can be masked or stopped off to prevent coverage. Plating can be applied as a very thin layer for applications requiring only a pleasing appearance or mild corrosion resistance; thicker plating can be applied for more wear resistance, longer corrosion resistance, or to replace lost metal (Table 6).

Electrodeposition is done by making clean iron castings cathodic in an aqueous solution containing a salt of the coating metal and then passing a direct electrical current through the solution. The effective metal content in the plating bath can be replenished by using anodes made of the coating metal to complete the electrical circuit. Variations in the properties of the deposited coating are influenced by the composition, temperature, pH, and agitation of the bath and by current density. In addition, further variations in the coating can result from the design of the casting, the distance of the casting from the anode, and the preparation of the surface before plating.

This section will review the types of platings applied to cast irons for corrosion or wear resistance. More detailed information on the equipment and plating solutions used for these processes can be found elsewhere in this Volume (see the articles in the Section on "Plating and Electroplating"). Additional information on corrosion and wear characteristics of electroplated coatings can also be found in Volume 13, *Corrosion,* and Volume 18, *Friction, Lubrication, and Wear Technology,* of the *ASM Handbook.*

**Chromium Plating.** Both hard and decorative chromium electroplates are deposited on cast iron substrates. Commercially, hard chromium is deposited from four types of efficiency etch-free baths. All of the baths contain chromic acid ($CrO_3$) and sulfate ($SO_4^{2-}$). The $SO_4^{2-}$ acts as a catalyst. Chromium cannot be electrodeposited from an aqueous $CrO_3$ solution unless one or more catalysts are present. Depending on which catalysts are present and the plating parameters, between 10 and 45% of the cathodic current will be used to reduce hexavalent chromium ($Cr^{6+}$) to chromium metal. The properties of the electrodeposits are influenced by the ratio of $CrO_3$ to the catalysts, plating temperature, and current density. Chromic acid to sulfate ratios vary between 75 to 1 and 120 to 1, plating temperatures range from 45 to 65 °C (110 to 150 °F), and current densities from 10 to 90 A/dm$^2$ (0.65 to 6 A/in.$^2$).

Hard chromium plating, which is also known as industrial chromium plating, differs from decorative chromium plating in the following ways:

- Hard chromium deposits are intended primarily to increase service life of function parts by increasing their resistance to wear, abrasion, heat, or corrosion. Deposits are also applied to restore dimensions of undersized parts
- Hard chromium normally is deposited to thicknesses ranging from 2.5 to 500 μm (0.1 to 20 mils) and for certain applications to considerably greater thicknesses (up to 6000 μm, or 240 mils) whereas decorative coatings seldom exceed 1.3 μm (0.05 mil)
- With certain exceptions, hard chromium is applied directly to the base metal; decorative chromium is applied over undercoats of nickel or of copper and nickel, and is either buffed or used in the as-plated condition

One of the most prevalent applications for chromium plated cast irons is that of hard plated piston rings. Gray cast iron, with a hardness ranging from 200 to 400 HB, is the most commonly used material for piston rings. Table 7 shows the various types of cast irons used in gasoline engine piston rings. Pearlitic gray iron produced by either centrifugal or sand casting methods has the widest use. In heavy-duty engine applications, alloy cast iron, ductile iron, and malleable iron are used. Harder materials, such as carbon steel or even bearing steels, may also be used.

**Table 7 Typical piston ring materials**

| Type | Approximate specification | Manufacturing method | Range of composition, wt% (balance iron) | | | | | | | | | Tensile strength | | Modulus of elasticity | | Hardness HB |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | C | Si | Mn | S | P | Ni | Cr | Mo | Other | MPa | ksi | GPa | psi × $10^6$ | |
| Gray cast iron | BSS 4K6 | Centrifugally cast | 3.5 max | 1.8-2.5 | 1.2 max | 1.0 max | 0.40-0.65 | 0.4 max | 0.5 max | 0.4 max | . . . | 245 | 36 | 117 | 17 | 210 min |
| | BSS 4K6 | Sand cast | 3.5 max | 1.0-1.8 | 0.6-1.2 | 0.15 max | 0.25-0.60 | 0.4 max | 0.4 max | 0.4 max | . . . | 245 | 36 | 103 | 15 | 200-245 |
| | DTD 233A | Centrifugally cast | 3.1-3.4 | 2.1-2.5 | 0.7-1.0 | 0.08 max | 0.40-0.65 | . . . | 0.3-0.6 | 0.5-1.0 | . . . | 310 | 45 | 110 | 16 | 255-296 |
| Carbidic/malleable iron | DTD 485A | Individually cast | 2.7-3.3 | 2.0-3.0 | 0.5-0.9 | 0.1 max | 0.5 max | . . . | 0.5-0.85 | . . . | V, 0.4 max | 585 | 85 | 159 | 23 | 270-320 |
| | DTD 485A | Centrifugally cast | 2.75-3.3 | 1.8-2.5 | 0.6-1.0 | 0.12 max | 0.3-0.5 | 0.3 max | 0.65-1.15 | 0.7-1.0 | Al, 0.5 max | 400 | 58 | 155 | 22 | 269-302 |
| Malleable/nodular iron | . . . | Centrifugally cast | 3.0-3.3 | 1.0-1.4 | 0.6-0.9 | 0.1 max | 0.1 max | 0.3 max | 0.1-0.5 | . . . | . . . | 540 | 78 | 155 | 22 | 200-400 |
| | BS2789 SNG | Sand or centrifugally cast | Varies according to mechanical properties required | | | | | | | | | 570 | 83 | 165 | 24 | 240-297 |

Source: Ref 8

Relatively thick coatings (up to 0.2 mm, or 0.008 in.) of plated chromium on the ring periphery provide the best compromise between scuffing, wear, and corrosion resistance and low friction and oxidation resistance at high temperatures. Generally, the use of chromium-plated top rings (with a hardness of 700 to 900 HV) run against cast iron cylinder liners can reduce the ring and liner wear by a factor of 2 to 3 (Ref 8). More detailed information on chromium plating can be found in the articles "Industrial (Hard) Chromium Plating" and "Decorative Chromium Plating" in this Volume.

**Electrolytic nickel plating** may be categorized as general purpose, special purpose wear-resistant, or bright. General purpose nickel plating is applied for protection against corrosive attack but is also used to build up worn or undersized parts. Wear-resistant nickel plating is used in engineering applications that require abrasion and corrosion resistance as well as surface smoothness. Bright nickel plating is used to provide decorative finishes and is frequently used as a base for a very thin chromium plate. Unless polished occasionally, all nickel plate will tarnish with a yellow cast after long exposure. Severely corrosive atmospheres will turn nickel green. Nickel plating of iron castings does not present any unusual problems, and the cleaning techniques prior to plating often are the same as for low-carbon steel. Three types of general-purpose baths are used for nickel plating: Watts, sulfamate, and fluoborate. A variety of proprietary organic and metallic brighteners, levelers, and antipitting agents are available to tailer the degree of brightness, reflectivity, and hardness desired.

The hardness of nickel deposits can vary from about 150 to 500 HV depending on the plating conditions (current density, solution pH and temperature, and composition). The widest use of electroplated nickel for wear applications is as an undercoat for chromium (Ref 9). If thick deposits are needed, for example, in building up heavily worn parts, it is usually not practical to do so using only chromium plating, because of its low current efficiency and high internal stress. In such cases, most of the deposit thickness is composed of nickel, with chromium constituting only a thin outer layer. For additional information, see the articles "Nickel Plating" and "Nickel Alloy Plating" in this Volume.

**Electroless nickel plating** is used to deposit nickel without the use of an electric current. The coating is deposited by an autocatalytic chemical reduction of nickel ions by sodium hypophosphite, sodium borohydride, or organic aminoboranes. When sodium hypophosphite is the reducing agent, the deposit generally contains between 3 and 11 wt% phosphorus. The boron contents of electroless nickel range from 0.2 to 4 wt% and from 4 to 7 wt% when the reducing agents are an aminoborane and sodium borohydride, respectively.

The structure of the deposit changes from microcrystalline to amorphous, with increasing alloy content. If the phosphorous content is above about 10 wt%, the coating is amorphous and therefore lacks grain boundaries or other crystalline defects at which corrosion can be initiated. Electroless nickel has some advantage over electrolytic nickel in that its thickness and phosphorus content are uniform over the substrate and independent of substrate geometry.

Electroless nickel can be heat treated to hardnesses comparable to those of electrodeposited chromium. The maximum hardness can be attained in 1 h at about 400 °C (750 °F) or 10 h at 260 °C (500 °F). The hardness of as-plated Ni-P alloys varies from 500 to 650 HV. As-plated Ni-B deposits are generally harder than the Ni-P ones. The ability of electroless nickel deposits to maintain their hardness under elevated-temperature service conditions increases with increasing phosphorus or boron content, but decreases rapidly above 385 °C (725 °F). Nickel-boron coatings tend to better withstand wear at elevated temperatures and are therefore more widely used under these conditions.

Electroless nickel is most frequently used in wear applications in the precipitation-hardened condition. The improved abrasion and wear resistance after heat treating is evident from Fig. 5. Although the greatest hardness was obtained by heat treatment at 400 °C (750 °F), the electroless nickel that was heat treated at 600 °C (1110 °F) showed the least wear. However, the corrosion resistance of as-plated Ni-P coatings, which is one of the main reasons for their use, deteriorates upon heat treating to the maximum hardness, because of cracking. Therefore, under corrosion or corrosive wear applications, the higher hardness should be avoided.

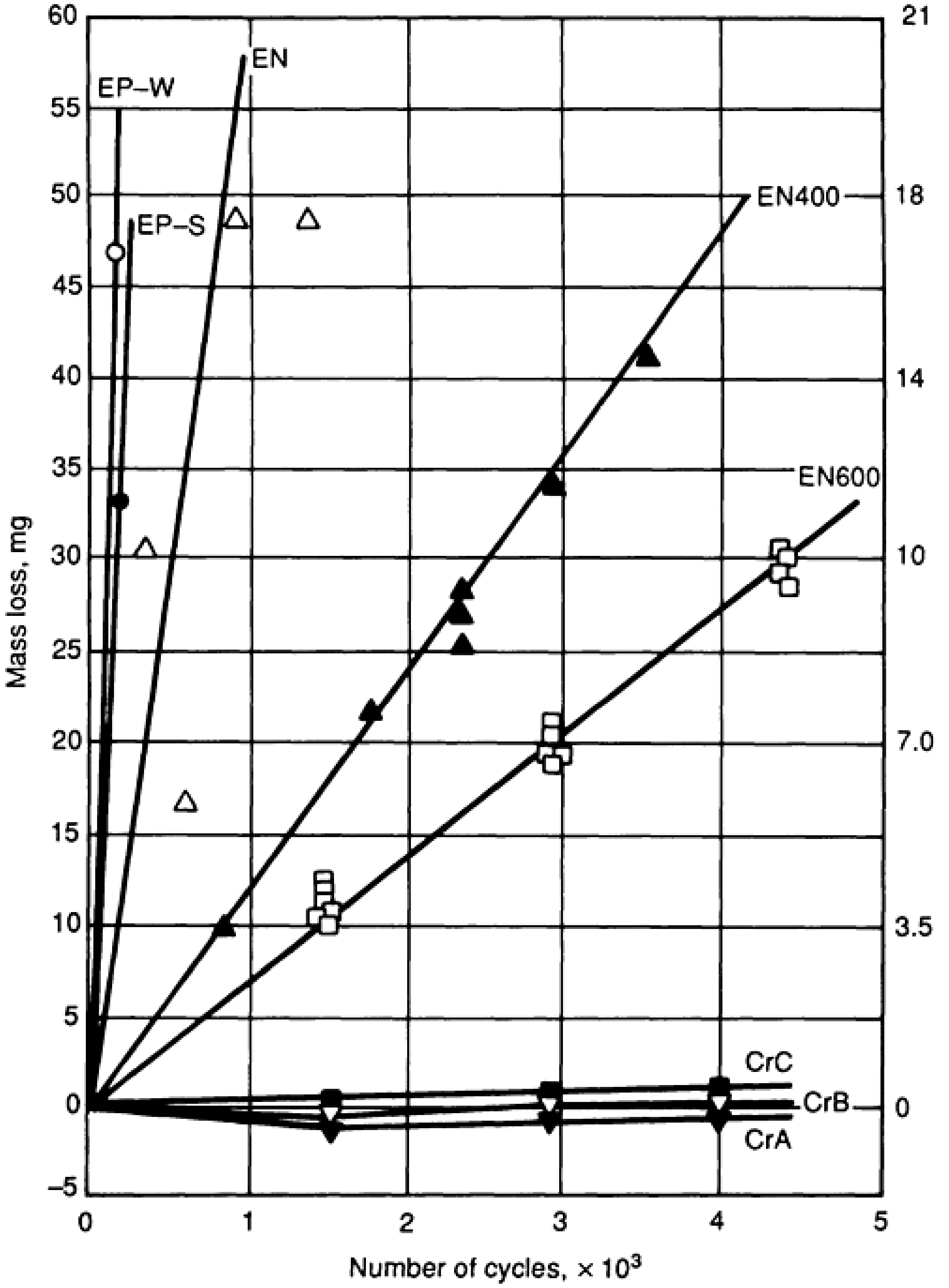

**Fig. 5 Effect of number of cycles on wear loss of plated pin versus steel blocks in a Falex test for three chromium deposits (CrA, CrB, and CrC), heat treated electroless nickel deposits (EN400 and EN600), a non-heat-treated electroless nickel deposit (EN), and two electroplated nickel deposits from a sulfamate solution (EP-S) and a Watts solution (EP-W). Source: Ref 9**

The widest use of electroless nickel for both corrosion and wear resistance is in complex-shaped cast iron valves that control the flow of either liquids or gases. Another important application for electroless nickel-plated cast irons is printing rolls which must have an especially uniform surface to function properly.

**Copper Plating** (Ref 7). Electroplated copper usually functions as an underplate for nickel and chromium plating. It provides a desirable base surface because it can be easily deposited in a uniform, pore-free, and ductile condition. Copper underplates also enhance buffing and polishing when multiple-layer plating is used. Copper itself is relatively corrosion resistant, but is subject to tarnishing and staining. It is occasionally used alone for decorative effect, but should be provided with an overcoat of lacquer. Some use of copper plating is made to facilitate soldering iron to other materials, such as copper tubing.

**Anodic Electroplates.** Electrodeposits of cadmium and zinc are used extensively to protect cast iron against corrosion. Because these metals are anodic to iron, the underlying ferrous metal is protected at the expense of the electroplate, even if the coating becomes scratched or nicked, exposing the substrate. Cadmium is generally preferred for the protection of cast irons in marine atmospheres and zinc is preferred in industrial environments. Cadmium is much more toxic than zinc, and applications in which its corrosion products may get into the environment should be avoided. The corrosion performance of both cadmium and zinc is greatly enhanced by chromate conversion coatings.

Most cadmium plating is carried out in alkaline cyanide baths prepared by dissolving cadmium oxide (CdO) in a sodium cyanide (NaCN) solution. Sodium hydroxide (NaOH) and sodium carbonate ($Na_2CO_3$) are formed by reactions within and are part of this bath. Cadmium balls suspended in steel wire cages serve as the plating anodes. Typical bath compositions suitable for various plating methods and workpieces are summarized in Table 8.

**Table 8 Alkaline cyanide cadmium plating baths**

| Total NaCN-to-Cd ratio | Concentration, g/L (oz/gal) | | | | |
|---|---|---|---|---|---|
| | Cd | CdO | NaCN | NaOH | $Na_2CO_3$ |
| 4.0 | 19.5 (2.6) | 22.5 (3.0) | 77.9 (10.4) | 14.2 (1.9) | 30-75 (4-10) |
| 4.1 | 19.5 (2.6) | 22.5 (3.0) | 80.1 (10.7) | 59.9 (8.0) | 30-45 (4-6) |
| 4.5 | 36 (4.8) | 41.2 (5.5) | 161.8 (21.6) | 25.5 (3.4) | 30-45 (4-6) |
| 5.0 | 20.2 (2.7) | 22.5 (3.0) | 101.1 (13.5) | 14.2 (1.9) | 30-60 (4-8) |
| 7.2 | 19.5 (2.6) | 22.5 (3.0) | 136.3 (18.2) | 14.2 (1.9) | 30-45 (4-6) |

The choice of a plating bath depends on the size and configuration of the workpiece being plated. Large numbers of small parts are most conveniently barrel plated with solutions of a lower NaCN-to-Cd ratio, while larger parts with intricate and recessed surfaces must be coated by still plating techniques of high throwing power. Automatic plating is normally used for intermediate size products which are arranged on racks and then automatically sequenced through a plating procedure.

Organic or metallic compounds are often added to alkaline cyanide cadmium plating baths to influence the formation of the electrodeposited cadmium crystals and thus the brightness of the coating. They are largely proprietary and, among the organics, include:

- Aldehydes
- Coumarin
- Dextrin
- Furfural
- Gelatin
- Milk
- Molasses
- Sugar

- Some sulfonic acids

Metallic brighteners include nickel, cobalt, molybdenum and selenium compounds.

Best results are achieved by a moderate use of both types. Excessive amounts of the organic brighteners are less harmful in that they ultimately hydrolyze and become harmless. Metallic brighteners should never be used unless technical facilities and competent personnel are available. Baths which are used excessively and which contain large amounts of organic brighteners must be filtered frequently or continuously. Other considerations in bath selection for both cyanide and non-cyanide plating baths can be found in the article "Cadmium Plating" in this Volume.

As shown in Table 9, cadmium is usually applied as a thin coating (less than 25 μm, or 1 mil thick) intended to withstand atmospheric corrosion. It is seldom used as an undercoating for other metals, and its resistance to corrosion by most chemicals is low.

**Table 9 Recommended minimum thicknesses and corrosion characteristics for zinc and cadmium coatings electrodeposited on cast iron**

| **Service conditions** | **Coating thickness** | | **Chromate finish** | **Time to white corrosion in salt spray, h** |
|---|---|---|---|---|
| | **μm** | **mils** | | |
| **Electrodeposited zinc** | | | | |
| Mild (indoor atmosphere; minimum wear and abrasion) | 5 | 0.2 | None | . . . |
| | | | Clear | 12-24 |
| | | | Iridescent | 24-72 |
| | | | Olive drab | 72-100 |
| Moderate (mostly dry indoor atmosphere; occasional condensation, wear, and abrasion) | 8 | 0.3 | None | . . . |
| | | | Clear | 12-24 |
| | | | Iridescent | 24-72 |
| | | | Olive drab | 72-100 |
| Severe (exposure to condensation; infrequent wetting by rain; and cleaners) | 13 | 0.5 | None | . . . |
| | | | Clear | 12-24 |
| | | | Iridescent | 24-72 |

| | | | | |
|---|---|---|---|---|
| | | | Olive drab | 72-100 |
| Very severe (exposure to bold atmospheric conditions; frequent exposure to moisture, cleaners, and saline solutions; likely damage by abrasion or wear) | 25 | 1 | None | . . . |
| **Electrodeposited cadmium** | | | | |
| Mild (see above) | 5 | 0.2 | None | . . . |
| | | | Clear | 12-24 |
| | | | Iridescent | 24-72 |
| | | | Olive drab | 72-100 |
| Moderate (see above) | 8 | 0.3 | None | . . . |
| | | | Clear | 12-24 |
| | | | Iridescent | 24-72 |
| | | | Olive drab | 72-100 |
| Severe (see above) | 13 | 0.5 | None | . . . |
| | | | Clear | 12-24 |
| | | | Iridescent | 24-72 |
| | | | Olive drab | 72-100 |
| Very severe (see above)(a) | 25 | 1 | None | . . . |
| | | | Clear | 24 |
| | | | Iridescent | 24-72 |
| | | | Olive drab | 72-100 |

Thickness specified is after chromate conversion coating, if used.

Source: Ref 11

(a) There are some applications for cadmium coatings in this environment; however, these are normally satisfied by hot-dipped or sprayed coatings.

Zinc, like cadmium, is also anodic to cast iron and therefore offers more protection when applied in thin films of 7 to 15 μm (0.3 to 0.5 mil) than similar thicknesses of nickel and other cathodic coatings. Because it is relatively inexpensive and readily applied in barrel, tank, or continuous plating facilities, zinc is often preferred for coating iron and steel parts when protection from either atmospheric or indoor corrosion is the primary objective. Table 9 lists the recommended minimum thicknesses and corrosion characteristics of zinc electrodeposits.

The adherence of electrodeposited zinc coatings depends on the metal-to-metal bond between the plated coating and the underlying cast iron surface. Therefore, particular attention must be given to the preparation of the surface before plating to obtain a coating in true physical contact with the entire casting surface.

The usual method of removing all rust, scale, and grease from the cast iron surface involves cleaning the surface thoroughly in a hot alkaline bath by soaking the parts for a short period of time. This is often followed by use of an electrolytic alkaline cleaner and a spray alkaline cleaner. An acid dip is then carried out to remove oxides and scale. There must be adequate rinsing between the alkaline/acid baths and the acid/plating baths to avoid contamination of the plating bath by carryover from the cleaning baths.

Zinc plating is done in an acid or an alkaline bath. Although the alkaline-cyanide zinc baths are the most efficient and have the best throwing power, they do create a serious pollution problem. Therefore, more acid zinc baths are being used. Acid bath compositions and operating conditions are described in the article "Zinc Plating" in this Volume.

Various brightening agents may be added to the baths to give a deposit that is more lustrous than that obtained from normal zinc plating baths. The amount of brightening agent requires very careful control, and the bath and the zinc anode must both be kept particularly pure when brighteners are used.

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## Hot Dip Coatings

Hot dip coating consists of immersing the casting in a bath of molten metal. A flux-coated and/or chemically cleaned surface is necessary to achieve satisfactory results. Aluminum, tin, zinc, and their alloys can be applied from a molten bath. Hot dip coatings are preferred because they are thicker than electroplates and because an alloy layer is formed between the coating metal and the iron. This provides additional durability and adhesion. Castings of complex shape are easily coated by these processes, although air may become trapped in blind holes unless the castings are rotated. More detailed information on hot dip coating is available in the articles "Continuous Hot Dip Coatings" and "Batch Hot Dip Galvanized Coatings" in this Volume.

**Hot dip zinc coating (galvanizing)** is widely used on iron castings, particularly pipe, valves, and fittings. The uniform and adherent coating provides a barrier against corrosive attack and will further protect an iron casting by acting as a sacrificial anode or by undergoing preferential corrosion. Successful galvanizing depends on surface preparation. Pickling followed by dipping in a bath of zinc ammonium chloride or other flux is done prior to dipping in molten zinc. Excess zinc may be drained or centrifuged from the castings before quenching. Quenching improves the brightness of the coating. Iron castings of any type and any composition can be hot dip galvanized.

**Hot dip tin coating (hot tinning)** provides a protective, decorative, and nontoxic coating for food equipment, a bonding layer for babbitted bearings, or a precoated surface for soldering. Surface preparation is particularly important, and when maximum adherence is desired, such as when tinning is used to prepare a casting for the application of babbitt, electrolytic cleaning in a molten salt is preferred.

**For the hot dip lead coating** of iron castings, lead-base alloys are preferred over pure lead; with pure lead, bonding is mechanical rather than metallurgical. Tin is the element most widely used to enhance bonding. Lead coatings are noted for their resistance to fumes from sulfuric and sulfurous acids.

**The aluminum coating (aluminizing)** of iron castings imparts resistance to corrosion and heat. The coating oxidizes rapidly, thus passivating the surface. The resultant aluminum oxide is refractory in nature; it seals the surface and resists degradation at high temperatures. An aluminized surface has limited resistance to sulfur fumes, organic acids, salts, and compounds of nitrate-phosphate chemicals.

## Hardfacing and Weld Cladding

**Hardfacing** can be used when a casting requires an unusually hard and wear-resistant surface and when it is impractical to produce a hard surface in the casting process or by selective heat treatment. Frequently, hardfacing is used to repair worn castings by building up an overlay of new material.

Hardfacing is basically a welding operation in which an alloy is fused to the base metal by oxyfuel welding, arc welding, laser welding, or thermal spray processes. Hardfacing materials include a wide variety of alloys, carbides, and combinations of these materials. Conventional hardfacing materials, also referred to as weld overlays, are normally classified as steels or low-alloy ferrous materials, high-chromium white irons or high-alloy ferrous materials, carbides, nickel-base alloys, or cobalt-base alloys. A few copper-base alloys are sometimes used for hardfacing applications, but for the most part, hardfacing alloys are either iron-, nickel-, or cobalt-base.

Microstructurally, hardfacing alloys generally consist of hard phase precipitates such as borides, carbides, or intermetallics bound in a softer iron-, nickel, or cobalt-base alloy matrix. Carbides are the predominant hard phases in iron- and cobalt-base hardfacing alloys. Carbon contents of iron- and cobalt-base hardfacing alloys generally range up to 4 wt%. Borides, as well as carbides, are the predominant hard phases in nickel-base hardfacing alloys. Combined carbon plus boron contents generally range up to 5 wt%. The specific carbide and/or boride phases that form are determined by matrix alloying additions.

Hardfacing alloys usually are available as bare rod, flux-coated rod, long-length solid wires, long-length tube wires (with and without flux), or powders. The most popular processes, and the forms most commonly associated with each process, are:

| **Hardfacing process** | **Consumable form** |
|---|---|
| Oxyfuel/oxyacetylene (OFW/OAW) | Bare cast or tubular rod |
| Shielded metal arc (SMAW) | Coated solid or tubular rod (stick electrode) |
| Gas-tungsten arc (GTAW) | Bare cast or tubular rod |
| Gas-metal arc (GMAW) | Tubular or solid wire |
| Flux-cored open arc | Tubular wire (flux cored) |

| | |
|---|---|
| Submerged arc (SAW) | Tubular or solid wire |
| Plasma transferred arc (PTA) | Powder |
| Laser beam | Powder |

Detailed information on hardfacing materials, hardfacing alloy selection, and hardfacing process selection can be found in Ref 12. Producers of hardfacing alloys should also be consulted for technical assistance.

**A weld clad** is a relatively thick layer of filler metal applied to a cast iron base metal for the purpose of providing a corrosion-resistant surface. Weld cladding is normally carried out by arc welding. Materials deposited on cast irons to improve their corrosion performance include copper-base alloys, stainless steels, and nickel-base alloys.

Problems due to dilution of stainless steel or nickel-base filler metals can be minimized by first depositing a buffer layer of low-carbon nickel prior to the application of the cladding alloy. Dilution of the base iron casting into the weld deposit can also be kept to a minimum by:

- Maximizing the amount of metal deposited per unit length. The beads being deposited should be overlapped as much as possible
- Minimizing the amount of heat input in order to reduce the amount of base metal melting. The use of straight-polarity dc current will help decrease the penetration

Caution must be exercised when considering the reduction in penetration or melting of the cast iron substrate. The deposited weld metal must melt part of the casting to adhere properly. A rule of thumb is that a minimum of 5 to 10% dilution is needed for complete fusion.

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12. J.R. Davis, Hardfacing, Weld Cladding, and Dissimilar Metal Joining, *Welding, Brazing, and Soldering,* Vol 6, *ASM Handbook,* ASM International, 1993, p 789-829

## Thermal Spraying

Thermal spraying comprises a group of processes in which divided molten metallic or nonmetallic material is sprayed onto a prepared substrate to form a coating. The sprayed material is originally in the form of wire, rod, or powder. As the coating materials are fed through the spray unit, they are heated to a molten or plastic state and propelled by a stream of compressed gas onto the substrate. As the particles strike the surface, they flatten and form thin platelets that conform and adhere to the irregularities of the prepared surface and to each other. They cool and accumulate, particle by particle, into a lamellar, castlike structure. In general, the substrate temperature can be kept below approximately 200 °C (400 °F), eliminating metallurgical change of the substrate material. The spray gun generates the necessary heat for melting through combustion of gases, an electric arc, or a plasma. Figure 6 illustrates a general thermal spraying process. Figure 7 illustrates the microstructure that results from the thermal spray process. As shown in this figure, the molten particles spread out and deform (splatter) as they impact the substrate, at first locking onto irregularities on the roughened surface, then interlocking with each other.

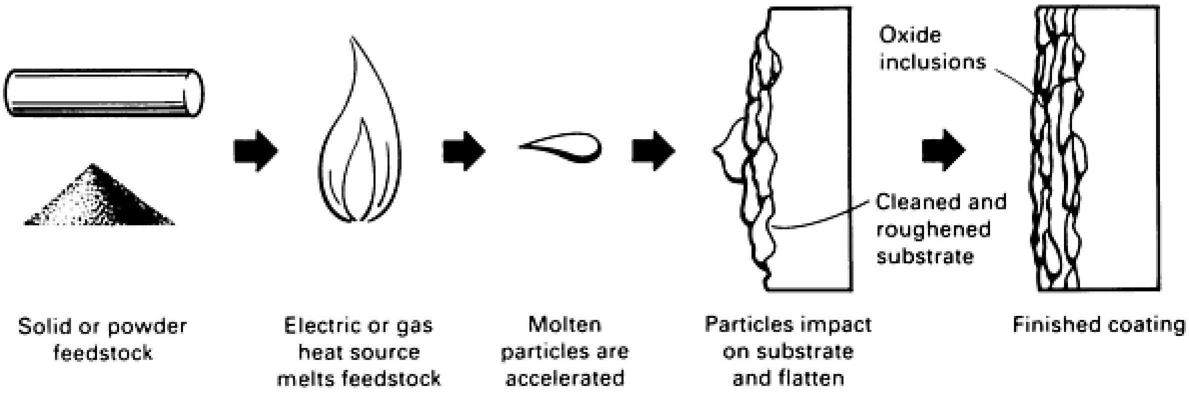

**Fig. 6 Schematic of the general thermal spray process. Source: Ref 12**

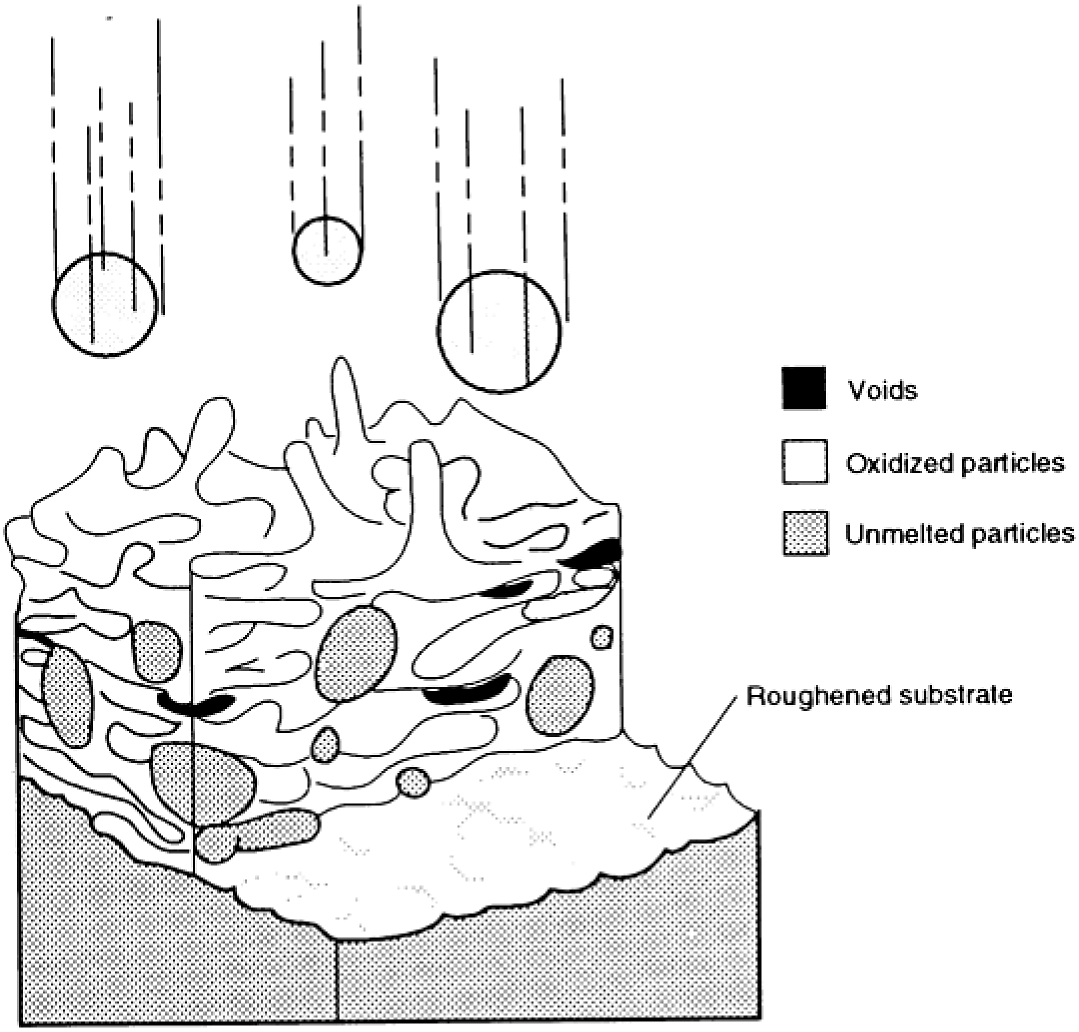

**Fig. 7 Schematic showing the buildup of a thermal spray coating. Molten particles spread out and deform (splatter) as they strike the target, at first locking onto irregularities on the substrate, then interlocking with each other. Voids can occur if the growing deposit traps air. Particles overheated in the flame become oxidized. Unmelted particles may simply be embedded in the accumulating deposit. Source: Ref 12**

Currently, five different commercially available thermal spray methods are in use:

- Oxyfuel wire (OFW) spray
- Electric arc wire (EAW) spray
- Oxyfuel powder (OFP) spray
- Plasma arc (PA) powder spray
- High-velocity oxyfuel (HVOF) powder spray

Selection of the appropriate thermal spray method is typically determined by the desired coating material, coating performance requirements, economics, and part size and portability. Reference 12 provides detailed information on thermal spray process selection.

Thermal spray coatings are deposited on cast iron substrates for:

- Corrosion resistance
- Wear resistance
- Oxidation resistance
- Dimensional restoration
- Thermal barriers

**Corrosion Resistance.** Zinc and aluminum and their alloys are the metals most widely used for thermal spray anticorrosion coatings. They are extensively used for the corrosion protection of iron and steel in a wide range of environments and have been shown to provide very long-term protection (over 20 years) in both marine and industrial locations.

**Wear coatings** are used to resist abrasion, erosion, cavitation, and fretting, and to reduce friction. These coatings consist of a wide range of metals and their alloys, ceramics, cermets, carbides, and even low-friction plastics. Typical coating hardness ranges from 20 to 70 HRC. Metal matrices are hardened by rapid solidification, by dispersions introduced from the spray process, by the addition of separate hard phases (for example, carbides of chromium, tungsten, titanium, and/or tantalum), or by oxide inclusions.

**Oxidation protection.** Thermal spray coatings are extensively used by industry to protect cast iron components and structures from heat oxidation at surface temperatures to 1095 °C (2000 °F). By ensuring long-term protection, thermal spray coatings show real economic advantages during the service lives of such items. Oxidation-resistant coatings include aluminum, aluminum-iron, nickel-chromium, and MCrAlY materials.

**Dimensional Restorative Coatings.** Thermal spray is used as a coating to repair or resurface (up to 3 mm, or 0.12 in. thick) worn and/or corroded parts, as well as to repair new part errors (for example, undersize parts), to repair nicks or other blemishes, or to renew surfaces that are corroded or worn in use.

**Thermal barrier coatings** consist of a low-conductivity (thermal) ceramic deposited over an MCrAlY bond coat. The ceramic of choice is partially-stabilized zirconia (7 to 8 wt% $Y_2O_3$-$ZrO_2$) deposited at a thickness of 0.25 mm (0.010 to 0.040 in.) with 10 to 15% porosity. A bond coat of NiCrAlY or CoCrAlY is used at a thickness of 0.125 mm (0.005 in.). Both coatings are used on components used in gas turbine engines and adiabatic engines to improve efficiency and reduce metal temperatures or cooling requirements.

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## Laser Surface Processing (Ref 13)

High-power lasers have been used to process materials to improve their wear resistance since the late 1960s. Laser surface modification techniques that are used to improve the wear resistance of cast irons include transformation hardening, melting, and alloying. The processing conditions, examples of microstructures, wear characteristics, and applications associated with each technique are discussed in greater detail in Ref 13.

**Laser Transformation Hardening.** The wear resistance of highly stressed ferrous alloy components, such as gears and bearings, can be improved by transformation hardening. Because ferrous materials are very good heat conductors, the high heat fluxes generated by lasers are most suitable to heat the surface layer to austenitization levels without affecting the bulk temperature of the sample. The ensuing self-quenching is rapid enough to eliminate the need for external quenching to produce the hard martensite in the heated surface. Because ferrous alloys have high reflectivity, absorptive coatings such as manganese phosphate and graphite are applied to the workpiece for efficient laser heating. Most of these coatings burn off and normally do not affect the microstructure. Processing conditions for laser transformation hardening are typically power densities that range from 5 to 100 MW/m$^2$ (3.2 to 64.5 kW/in.$^2$) and interaction times ranging from 0.01 to 10 s. Usually, inert gas shielding is used. A rectangular beam is often used for laser transformation hardening. The case depth depends on the hardenability of the material and rarely exceeds 2.5 mm (0.1 in.).

In cast irons, laser heat-treated surfaces appear in light contrast, as shown in Fig. 8(a) for gray iron and in Fig. 8(b) for ductile iron. The microstructure of laser-hardened gray cast iron is generally fine martensite that contains flake graphite, as shown in Fig. 9(a). Acicular bainite can sometimes occur in the martensite matrix. The microstructure of laser-hardened ductile iron is also fine martensite, but contains "bull's eye" graphite nodules, as shown in Fig. 9(b). A closer examination of Fig. 9(b) reveals a narrow region of martensite between the graphite nodule and the ferrite ring, which indicates the extent of carbon diffusion occurring during processing.

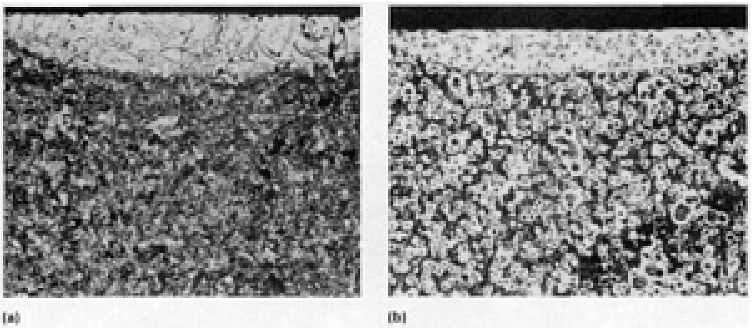

**Fig. 8 Cross sections of laser heat-treated surfaces in cast irons. (a) Gray iron. (b) Ductile iron. Source: Ref 13**

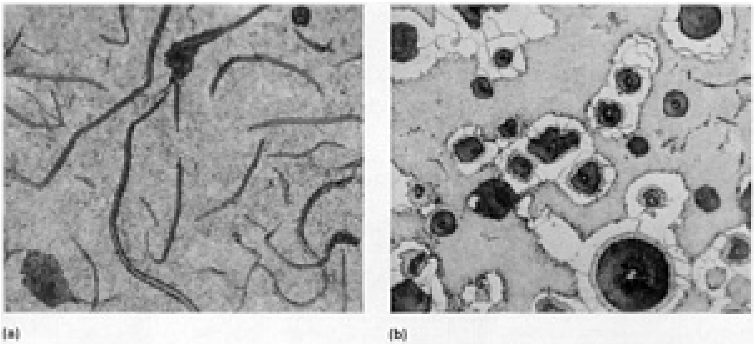

**Fig. 9 Microstructures of laser-hardened cast irons. (a) Gray iron. (b) Ductile iron. Source: Ref 13**

According to Molian and Baldwin (Ref 14), the extensive case that developed during laser hardening of gray and ductile irons was made up of sequential regions with varying degrees of microstructural modification. The region just below a very thin melt zone contained plate martensite, retained austenite, and graphite, whereas the region just above the base metal contained a mixture of refined martensite and untransformed pearlite.

From their study of pin-on-disk wear behavior of laser-hardened gray and ductile cast irons, Molian and Baldwin (Ref 14) found an improvement in scuffing and sliding wear resistance with an increase in case depth, as shown in Fig. 10. On the same samples, erosive wear test results showed that the erosion rate depended on the surface hardness and the case depth, as shown in Fig. 11, and increased as the matrix microstructure varied from ledeburite to tempered martensite to pearlite (Ref 15).

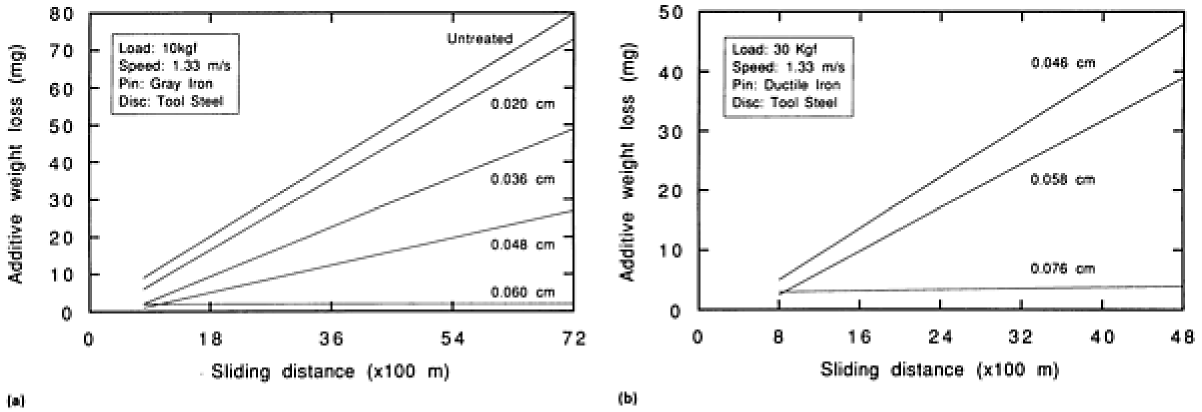

**Fig. 10 Sliding wear behavior of laser-hardened cast irons as a function of case depth. (a) Gray iron. (b) Ductile iron. Source: Ref 13**

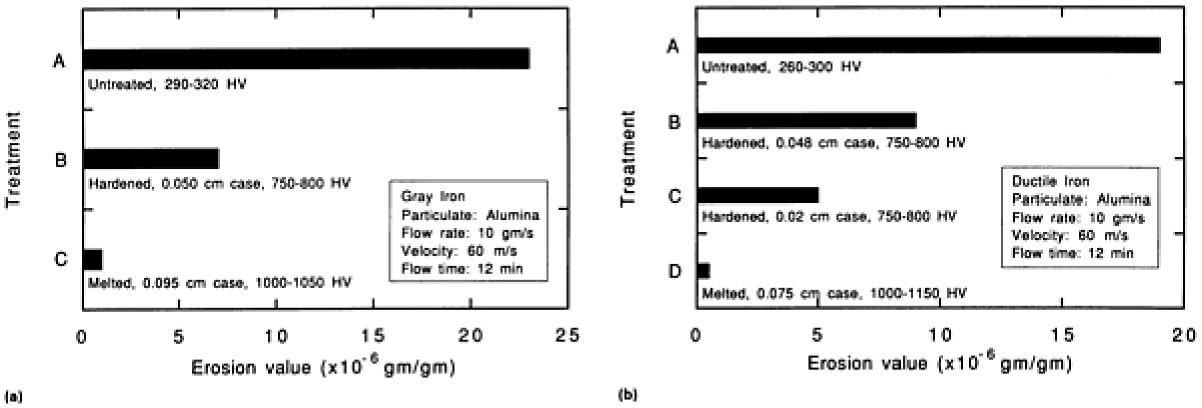

**Fig. 11 Erosive wear behavior of laser-hardened cast irons as a function of surface hardness and case depth. (a) Gray iron. (b) Ductile iron. Source: Ref 13**

Tomlinson et al. (Ref 16) observed that besides reducing wear, laser hardening of flake graphite iron resulted in very little plastic deformation, no graphite deposition on the opposing metal, and no adhesive damage. Trafford et al. (Ref 17) used a reciprocating pad-on-plate technique to evaluate the wear resistance of laser-processed gray iron and found that fully martensitic and surface-melted ledeburite microstructures had the lowest wear rates (Fig. 12).

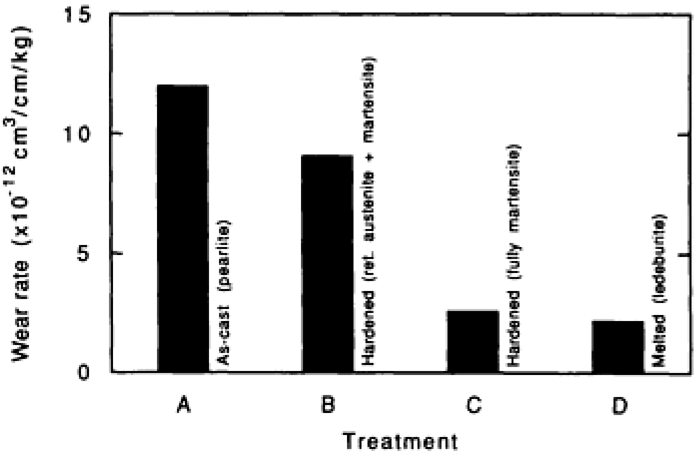

**Fig. 12** **Abrasive wear rates in gray iron as a function of microstructure arising from various laser-hardening treatments. Source: Ref 13**

## Example 1: Laser Surface Hardening of Cast Iron Camshaft Lobes

(Ref 18). The surface of the lobes of an automotive camshaft made from ductile cast iron (see Fig. 13) was to be surface hardened to increase wear resistance. The desired case depth, defined as the depth where the hardness was 50 HRC, was 0.5 to 1.0 mm (0.02 to 0.04 in.).

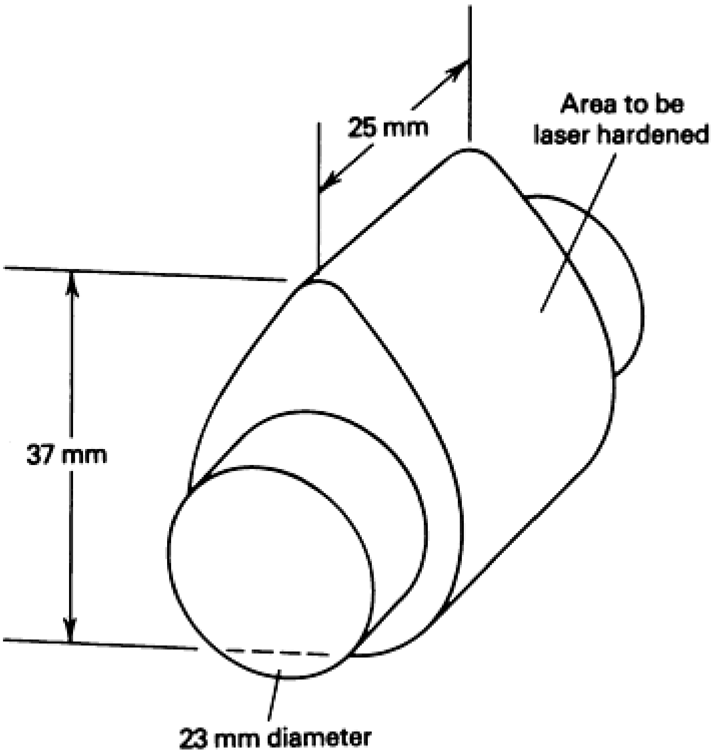

**Fig. 13** **Ductile cast iron cam from automotive camshaft. Source: Ref 18**

A 15 kW $CO_2$ laser was used for the processing. The optical system delivered a focused spot, with a diameter of 10 mm (0.4 in.) to the workpiece. This spot was scanned over a distance of 22 mm (0.9 in.) normal to the direction of processing. The frequency of scanning was 125 Hz in the normal direction, forming a rectangular spot 22 mm by 25 mm (0.9 by 1.0 in.) on the camlobe surface.

To obtain an even hardened case around the periphery of the camlobe, it was necessary to vary the angular speed of rotation of the lobe under the laser beam. The reason is that the angle of incidence of the laser beam to the workpiece changed during rotation, from nearly normal incidence at the cylindrical portion of the lobe to a grazing incidence of only 20 to 30° at the flat portion. Furthermore, at constant rotational speed, the linear speed of processing would vary as the lobe rotated. This was obtained by mounting the workpiece on a rotary table. The speed of rotation was varied by means of an electromechanical controller in a predetermined manner.

The camlobe was laser hardened using a manganese phosphate coating to increase energy absorption. Because of the design of the workpiece, it was difficult to predict the optimum processing parameters by calculations and the parameters were, therefore, evaluated by trial and error. The results were:

| | |
|---|---|
| Power input | 9 kW |
| Power density | 1600 W/cm$^2$ (10,300 W/in.$^2$) |
| Linear speed of processing | |
| at the cylindrical portion | 760 mm/min (30 in./min) |
| at the flat portion | 180 mm/min (7 in./min) |
| Depth of case | 0.55 mm (0.022 in.) |

The hardness profile of the surface layer of the camlobe is shown in Fig. 14.

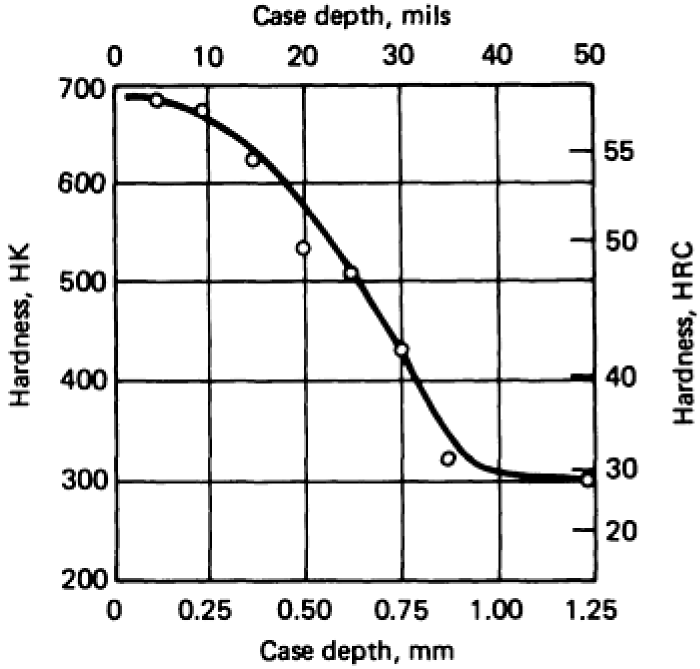

**Fig. 14 Hardness profile of laser surface hardened cast iron camlobe. Source: Ref 18**

**Laser melting** requires higher power densities than the levels used for laser transformation hardening. The workpiece is often made absorptive either by using coatings similar to those used for laser heating or by increasing surface roughness, for example, by sand blasting. Laser melting can harden alloys that cannot be hardened by laser transformation hardening. In ferritic malleable gray iron, melting enhances the diffusion of carbon, and the ensuing rapid quench produces a hardened region.

Processing conditions for laser melting are typically a power density from 10 to 3000 $MW/m^2$ (6.5 to 1935 $kW/in.^2$) and an interaction time from 0.01 to 1 s. Inert gas shielding is used to prevent oxidation of the surface.

Microstructural changes with laser melting are in the forms of grain refinement, solid solutions, and fine dispersions of precipitates. All of these can contribute to the hardening and strengthening of the surface. Laser-melted surfaces of cast irons appear dendritic, as shown in Fig. 15(a) for gray iron and in Fig. 15(b) for ductile iron. Below the melt zone is the heat-affected zone, which appears in lighter contrast in Fig. 15.

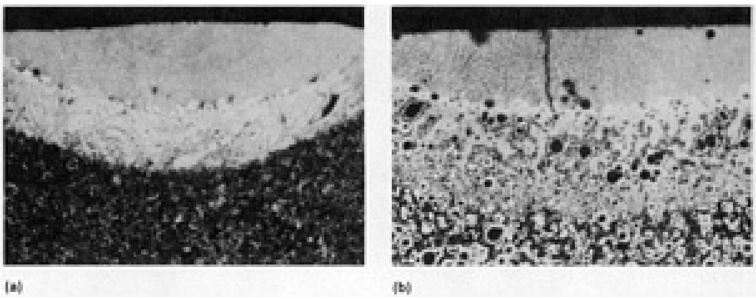

**Fig. 15 Cross section of laser-melted cast iron surfaces. (a) Gray iron. (b) Ductile iron. Source: Ref 13**

In the solidified melt in cast irons, a ledeburite (mixture of austenite and cementite) structure generally forms. Hardening is caused by graphite dissolution to form cementite and austenite transformation to martensite. Molian and Baldwin (Ref 14) described the formation of predominantly dendritic ledeburite with small amounts of plate-like, high-carbon martensite and retained austenite in the melt zone in gray and ductile irons.

Chen et al. (Ref 19) determined that microstructures in laser-melted ductile iron depended on the solidification rate. Dendritic retained austenite with a continuous interdendritic carbide, with a microhardness from 400 to 650 HV, formed at high solidification rates. A lamellar mixture of ferrite and cementite plates, with a microhardness from 1000 to 1250 HV, formed at low solidification rates.

Bamberger et al. (Ref 20) found that in laser-melted gray cast iron, full dissolution of the graphite occurred, leading to the formation of hot tears on the surface. On the other hand, in laser-melted nodular cast iron, partial dissolution of the graphite occurred, resulting in increased ductility and no hot tearing.

Bergmann (Ref 21) has summarized the wear properties of laser-melted cast irons. For laser-melted gray iron containing flake graphite in a pearlitic matrix, the dry pin-on-disk test demonstrated that the wear behavior improved by an order of magnitude and was better than a fully martensitic structure. In a test involving rolls that ran against one another with a fixed relative slip, it was found that the wear resistance of laser-melted ductile iron was superior to that of 0.6% C steel, case-hardened 16MnCr5 steel, nitrided or carburized 16MnCr5 steel, and a gas-tungsten arc welded melted surface.

Ju et al. (Ref 22) reported significant improvement in erosive wear behavior in laser-melted ductile and gray irons, as shown in Fig. 16. This improvement was due to the presence of mechanically metastable austenite that transforms to martensite when plastic deformation of the near-surface region occurs during wear.

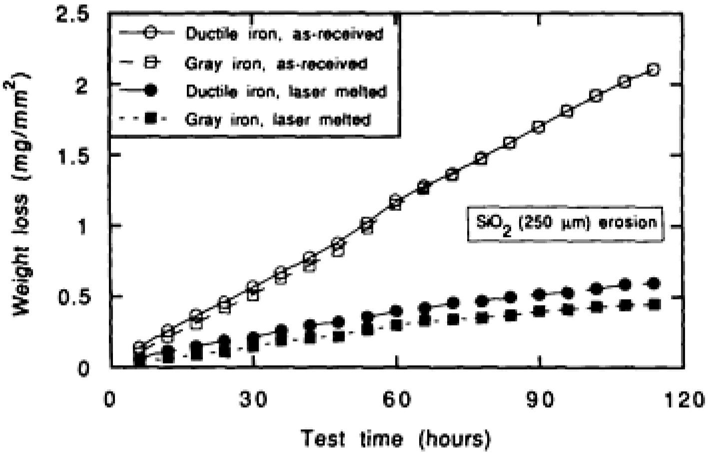

**Fig. 16 Erosive wear behavior of as-received and laser-melted gray and ductile irons. Source: Ref 22**

Tomlinson et al. (Ref 23) reported that laser melting reduced the amount of cavitation erosion of gray cast iron in distilled water by a factor of 0.3, and, in 3% saltwater, by a factor of 0.57.

**Laser Alloying.** A technique of localized alloy formation is laser surface melting with the simultaneous, controlled addition of alloying elements. These alloying elements diffuse rapidly into the melt pool, and the desired depth of alloying can be obtained in a short period of time. By this means, a desired alloy chemistry and microstructure can be generated on the sample surface; the degree of microstructural refinement will depend on the solidification rate. The surface of a low-cost alloy, such as cast iron, can be selectively alloyed to enhance properties, such as resistance to wear, in such a way that only the locally modified surface possesses properties typical of tribological alloys. This results in substantial cost savings, and reduces the dependence on strategic materials. Typical processing parameters for laser alloying are a power density from 10 to 3000 MW/m$^2$ (6.5 to 1935 kW/in.$^2$) and an interaction time from 0.01 to 1 s. An inert shielding gas is normally used.

One method of alloying is to apply appropriate mixtures of powders on the sample surface, either by spraying the powder mixture suspended in alcohol to form a loosely packed coating, or by coating a slurry suspended in organic binders. The use of metal powders in laser alloying is the least expensive, but, with appropriate process modifications, alloys in the form of rods, wires, ribbons, and sheets can also be added.

Cast irons, primarily gray irons, have been laser alloyed with chromium, silicon, carbon, nickel, nickel-aluminum, cobalt, and cobalt-chromium powders. Figure 17 shows the improved cavitation erosion resistance of a gray cast iron containing 2.9 to 3.2% C, 1.7 to 2.1% Si, 0.5 to 0.8% Mn, ≤0.1% P, and 0.06 to 0.11% S that was laser alloyed with chromium. The resulting coating, which was approximately 0.5 mm (0.02 in.) thick, contained 22% Cr and had a hardness value of 700 HV.

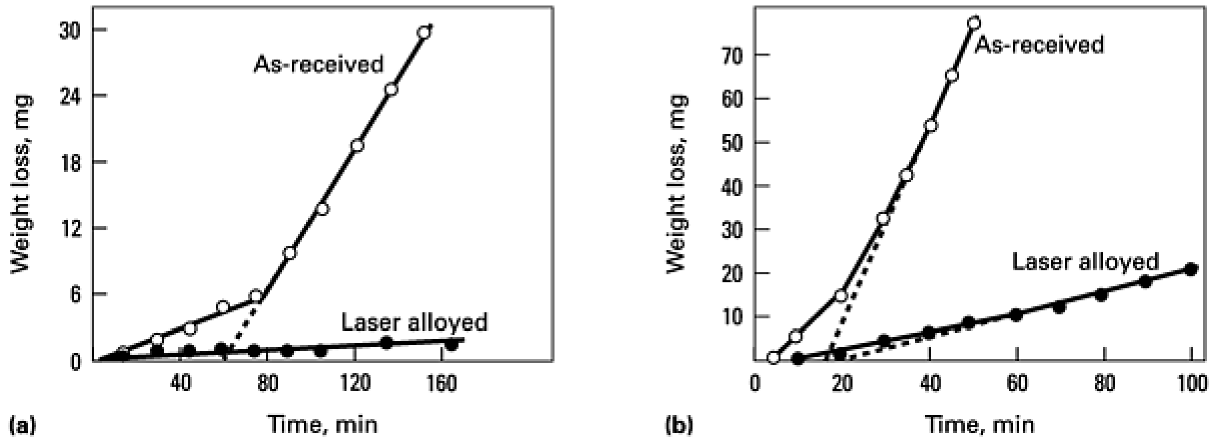

**Fig. 17 Effect of laser alloying with chromium on the cavitation erosion resistance of gray cast iron in distilled water (a) and 3% sodium chloride solution (b). Source: Ref 24**

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## Surface Hardening

Surface hardening is a generic term covering several processes applicable to a suitable ferrous alloy that produces a surface layer that is harder or more wear resistant than the core. The processes commonly used to surface harden cast irons which will be described in this section include flame hardening, induction hardening, and nitriding. Laser transformation hardening, which is a rapidly emerging technology for improving the performance of iron castings, was described in the previous section on "Laser Surface Processing." Other less commonly used methods for surface hardening of cast irons include boriding, nitrocarburizing, and the thermoreactive deposition/diffusion process (Toyota diffusion coating process). More detailed information on surface hardening can be found in Volume 4, *Heat Treating,* of the *ASM Handbook.*

### *Flame Hardening of Gray Iron*

Flame hardening is the method of surface hardening most commonly applied to gray iron. After flame hardening, a gray iron casting consists of a hard, wear-resistant outer layer of martensite and a core of softer gray iron, which during treatment does not reach the $A_1$ transformation temperature (in fact, the unhardened metal immediately below the hardened case, which has been heated by the flame to some extent, may even be partially annealed during flame hardening if it is unalloyed).

**Recommended Composition.** Both unalloyed and alloyed gray irons can be successfully flame hardened. However, some compositions yield much better results than do others. One of the most important aspects of composition is the combined carbon content, which should be in the range of 0.50 to 0.70%, although irons with as little as 0.40% combined carbon can be flame hardened. In general, flame hardening is not recommended for irons that contain more than 0.80% combined carbon because such irons (mottled or white irons) may crack in surface hardening.

The stability of the microconstituents from which the carbon precipitates is a factor in determining the hardness of the flame-hardened iron. One user observed that the stability of microconstituents containing combined carbon is indicated by the hardness of test specimens annealed at 845 °C (1550 °F). A test of four pearlitic irons from different sources, containing 3.30% C max, 1.40 to 1.60% Si, 0.80 to 1.10% Mn, and 0.15 to 0.20% Cr, gave the results:

| **Iron** | **Hardness, HB** | | **Hardness[(a)], HRC** |
|---|---|---|---|
| | **As-cast** | **Annealed** | |
| A | 220 | 200 | 47-50 |
| B | 190 | 180 | 47-50 |
| C | 200 | 140 | 35-38 |

(a) After flame hardening as-cast iron

For maximum hardness, it is advisable to use an iron containing as small an amount of total carbon as is consistent with the production of sound castings free from any danger of cracking. The coarse graphite flakes typical of high-carbon irons should be avoided because they may be burned out during flame heating, thereby producing a porous and unattractive surface.

Because silicon promotes the formation of graphite and of a low combined carbon content, a relatively low silicon content is also advisable. Several users report that silicon content should not exceed 2% in any iron submitted to a flame-hardening operation, although alloy irons containing 2.4% Si can be hardened successfully. They also recommend that manganese content be held in the range of 0.80 to 1.00% to increase carbon solubility in austenite.

Gray iron to be flame hardened should be as free as possible from porosity and from foreign matter such as sand or slag because porosity and even small inclusions of foreign matter can produce a rough surface or result in cracking after hardening. Rough casting surfaces should be sand or shot blasted prior to heat treatment because skin or scale on the surface acts as a heat insulator and reduces the effectiveness of flame hardening.

**Effects of Alloying Elements.** In general, alloyed gray irons can be flame hardened with greater ease than can unalloyed irons, partly because alloyed gray irons have increased hardenability. Final hardness also may be increased by alloying additions. The maximum hardness obtainable by flame hardening an unalloyed gray iron containing approximately 3% total carbon, 1.7% Si, and 0.60 to 0.80% Mn ranges from 400 to 500 HB. This is because the Brinell hardness value for gray iron is an average of the hardness of the matrix and that of the relatively soft graphite flakes. Actually, the matrix hardness on which wear resistance depends approximates 600 HB. With the addition of 2.5% Ni and 0.5% Cr, an average surface hardness of 550 HB can be obtained. The same result has been achieved using 1.0 to 1.5% Ni and 0.25% Mo. Small additions of chromium are particularly valuable in preventing softening and ensuring the retention of a high content of combined carbon during austenitizing for hardening. Automotive camshafts containing 1% Cr, 0.50% Mo, and 0.8% Mn are easily flame hardened to 52 HRC to a required depth. These parts are not tempered or stress relieved.

**Stress Relieving.** Whenever practicable or economically feasible, flame-hardened castings should be stress relieved at 150 to 200 °C (300 to 400 °F) in a furnace, in hot oil, or by passing a flame over the hardened surface. Such a treatment will minimize distortion or cracking and will increase the toughness of the hardened layer.

Stress relieving at 150 °C (300 °F) for 7 h was found to remove 25 to 40% of the residual stresses in a flame-hardened casting, while reducing the hardness of the surface by only 2 to 5 points on the HRA scale. Although stress relieving is desirable, it can often be safely omitted.

**Hardness.** The surface of flame-hardened gray iron typically has a somewhat lower hardness than the metal immediately below the surface (Fig. 18). This decrease in hardness may be caused by the retention of relatively soft austenite at the surface. Surface hardness often can be raised by heating in the range from 195 to 250 °C (380 to 480 °F).

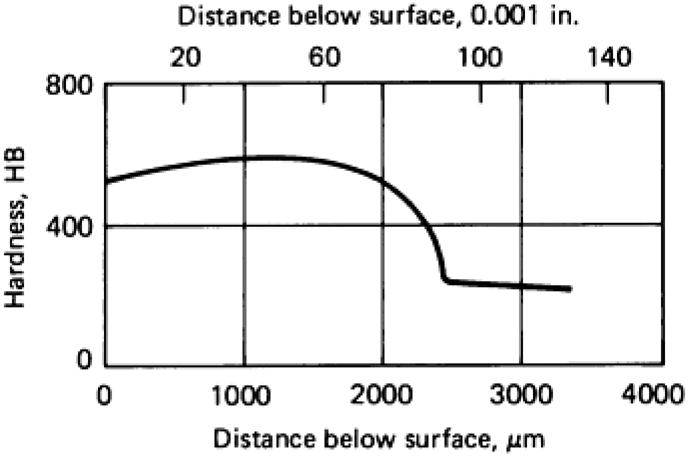

**Fig. 18 Typical hardness gradient produced in gray iron by flame hardening**

The depth and microstructure of the hardened layer depend on two other factors in addition to temperature: the amount of carbon and alloying elements in solution when the flame-hardened surface is quenched, and the efficiency of quenching. If softness is due to the presence of austenite in the microstructure, subjecting the part to -40 °C (-40 °F) for 1 h will transform the austenite and increase the hardness.

**Fatigue strength** is usually increased by surface hardening because the treatment induces compressive stresses at the surface. For example, flame or induction heating followed by water quenching induces high compressive stresses (>205 MPa, or 30 ksi) in the fillet areas of crankshafts; however, if self-quenching instead of water quenching is used, undesirable tensile stresses may result at the surface. The degree of improvement in fatigue strength by flame hardening cannot be produced by through hardening.

**Quenching.** The various methods of flame hardening influence the selection of the quenching medium. In the progressive method, only nonflammable media such as water, soluble-oil mixtures, and solutions of polyvinyl alcohol in water can be employed. Conventional oil cannot be used because of the fire hazard. In spot hardening or spinning methods, in which the flame head is withdrawn from the part before quenching, parts are quenched conventionally by immersion in hot oil.

When quenching is done with water, the water should be at about 30 °C (90 °F) for best results. Lower quenching rates, such as those obtained with 5 to 15% soluble-oil mixtures, compressed air, or compressed air and water at low pressure, are used to prevent cracking. Air quenching is especially suited to highly alloyed cast irons because of their susceptibility to cracking.

### *Induction Hardening of Gray Iron*

Gray iron castings can be surface hardened by the induction method when the number of castings to be processed is large enough to warrant the relatively high equipment cost and the need for special induction coils. Considerable variation in the hardness of the cast irons may be expected because of a variation in the combined carbon content. A minimum combined carbon content of 0.40 to 0.50% C (as pearlite) is recommended for cast iron to be hardened by induction, with the short heating cycles that are characteristic of this process. Heating castings with lower combined carbon content to high hardening temperatures for relatively long periods of time may dissolve some free graphite, but such a procedure is likely to coarsen the grain structure at the surface and will result in undesirably large amounts of retained austenite in the surface layers. The recommended minimum induction hardening temperature for gray iron is 870 to 925 °C (1600 to 1700 °F).

**The surface hardness** attained from the induction hardening of gray iron is influenced by the carbon equivalent (%C + 1/3% Si) when this hardness is measured by conventional Rockwell tests. The more graphite that is present in the microstructure, the lower the surface hardness will appear to be after hardening. Table 10 shows the surface hardness of induction-hardened gray iron castings of various carbon equivalents from 3.63 to 4.23. The microstructure of these castings, which were cast in the same manner and cooled at similar rates, contained more and larger graphite flakes as the carbon equivalent increased. This resulted in lower apparent surface hardness after hardening, yet the hardened matrix was consistently 57 to 61 HRC (converted from microhardness).

**Table 10 Effect of carbon equivalent on surface hardness of induction-hardened gray irons**

| Composition, %(a) | | Carbon equivalent(b) | Hardness HRC, converted from | | |
|---|---|---|---|---|---|
| C | Si | | As read | Rockwell 30-N | Microhardness |
| 3.13 | 1.50 | 3.63 | 50 | 50 | 61 |
| 3.14 | 1.68 | 3.70 | 49 | 50 | 57 |
| 3.19 | 1.64 | 3.74 | 48 | 50 | 61 |
| 3.34 | 1.59 | 3.87 | 47 | 49 | 58 |
| 3.42 | 1.80 | 4.02 | 46 | 47 | 61 |
| 3.46 | 2.00 | 4.13 | 43 | 45 | 59 |
| 3.52 | 2.14 | 4.23 | 36 | 38 | 61 |

(a) Each iron also contained 0.50 to 0.90 Mn, 0.35 to 0.55 Ni, 0.08 to 0.15 Cr, and 0.15 to 0.30 Mo.

(b) Carbon equivalent = $\%C + \frac{1}{3}\% Si$.

**Distortion.** Induction hardening causes less distortion than would a similar quenching treatment from a furnace. The maximum warpage in a 560 mm (22 in.) length of bar was found to be 0.03 mm (0.0015 in.) after induction hardening, compared with 0.17 to 0.25 mm (0.007 to 0.010 in.) for the same bars quenched from a furnace. For thin-walled cylinders, distortion is not a problem unless the thickness of the induction-hardened layer exceeds 20% of the wall thickness.

For selective hardening, in place or by scanning, to depths up to 3.8 mm (0.150 in.), water quenching can be used safely. However, the hardening of keyways, cross-drilled holes, or extremely thin walls may require the use of oil to prevent excessive distortion or cracking.

### *Surface Hardening of Ductile Iron*

Ductile iron responds readily to surface hardening by flame, induction, or laser heating, or by nitriding. Because of the short heating cycle in these processes, the pearlitic types of ductile iron ASTM 80-60-03 and 100-70-03 are preferred. Irons without free ferrite in their microstructure respond almost instantly to flame or induction heating and require very little holding time at the austenitizing temperature in order to be fully hardened.

With a moderate amount of free ferrite, the response may be satisfactory, but an entirely ferritic matrix, typical of the grades with high ductility, requires several minutes at 870 °C (1600 °F) to be fully hardened by subsequent cooling. A matrix microstructure of fine pearlite, readily obtained by normalizing, has a rapid response to surface hardening and provides excellent core support for the hardened case.

With proper technique and the control of temperature between 845 and 900 °C (1550 and 1650 °F), the ranges of surface hardness for ductile iron with different matrices expected in commercial production are:

- Ductile iron, fully annealed (ferritic), water quenched behind the flame or induction coil, 35 to 45 HRC
- Ductile iron, predominantly ferritic (partly pearlitic), stress relieved prior to heating, self quenched, 40 to 45 HRC
- Ductile iron, predominantly ferritic (partly pearlitic), stress relieved prior to heating, water quenched, 50 to 55 HRC
- Ductile iron, mostly pearlitic, stress relieved before heating, water quenched, 58 to 62 HRC

Heating time and temperature, amount of dissolved carbon, section size, and rate of quench help to determine final hardness values. Often soluble-oil or polymer quench media are used to minimize quench cracking where the casting section changes.

Flame or induction-hardened ductile iron castings have been used for heavy-duty applications such as foils for cold working titanium, ring gears for paper-mill drives, crankshafts, and large sprockets for chain drives.

**The response of ductile iron to induction hardening** is dependent on the amount of pearlite in the matrix of as-cast, normalized, and normalized and tempered prior structures. In quenched and tempered iron, the secondary graphite nodules formed during tempering are close enough together to supply sufficient carbon to the matrix by re-solution during induction heating.

***In the as-cast condition,*** a minimum of 50% pearlite is considered necessary for satisfactory hardening with induction heating cycles of 3.5 s and longer and hardening temperatures of 955 to 980 °C (1750 to 1800 °F). Structures containing less pearlite can be hardened by using higher temperatures, but at the risk of retaining austenite, forming ledeburite, and damaging the surface. With more than 50% pearlite, hardening temperatures may be reduced to within the range of 900 to 925 °C (1650 to 1700 °F).

***In the Normalized Condition.*** For heating cycles of 3.5 s and longer, at temperatures of 955 to 980 °C (1750 to 1800 °F), 50% pearlite in a prior structure would be considered a minimum. Normalized and tempered irons exhibit a poor response with lower pearlite content because of the depletion of the matrix carbon. In the tempering operation, the carbon migrates from the pearlite matrix to the graphite nodules. In the heating cycle, carbon is reabsorbed in the matrix from the nodule; however, there is insufficient time for it to migrate throughout the ferritic areas. Another factor in the response of ductile iron is the graphite nodule count; the greater the number of nodules per unit area, the deeper the hardening for any given heat cycle. This effect is more evident as the percentage of ferrite increases (Fig. 19).

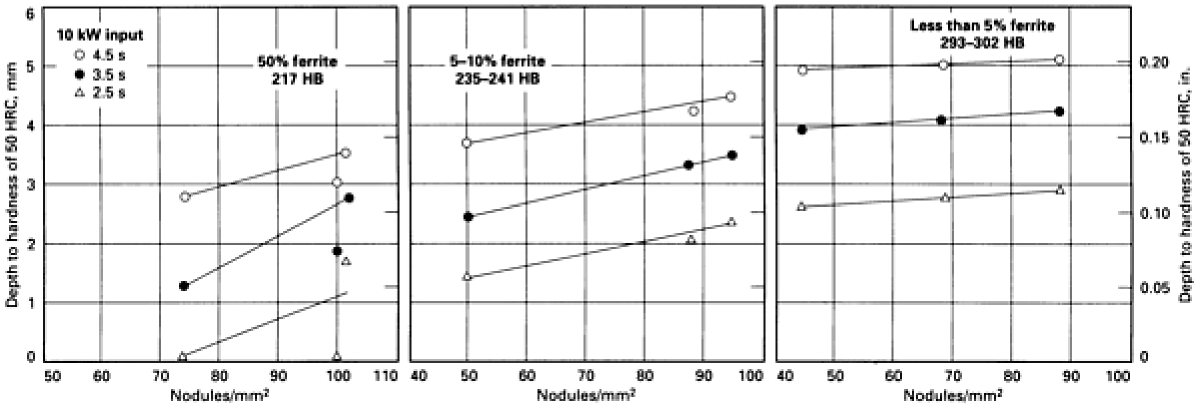

**Fig. 19 Relationship between depth of induction hardening to 50 HRC and graphite nodule count in normalized and tempered ductile (nodular) iron**

***Quenched and Tempered.*** The response of quenched and tempered nodular iron to induction hardening is excellent over a wide range of microstructures containing up to 95% ferrite. As a prior treatment, quenching and tempering has the advantage of permitting a lower prior hardness; there is a risk of distortion and quench cracking, however.

**Nitriding** is a case-hardening process that involves the diffusion of nitrogen into the surface at a temperature of about 550 to 600 °C (1020 to 1110 °F). Usually the source of nitrogen is ammonia, and the process produces a surface layer about 0.1 mm (0.004 in.) deep with a surface hardness approaching 1100 HV. The surface layer is typically white and featureless in an etched microstructure, but nitride needles can be found just below it. Alloying elements can be used to increase case hardness, and 0.5 to 1% Al, Ni, and Mo have been reported to achieve useful results. Nitrided cases provide, in addition to very high hardness, increased wear resistance and antiscuffing properties, improved fatigue life, and improved corrosion resistance. Typical applications are for cylinder liners, bearing pins, and small shafts.

Nitriding can also be carried out in liquid salt baths based on cyanide salts. Such processes have lower temperatures of treatment, although case depth may be decreased. More recently, processes for nitriding in a plasma have been developed and applied with success to ductile iron, but the process may be more restricted because of the special equipment and cost likely to be involved.

### *Surface Hardening of Pearlitic Malleable Iron*

Fully pearlitic malleable iron may be surface hardened by either induction heating and quenching or flame heating and quenching. Laser and electron beam techniques also have been used for hardening selected areas on the surface of pearlitic and ferritic malleable iron castings that are free from decarburization. Generally, hardness in the range from 55 to 60 HRC is attainable, with the depth of penetration being controlled by the rate of heating and by the temperature developed at the surface of the part being hardened. In induction hardening, this is accomplished by the close regulation of power output, operating frequency, heating time, and alloy content of the iron.

The maximum hardness obtainable in the matrix of a properly hardened part is 67 HRC; however, conventional hardness measurements show less than the true matrix hardness because of the temper carbon nodules that are averaged into the hardness. Generally, a casting with a matrix microhardness of 67 HRC will have about 62 HRC average hardness, as measured with the standard Rockwell tester.

Rocker arms and clutch hubs are examples of automotive production parts that are surface hardened by induction. Flame hardening requires close control for these applications in order to avoid distortion that would interfere with their operation.

## Conversion Coatings

Chemical reactions at casting surfaces can produce iron-containing compounds that provide wear resistance or an attractive appearance or that serve as excellent bonding agents for subsequent organic coatings. Table 11 details common conversion coatings and their useful properties (chromate and phosphate conversion coatings are discussed in greater detail in the articles "Chromate Conversion Coatings" and "Phosphate Coatings" in this Volume). Most of the successful processes are proprietary, and reproducibility of consistently good finishes is one of the important features.

**Table 11 Chemical conversion coatings, structures, and characteristics**

| Type | Coating structure | Properties | Uses |
|---|---|---|---|
| Chromate | Nonporous film acts as moisture barrier | High corrosion resistance; inhibits corrosion if surface is broken; can be colored | Marine applications; can be decorative; nonporous bond layer for paint |
| Oxide | Ferric oxide formed from iron | Inhibits formation of ferrous oxide; highly absorbent; some wear resistance | Decorative blue-black coating; readily absorbs overlays of wax or oil |
| Phosphate | Iron zinc or manganese phosphates are crystalline structures formed on the surface by deposition from chemical solution | Chemically neutral and high adherence to iron surfaces; highly absorbent | Excellent for bonding paint to iron; prevents abnormal wear or seizing during break-in |

Source: Ref 7

**Phosphate coating** is the treatment of cast iron with a dilute solution of phosphoric acid and other chemicals in which the surface of the metal, reacting chemically with the phosphoric acid medium, is converted to an integral, mildly protective layer of insoluble crystalline phosphate. The coating reduces corrosion, prevents surface seizure on initial wear contact, and provides an excellent base for organic paint bonding.

Gray, ductile, and malleable iron castings all lend themselves readily to phosphating. The ability of a cast iron to accept a phosphate coating is not affected by alloy content, but hinges primarily on two requirements: a clean surface, and a metal temperature approximately equal to that of the phosphating bath. Dry machined surfaces need no further cleaning; cast surfaces can be prepared by blasting or other cleaning methods to remove scale and sand.

**Oxide Coatings** (Ref 7). Conversion of the surface of an iron casting to a magnetic oxide, $Fe_3O_4$, gives a thin black finish. These films have a certain degree of wear resistance, provide a good bond for paint or lacquer, and have pleasing decorative features. The film layer, if oiled or waxed, provides satisfactory corrosion resistance against handling and storage and is useful with lubrication for sliding and rotating wear applications. The original method of forming a strongly adherent black oxide film is still useful today. The process involves use of steam around an iron part heated above 480 °C (900 °F) and yields a tight oxide coating. Steam generally is introduced to furnace atmospheres to completely replace air while the parts are heated to 590 °C (1100 °F). Twenty minutes at temperature in this atmosphere is sufficient for buildup of a thick, wear-resisting film.

Oxide film finishes can also be produced in a wide variety of proprietary basic-nitrate media. Reproducibility of consistent finishes in large-volume operations is one of their prime features. These provide thinner films that are more suitable for decorative purposes. Sodium carbonate and sodium and potassium nitrates constitute the bulk of the bath solutions. Often these are supplemented with additional agents, such as manganese, to give a mixed oxide film.

**Chromate conversion coating** is accomplished by immersion of iron in an aqueous solution of chromic acid or chromium salts. This solution can be used as a supplement to cadmium and zinc plating to prevent the formation of powder corrosion products (see Table 9) and it also provides an excellent bond for paints.

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## Reference cited in this section

7. C.F. Walton and T.J. Ajar, Ed., *Iron Castings Handbook,* Iron Casting Society, 1981, p 755-799

## Porcelain Enameling

Porcelain enamels are inorganic vitreous coatings that are matured by heat. The inherently good heat transfer, thermal stability, and rigidity of iron at firing temperatures, coupled with the excellent adherence of vitreous ceramic frits as they fuse onto the cast surface, make the combination of porcelain on iron an excellent product. General corrosion resistance or resistance to specific chemicals can be obtained by selecting the proper porcelain enamel. The scratch resistance and hardness of the enamel coating, which allow the surface to resist abrasion, are almost equal in importance to the corrosion resistance.

Four processes are used to apply enamels: dry, wet, thermal spray (or plasma spray), and electrostatic precipitation. The latter two methods are seldom used on iron castings. Preparations for enameling start by blasting with sand, steel shot, or iron grit.

Dry coating methods use formulations that are mainly silica; these formulations generate a surface with the hardness and abrasion resistance of glass. Fluxes and opacifiers are mixed into the silica, and the mixture is then melted, quenched, and ground to make frit. (Frit is the term applied to the basic coating materials.) After application of a bonding ground coat, relatively heavy, smooth coatings (such as those on sinks and bathtubs) can be obtained by multiple firing. Each firing is followed by hot dusting with additional powdered frit, until the desired finish has been achieved.

Wet methods produce thinner coatings. The powdered frit is suspended in a solution of electrolytes and water or in an organic solvent and is applied by spraying or dipping over the ground coat. The sprayed or dipped coating must be dried prior to firing.

Ground coats that wet iron readily, adhere well, and are compatible with the cover coat are essential to the enameling process. Good ground coats promote adhesion between the enamel layer and the substrate, seal and smooth the irregularities of the surface, and prevent oxidation of the iron casting at firing temperatures. Top coats (cover coats) must provide the desired appearance and must be compatible with the ground coat. Formulation of frits requires the judgment and experience of a frit manufacturer to ensure that the coating provides successful results.

Cast iron for enameling usually has a composition that falls within the following limits:

| **Constituent** | **Amount, %** |
|---|---|
| Total carbon | 3.20-3.60 |
| Silicon | 2.30-3.00 |
| Manganese | 0.30-0.60 |
| Sulfur | 0.50-0.12 |
| Phosphorus | 0.40-0.80 |

Total carbon and silicon should vary in opposite directions within the ranges shown. If both are low, the iron tends to be brittle and to blister during porcelain enameling. If both are high, the iron is soft and warps easily when reheated for porcelain enameling. Manganese and sulfur should range in the same direction, so that all of the sulfur is converted to manganese sulfide. Within the normal range, phosphorus has a negligible effect on the strength of the cast iron at porcelain enameling firing temperatures.

The primary applications for porcelain enameled cast irons are in the manufacture of bathtubs, kitchen sinks, and lavatories. See the article "Porcelain Enameling" in this Volume for more detailed information.

## Organic Coatings

Organic coatings have a wide variety of properties, but their primary uses require corrosion resistance combined with a pleasing colored appearance. An organic-base film is often resistant to certain environmental substances but not to others, and so must be chosen for a specific set of well-defined service conditions. For example, a vinyl paint might be used on a pump casing that must operate in contact with acidic industrial waters. However, if the same casing is expected to contact hydrocarbons such as gasoline or solvents, a styrene, epoxy, or phenolic coating would most likely provide superior protection.

**Types of Organic Coatings.** The term paint was once commonly used to designate all liquid organic coatings, but it is considered inadequate to describe modern liquid organic coatings, which in general are subdivided into enamels, lacquers, aqueous mixtures, suspensions, bituminous substances, and rubber-base products. Resins dispersed in a vehicle--for example, enamels or lacquers--cure to relatively hard gels by polymerization, oxidation, or solvent evaporation. A comparison of the chemical and environmental resistance of common resins is given in Table 12.

**Table 12 Properties of organic coatings on iron castings**

| **Resin** | **Resistance to chemicals and environment**(a) | | | | | | | | | | **Application method** | | | | **Curing Method** | | **Typical applications** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | **Hydro-carbons** | **Solvents** | **Acids** | **Alkalies** | **Salts** | **Water** | **Weathering** | **Heat** | **Cold** | **Abrasion** | **Need for primer** | **Spray** | **Dip** | **Fluidized bed** | **Air dry** | **Bake** | |
| **Low cost** | | | | | | | | | | | | | | | | | |
| Phenolic | E | E | E | F | E | E | E | G | E | E | no | yes | yes | no | yes | yes | Appliances |
| Urea | E | G | E | E | E | G | G | G | G | E | no | yes | yes | no | no | yes | Appliances |
| Polyester | G | G | G | F | E | G | G | G | G | G | no | yes | yes | no | yes | yes | Thick coatings |
| Alkyd | G | P | F | F | E | G | E | F | G | G | yes | yes | yes | no | yes | yes | General purpose |
| Epoxy | E | E | E | E | E | G | G | E | E | E | no | yes | yes | yes | yes | yes | Scratch-resistant finish |
| Polyethylene | G | E | E | E | E | E | G | F | E | F | no | no | no | yes | no | yes | Coatings |
| Styrene-butadiene | E | G | E | E | E | E | G | G | E | G | no | yes | yes | no | yes | yes | General purpose |
| Urethane | G | E | G | G | E | E | E | E | G | G | yes | yes | yes | no | yes | yes | Scuff-resistant coatings: chemical and marine finishes |
| **Moderate cost** | | | | | | | | | | | | | | | | | |

| | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Vinyl chloride | G | F | E | E | E | E | E | G | G | E | yes | yes | yes | yes | yes | yes | Chemical equipment |
| Melamine | E | G | E | E | E | G | E | G | G | E | no | yes | yes | no | no | yes | Appliances |
| Polyamide | F | G | F | E | E | F | P | G | G | E | no | yes | yes | yes | yes | yes | Abrasion-resistant coatings |
| Vinyl butyral | G | F | F | G | G | G | E | G | E | E | no | yes | yes | no | yes | yes | General purpose, primers |
| Cellulose nitrate | F | F | G | F | E | E | E | P | G | F | yes | yes | yes | no | yes | yes | High-gloss lacquer |
| Acrylic | F | P | F | G | E | E | E | P | F | F | yes | yes | yes | no | yes | yes | Water-resistant finishes |
| Vinyl acetate | F | P | F | F | F | G | E | F | F | E | no | yes | yes | no | yes | yes | Decorative |
| Cellulose acetate butyrate | F | F | F | F | G | F | E | P | G | F | yes | yes | yes | no | yes | yes | Decorative |
| **High cost** | | | | | | | | | | | | | | | | | |
| Chlorinated polyether | G | E | E | E | E | E | E | G | E | F | no | no | no | yes | no | yes | Chemical equipment |
| Fluorocarbon | E | E | E | E | E | E | E | E | G | P | yes | yes | no | yes | no | yes | Chemical equipment, nonstick surfaces |

| | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Silicone | G | F | G | G | G | E | E | E | E | G | yes | yes | yes | no | yes | yes | Heat-resistant finishes |

Source: Ref 7

(a) E, excellent; G, good; F, fair; P, poor.

Enamels consist of milled pigments and other additives dispersed in resins and solvents and are converted from liquids to hard films by oxidation or polymerization. Lacquers are thermoplastic resins dissolved in organic solvents that dry rapidly by evaporation. In aqueous coatings, water is the principal vehicle or reducer. The advantages of water-base paints are nominal cost, nonflammability, true odorlessness, and nontoxicity. The disadvantages are difficulties in wettability, flow, and drying. Rubber-base coatings are noted for their mechanical properties and corrosion resistance rather than their decorative effects. Bituminous paints are black materials in which coal tar is dissolved in a solvent that evaporates. The major uses of bituminous paints are those that require extremely low permeability and high resistance to water. Unusual protection against chemical solutions, or special decorative effects, can be obtained by the use of asphaltic coatings or those produced by japanning, both of which are also considered bituminous coatings.

Fluorocarbon coatings produce an unusual combination of properties. They are tough, stain resistant, and nonsticking, and have a very low coefficient of friction. Fluorocarbon coatings resist all common industrial acids and temperatures to 300 °C (570 °F). Domestic cookware and chemical-processing equipment are two major applications of fluorocarbon coatings on iron castings. Fluorocarbon coatings are sprayed as emulsions of proprietary products onto a primed surface and then fused at temperatures of 385 to 425 °C (725 to 800 °F).

**Methods of Application.** Organic coatings are applied by spraying, dipping, flow coating, fluidized bed coating, electrostatic deposition, and electrophoresis (electrocoating).

Spraying is adaptable to both low-volume and high-volume workloads. It is done by propelling the coating material toward the workpiece by compressed air, hot spraying, hydraulic-airless, and airless-electrostatic methods. Overspraying is most troublesome with compressed air methods and least troublesome with electrostatic methods.

Dipping has been used for centuries; modern refinements include flow coating and electrophoresis. Not all shapes can be painted by dipping. Pockets can exclude paint from surfaces. The shape of the casting should allow easy draining after dipping. The coating should be selected to inhibit sagging or the formation of droplets on edges. The dipping process is easily automated and can be very efficient in use of materials. A thorough review of organic coatings and their applications, advantages, and limitations is available in Ref 25 and in the articles "Painting" and "Elastomeric Coatings and Linings" in this Volume.

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### References cited in this section

7. C.F. Walton and T.J. Ajar, Ed., *Iron Castings Handbook,* Iron Casting Society, 1981, p 755-799

25. K.B. Tator, Organic Coatings and Linings, *Corrosion,* 9th ed., Vol 13, *Metals Handbook,* ASM International, 1987, p 399-418

## Fused Dry-Resin Coatings

Dry-resin polymers can be applied (by fusion bonding) to iron castings for many of the same applications for which liquid organic coatings are used. Generally, the fused coatings are thick and can be applied very rapidly--often in minutes; in contrast, several hours are required for the drying and curing of a liquid organic coating.

The fusion bonding of polymers on iron castings can be readily accomplished by the application of dry solvent-free powder by fluidized bed coating or electrostatic deposition. The advantages of the process include the use of resins that are insoluble in ordinary solvents, the elimination of carrier solvents, and the ability to combine various plastics in the coating for maximum effectiveness. Sandblasted castings are excellent bases for this process. The plastic films can be easily machined, which contributes to flexibility in manufacturing. Two disadvantages are that thin films are not easily applied and that finding a suitable holding point on a part to be coated in a fluidized bed may be difficult. The six basic types of plastic fusion-bonded finishes, as well as a comparison of their characteristics, are given in Table 13.

**Table 13 Relative effectiveness of fusion-bonding resin coatings**

| | Effectiveness[(a)] | | | | | |
|---|---|---|---|---|---|---|
| | Vinyl | Cellulose | Epoxy | Nylon | Chlorinated | Polyethylene |

|  |  |  |  |  | **polyether** |  |
|---|---|---|---|---|---|---|
| Exterior durablity | E | VG | F | F | F | F |
| Salt spray resistance | E | G | VG | VG | F | F |
| Water resistance | E | VG | G | G | E | F |
| Acid resistance | VG | G | VG | F | E | E |
| Alkali resistance | VG | G | VG | G | E | E |
| Solvent resistance | G | F | F | E | VG | G |
| Abrasion resistance | E | VG | E | E | VG | P |
| Impact resistance | E | G | (b) | VG | G | P |
| Heat resistance | VG | G | VG | VG | VG | P |
| Flexibility | E | G | (b) | G | F | E |
| Electrical characteristics | VG | VG | E | G | VG | VG |
| Color range | E | E | P | F | P | F |
| Gloss | E | E | VG | VG | G | G |

Source: Ref 7

(a) E, excellent; VG, very good; G, good; F, fair; P, poor.

(b) Ranges from excellent to poor depending on composition.

In a fluidized bed, castings heated to 175 to 310 °C (350 to 590 °F) are placed in a chamber containing resin powder suspended by upward-moving air. The dry resin floats around the casting, adhering to all the surfaces regardless of the complexity of the shape. Heating fuses the coating into a continuous film. This method produces a uniform coating that covers sharp corners, edges, and projections and that can be applied in a wide range of thicknesses (up to 1.5 mm, or 0.06 in.) in a single application.

In electrostatic deposition, the powdered resin is conveyed to a gun, in which it is given an electrostatic charge. The casting has the opposite charge. The charged powder is attracted to the surface, where it is deposited evenly. The electrostatic process is especially useful for applying thinner coatings because the residual charge on the workpiece is discharged by the powder, or leaks off, thus limiting the amount of powder that can be deposited. Preheating of the casting permits thicker coatings because the initial powder layer fuses as it is applied. Curing is done by reheating the casting to fuse the resin coating. Primers may be needed for some types of polymers (such as butyrates and vinyls) in order to achieve adequate bonding.

## Reference cited in this section

7. C.F. Walton and T.J. Ajar, Ed., *Iron Castings Handbook*, Iron Casting Society, 1981, p 755-799

# Surface Engineering of Carbon and Alloy Steels

**J.R. Davis, Davis & Associates**

## Introduction

CARBON AND ALLOY STEELS, the most widely used metallic material, account for more than 80 million tons, or approximately 98% of the annual steel production in the United States (Table 1). Steels are a popular material of choice because they can be manufactured relatively inexpensively in large quantities to very precise specifications. They also provide a wide range of mechanical properties, from moderate yield strength levels (200 to 300 MPa, or 30 to 40 ksi) with excellent ductility to yield strengths exceeding 1400 MPa (200 ksi) with fracture toughness levels as high as 110 MPa $\sqrt{m}$ (100 ksi $\sqrt{in}$ ).

**Table 1 Net shipment of U.S. steel mill products--all grades**

| Steel products | 1992 | | 1991 | |
|---|---|---|---|---|
| | Tons [(a)] | % | Tons [(a)] | % |
| Ingots and steel for castings | 215 | 0.3 | 244 | 0.3 |
| Blooms, slabs, billets | 2,255 | 2.7 | 2,305 | 2.9 |
| Wire rods | 4,511 | 5.5 | 4,366 | 5.5 |
| Structural shapes (≥ 75 mm, or 3 in.) | 5,081 | 6.2 | 5,245 | 6.7 |
| Steel piling | 454 | 0.6 | 430 | 0.5 |
| Plates (cut lengths) | 4,362 | 5.3 | 4,275 | 5.4 |
| Plates (in coils) | 2,740 | 3.3 | 2,667 | 3.4 |
| Rails | | | | |
| Standard (over 27 kg, or 60 lb) | 435 | 0.5 | 382 | 0.5 |
| All other | 5 | 0.0 | 16 | 0.0 |

| | | | | |
|---|---|---|---|---|
| Railroad accessories | 122 | 0.1 | 89 | 0.1 |
| Bars | | | | |
| Hot rolled | 5,806 | 7.1 | 5,431 | 6.9 |
| Bar-size light shapes | 1,119 | 1.4 | 1,157 | 1.5 |
| Reinforcing | 4,781 | 5.8 | 4,859 | 6.2 |
| Cold finished | 1,458 | 1.8 | 1,341 | 1.7 |
| Tool steel | 64 | 0.1 | 51 | 0.1 |
| Pipe and tubing | | | | |
| Standard pipe | 1,062 | 1.3 | 970 | 1.2 |
| Oil country goods | 979 | 1.2 | 1,077 | 1.4 |
| Line | 1,110 | 1.3 | 1,439 | 1.8 |
| Mechanical | 790 | 1.0 | 744 | 0.9 |
| Pressure | 48 | 0.1 | 49 | 0.1 |
| Structural | 142 | 0.2 | 151 | 0.2 |
| Pipe for piling | 35 | 0.0 | 24 | 0.0 |
| Stainless | 32 | 0.0 | 34 | 0.0 |
| Wire-drawn | 900 | 1.1 | 865 | 1.1 |
| Black plate | 230 | 0.3 | 249 | 0.3 |
| Tin plate | 2,715 | 3.3 | 2,754 | 3.5 |
| Tin-free steel | 904 | 1.1 | 964 | 1.2 |

|  |  |  |  |  |
|---|---|---|---|---|
| Tin-coated sheets | 78 | 0.1 | 74 | 0.1 |
| Sheets |  |  |  |  |
| Hot rolled | 13,361 | 1.62 | 13,161 | 16.7 |
| Cold rolled | 12,692 | 15.4 | 11,532 | 14.6 |
| Sheets and strip |  |  |  |  |
| Galvanized-hot dipped | 8,199 | 10.0 | 6,910 | 8.8 |
| Electrolytic | 2,390 | 2.9 | 2,099 | 2.7 |
| All other metallic coated | 1,348 | 1.6 | 1,146 | 1.5 |
| Electrical | 436 | 0.5 | 458 | 0.6 |
| Strip |  |  |  |  |
| Hot rolled | 550 | 0.7 | 533 | 0.7 |
| Cold rolled | 832 | 1.0 | 755 | 1.0 |
| **Total Steel Mill Products** | **82,241** | **100.0** | **78,846** | **100.0** |
| Carbon | 76,625 | 93.2 | 73,480 | 93.2 |
| Stainless | 1,514 | 1.8 | 1,449 | 1.8 |
| Alloy (other than stainless) | 4,101 | 5.0 | 3,917 | 5.0 |

Source: American Iron and Steel Institute

(a) Thousands of net tons.

Following a brief review of the classification of steels, this article will review the following:

- Cleaning methods
- Finishing methods
- Conversion coatings
- Hot dip coating processes

- Electrogalvanizing
- Electroplating
- Metal cladding
- Organic coatings
- Zinc-rich coatings
- Porcelain enameling
- Thermal spraying
- Hardfacing
- Vapor deposited coatings
- Surface modification
- Surface hardening via heat treatment

Emphasis will be placed on the most commonly used methods for surface engineering of steels. No attempt is made at providing detailed information on any given process as this can be found in the cited articles found throughout this Volume. In terms of the coating, surface modification, and surface hardening processes described, the resulting property improvements (corrosion and/or wear resistance) will be stressed rather than the details of the process itself (equipment, plating bath compositions, process controls, etc.). Information on the surface engineering of stainless steels, tool steels, maraging steels, electrical steels, and ferrous powder metallurgy alloys can be found in the articles "Surface Engineering of Stainless Steels" and "Surface Engineering of Specialty Steels" which immediately follow in this Section of the Handbook.

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## Classification of Steels

Steels can be classified by a variety of different systems depending on:

- *The composition,* such as carbon, low-alloy, or stainless steels
- *The manufacturing methods,* such as open hearth, basic oxygen process, or electric furnace methods
- *The finishing method,* such as hot rolling or cold rolling
- *The product form,* such as bar, plate, sheet, strip, tubing, or structural shape
- *The deoxidation practice,* such as killed, semikilled, capped, or rimmed steel
- *The microstructure,* such as ferritic, pearlitic, and martensitic
- *The required strength level,* as specified in ASTM standards
- *The heat treatment,* such as annealing, quenching and tempering, and thermomechanical processing
- *Quality descriptors,* such as forging quality and commercial quality

Of the aforementioned classification systems, chemical composition is the most widely used and will be discussed below. More detailed information on the classification and designation of carbon and alloy steels can be found in Ref 1.

### *Carbon Steels*

The American Iron and Steel Institute defines carbon steel as follows:

> Steel is considered to be carbon steel when no minimum content is specified or required for chromium, cobalt, columbium [niobium], molybdenum, nickel, titanium, tungsten, vanadium or zirconium, or any other element to be added to obtain a desired alloying effect; when the specified minimum for copper does not exceed 0.40 per cent; or when the maximum content specified for any of the following elements does not exceed the percentages noted; manganese 1.65, silicon 0.60, copper 0.60.

Carbon steel can be classified, according to various deoxidation practices, as rimmed, capped, semikilled, or killed steel. Deoxidation practice and the steelmaking process will have an effect on the characteristics and properties of the steel. However, variations in carbon have the greatest effect on mechanical properties, with increasing carbon content leading to increased hardness and strength. As such, carbon steels are generally categorized according to their carbon content. Generally speaking, carbon steels contain up to 2% total alloying elements and can be subdivided into low-carbon steels, medium-carbon steels, and high-carbon steels.

As a group, carbon steels are by far the most frequently used steel. Table 1 indicates that more than 93% of the steel produced and shipped in the United States is carbon steel. Chemical compositions for selected carbon steels are provided in Table 2.

### Table 2 Carbon steel compositions

Applicable only to structural shapes, plates, strip, sheets, and welded tubing

| **UNS number** | **SAE-AISI number** | **Cast or heat chemical ranges and limits, %[(a)]** | | | |
|---|---|---|---|---|---|
| | | **C** | **Mn** | **P max** | **S max** |
| G10060 | 1006 | 0.08 max | 0.45 max | 0.040 | 0.050 |
| G10080 | 1008 | 0.10 max | 0.50 max | 0.040 | 0.050 |
| G10090 | 1009 | 0.15 max | 0.60 max | 0.040 | 0.050 |
| G10100 | 1010 | 0.08-0.13 | 0.30-0.60 | 0.040 | 0.050 |
| G10120 | 1012 | 0.10-0.15 | 0.30-0.60 | 0.040 | 0.050 |
| G10150 | 1015 | 0.12-0.18 | 0.30-0.60 | 0.040 | 0.050 |
| G10160 | 1016 | 0.12-0.18 | 0.60-0.90 | 0.040 | 0.050 |
| G10170 | 1017 | 0.14-0.20 | 0.30-0.60 | 0.040 | 0.050 |
| G10180 | 1018 | 0.14-0.20 | 0.60-0.90 | 0.040 | 0.050 |
| G10190 | 1019 | 0.14-0.20 | 0.70-1.00 | 0.040 | 0.050 |
| G10200 | 1020 | 0.17-0.23 | 0.30-0.60 | 0.040 | 0.050 |
| G10210 | 1021 | 0.17-0.23 | 0.60-0.90 | 0.040 | 0.050 |
| G10220 | 1022 | 0.17-0.23 | 0.70-1.00 | 0.040 | 0.050 |
| G10230 | 1023 | 0.19-0.25 | 0.30-0.60 | 0.040 | 0.050 |
| G10250 | 1025 | 0.22-0.28 | 0.30-0.60 | 0.040 | 0.050 |

| | | | | | |
|---|---|---|---|---|---|
| G10260 | 1026 | 0.22-0.28 | 0.60-0.90 | 0.040 | 0.050 |
| G10300 | 1030 | 0.27-0.34 | 0.60-0.90 | 0.040 | 0.050 |
| G10330 | 1033 | 0.29-0.36 | 0.70-1.00 | 0.040 | 0.050 |
| G10350 | 1035 | 0.31-0.38 | 0.60-0.90 | 0.040 | 0.050 |
| G10370 | 1037 | 0.31-0.38 | 0.70-1.00 | 0.040 | 0.050 |
| G10380 | 1038 | 0.34-0.42 | 0.60-0.90 | 0.040 | 0.050 |
| G10390 | 1039 | 0.36-0.44 | 0.70-1.00 | 0.040 | 0.050 |
| G10400 | 1040 | 0.36-0.44 | 0.60-0.90 | 0.040 | 0.050 |
| G10420 | 1042 | 0.39-0.47 | 0.60-0.90 z | 0.040 | 0.050 |
| G10430 | 0143 | 0.39-0.47 | 0.70-1.00 | 0.040 | 0.050 |
| G10450 | 1045 | 0.42-0.50 | 0.60-0.90 | 0.040 | 0.050 |
| G10460 | 1046 | 0.42-0.50 | 0.70-1.00 | 0.040 | 0.050 |
| G10490 | 1049 | 0.45-0.53 | 0.60-0.90 | 0.040 | 0.050 |
| G10500 | 1050 | 0.47-0.55 | 0.60-0.90 | 0.040 | 0.050 |
| G10550 | 1055 | 0.52-0.60 | 0.60-0.90 | 0.040 | 0.050 |
| G10600 | 1060 | 0.55-0.66 | 0.60-0.90 | 0.040 | 0.050 |
| G10640 | 1064 | 0.59-0.70 | 0.50-0.80 | 0.040 | 0.050 |
| G10650 | 1065 | 0.59-0.70 | 0.60-0.90 | 0.040 | 0.050 |
| G10700 | 1070 | 0.65-0.76 | 0.60-0.90 | 0.040 | 0.050 |
| G10740 | 1074 | 0.69-0.80 | 0.50-0.80 | 0.040 | 0.050 |
| G10750 | 1075 | 0.69-0.80 | 0.40-0.70 | 0.040 | 0.050 |

| | | | | | |
|---|---|---|---|---|---|
| G10780 | 1078 | 0.72-0.86 | 0.30-0.60 | 0.040 | 0.050 |
| G10800 | 1080 | 0.74-0.88 | 0.60-0.90 | 0.040 | 0.050 |
| G10840 | 1084 | 0.80-0.94 | 0.60-0.90 | 0.040 | 0.050 |
| G10850 | 1085 | 0.80-0.94 | 0.70-1.00 | 0.040 | 0.050 |
| G10860 | 1086 | 0.80-0.94 | 0.30-0.50 | 0.040 | 0.050 |
| G10900 | 1090 | 0.84-0.98 | 0.60-0.90 | 0.040 | 0.050 |
| G10950 | 1095 | 0.90-1.04 | 0.30-0.50 | 0.040 | 0.050 |

(a) When silicon ranges or limits are required, the following ranges and limits are commonly used; up to SAE 1025 inclusive, 0.10% max, 0.10-0.25%, or 0.15-0.35%. Over SAE 1025, 0.10-0.25% or 0.15-0.35%

**Low-carbon steels** contain up to 0.30% C. The largest category of this class of steel is flat-rolled products (sheet or strip) usually in the cold-rolled and annealed condition. The carbon content for these high-formability steels is very low, less than 0.10% C, with up to 0.4% Mn. Typical uses are in automobile body panels, tin plate, and wire products. For rolled steel structural plates and sections, the carbon content may be increased to approximately 0.30%, with higher manganese up to 1.5%. These latter materials may be used for stampings, forgings, seamless tubes, and boiler plate.

**Medium-carbon steels** are similar to low-carbon steels except that the carbon ranges from 0.30 to 0.60% and the manganese from 0.60 to 1.65%. Increasing the carbon content to approximately 0.5% with an accompanying increase in manganese allows medium-carbon steels to be used in the quenched and tempered condition. The uses of medium carbon-manganese steels include shafts, couplings, crankshafts, axles, gears, and forgings. Steels in the 0.40 to 0.60% C range are also used for rails, railway wheels, and rail axles.

**High-carbon steels** contain from 0.60 to 1.00% C with manganese contents ranging from 0.30 to 0.90%. High-carbon steels are used for spring materials and high-strength wires.

### *High-Strength Low-Alloy Steels*

High-strength low-alloy (HSLA) steels are designed to provide better mechanical properties and/or greater resistance to atmospheric corrosion than conventional carbon steels. They are not considered to be alloy steels in the normal sense because they are designed to meet specific mechanical properties rather than a chemical composition (HSLA steels have yield strengths greater than 275 MPa, or 40 ksi). The chemical composition of a specific HSLA steel may vary for different product thicknesses to meet mechanical property requirements. The HSLA steels have low carbon contents (0.05 to ~0.25% C) in order to produce adequate formability and weldability, and they have manganese contents up to 2.0%. Small quantities of chromium, nickel, molybdenum, copper, nitrogen, vanadium, niobium, titanium, and zirconium are used in various combinations. The types of HSLA steels commonly used include:

- *Weathering steels,* designed to exhibit superior atmospheric corrosion resistance
- *Control-rolled steels,* hot rolled according to a predetermined rolling schedule designed to develop a highly deformed austenite structure that will transform to a very fine equiaxed ferrite structure on cooling
- *Pearlite-reduced steels,* strengthened by very fine-grain ferrite and precipitation hardening but with low carbon content and therefore little or no pearlite in the microstructure

- *Microalloyed steels,* with very small additions (generally <0.10% each) of such elements as niobium, vanadium, and/or titanium for refinement of grain size and/or precipitation hardening
- *Acicular ferrite steel,* very low carbon steels with sufficient hardenability to transform on cooling to a very fine high-strength acicular ferrite (low-carbon bainite) structure rather than the usual polygonal ferrite structure
- *Dual-phase steels,* processed to a microstructure of ferrite containing small, uniformly distributed regions of high-carbon martensite, resulting in a product with low yield strength and a high rate of work hardening, thus providing a high-strength steel of superior formability

Table 3 lists chemical compositions for various HSLA steels.

**Table 3 Compositional limits for HSLA steel grades described in ASTM specifications**

| **ASTM specification** | **Type or grade** | **UNS designation** | **Heat compositional limits, %(a)** | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | **C** | **Mn** | **P** | **S** | **Si** | **Cr** | **Ni** | **Cu** | **V** | **Other** |
| A 242 | Type 1 | K11510 | 0.15 | 1.00 | 0.45 | 0.05 | . . . | . . . | . . . | 0.20 min | . . . | . . . |
| A 572 | Grade 42 | . . . | 0.21 | 1.35(b) | 0.04 | 0.05 | 0.30(b) | . . . | . . . | 0.20 min(c) | . . . | (d) |
| | Grade 50 | . . . | 0.23 | 1.35(b) | 0.04 | 0.05 | 0.30(b) | . . . | . . . | 0.20 min(c) | . . . | (d) |
| | Grade 60 | . . . | 0.26 | 1.35(b) | 0.04 | 0.05 | 0.30 | . . . | . . . | 0.20 min(c) | . . . | (d) |
| | Grade 65 | . . . | 0.23(b) | 1.65(b) | 0.04 | 0.05 | 0.30 | . . . | . . . | 0.20 min(c) | . . . | (d) |
| A 588 | Grade A | K11430 | 0.10-0.19 | 0.90-1.25 | 0.04 | 0.05 | 0.15-0.30 | 0.40-0.65 | . . . | 0.25-0.40 | 0.02-0.10 | . . . |
| | Grade B | K12043 | 0.20 | 0.75-1.25 | 0.04 | 0.05 | 0.15-0.30 | 0.40-0.70 | 0.25-0.50 | 0.20-0.40 | 0.01-0.10 | . . . |
| | Grade C | K11538 | 0.15 | 0.80-1.35 | 0.04 | 0.05 | 0.15-0.30 | 0.30-0.50 | 0.25-0.50 | 0.20-0.50 | 0.01-0.10 | . . . |
| | Grade D | K11552 | 0.10-0.20 | 0.75-1.25 | 0.04 | 0.05 | 0.50-0.90 | 0.50-0.90 | . . . | 0.30 | . . . | 0.04 Nb, 0.05-0.15 Zr |
| | Grade K | . . . | 0.17 | 0.5-1.20 | 0.04 | 0.05 | 0.25-0.50 | 0.40-0.70 | 0.40 | 0.30-0.50 | . . . | 0.10 Mo, 0.005-0.05 Nb |

| ASTM specification | Type or grade | UNS designation | Heat compositional limits, %(a) | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | C | Mn | P | S | Si | Cr | Ni | Cu | V | Other |
| A 606 | . . . | . . . | 0.22 | 1.25 | . . . | 0.05 | . . . | . . . | . . . | . . . | . . . | . . . |
| A 607 | Grade 45 | . . . | 0.22 | 1.35 | 0.04 | 0.05 | . . . | . . . | . . . | 0.20 min(c) | . . . | (d) |
| | Grade 50 | . . . | 0.23 | 1.35 | 0.04 | 0.05 | . . . | . . . | . . . | 0.20 min(c) | . . . | (d) |
| | Grade 55 | . . . | 0.25 | 1.35 | 0.04 | 0.05 | . . . | . . . | . . . | 0.20 min(c) | . . . | (d) |
| | Grade 60 | . . . | 0.26 | 1.50 | 0.04 | 0.05 | . . . | . . . | . . . | 0.20 min(c) | . . . | (d) |
| | Grade 65 | . . . | 0.26 | 1.50 | 0.04 | 0.05 | . . . | . . . | . . . | 0.20 min(c) | . . . | (d) |
| | Grade 70 | . . . | 0.26 | 1.65 | 0.04 | 0.05 | . . . | . . . | . . . | 0.20 min(c) | . . . | (d) |
| A 618 | Grade Ia | . . . | 0.15 | 1.00 | 0.15 | 0.05 | . . . | . . . | . . . | 0.20 min | . . . | . . . |
| | Grade Ib | . . . | 0.20 | 1.35 | 0.04 | 0.05 | . . . | . . . | . . . | 0.20 min(e) | . . . | . . . |
| | Grade II | K12609 | 0.22 | 0.85-1.25 | 0.04 | 0.05 | 0.30 | . . . | . . . | . . . | 0.02 min | . . . |
| | Grade III | K12700 | 0.23 | 1.35 | 0.04 | 0.05 | 0.30 | . . . | . . . | . . . | 0.02 min | 0.005 Nb min(f) |
| A 633 | Grade A | K10802 | 0.18 | 1.00-1.35 | 0.04 | 0.05 | 0.15-0.30 | . . . | . . . | . . . | . . . | 0.05 Nb |
| | Grade C | K12000 | 0.20 | 1.15-1.50 | 0.04 | 0.05 | 0.15-0.50 | . . . | . . . | . . . | . . . | 0.01-0.05 Nb |
| | Grade D | K02003 | 0.20 | 0.70-1.60(b) | 0.04 | 0.05 | 0.15-0.50 | 0.25 | 0.25 | 0.35 | . . . | 0.08 Mo |
| | Grade | K12202 | 0.22 | 1.15- | 0.04 | 0.05 | 0.15- | . . . | . . . | . . . | 0.04- | 0.01-0.05 Nb(c), |

| ASTM specification | Type or grade | UNS designation | Heat compositional limits, %[a] | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | C | Mn | P | S | Si | Cr | Ni | Cu | V | Other |
| | E | | | 1.50 | | | 0.50 | | | | 0.11 | 0.01-0.03 N |
| A 656 | Type 3 | . . . | 0.18 | 1.65 | 0.025 | 0.035 | 0.60 | . . . | . . . | . . . | 0.08 | 0.020 N, 0.005-0.15 Nb |
| | Type 7 | . . . | 0.18 | 1.65 | 0.025 | 0.035 | 0.60 | . . . | . . . | . . . | 0.005-0.15 | 0.020 N, 0.005-0.10 Nb |
| A 690 | . . . | K12249 | 0.22 | 0.60-0.90 | 0.08-0.15 | 0.05 | 0.10 | . . . | 0.40-0.75 | 0.50 min | . . . | . . . |
| A 709 | Grade 50, type 1 | . . . | 0.23 | 1.35 | 0.04 | 0.05 | 0.40 | . . . | . . . | . . . | . . . | 0.005-0.05 Nb |
| | Grade 50, type 2 | . . . | 0.23 | 1.35 | 0.04 | 0.05 | 0.40 | . . . | . . . | . . . | 0.01-0.15 | . . . |
| | Grade 50, type 3 | . . . | 0.23 | 1.35 | 0.04 | 0.05 | 0.40 | . . . | . . . | . . . | [g] | 0.05 Nb max |
| | Grade 50, type 4 | . . . | 0.23 | 1.35 | 0.04 | 0.05 | 0.40 | . . . | . . . | . . . | [h] | 0.015 N max |
| A 715 | . . . | . . . | 0.15 | 1.65 | 0.025 | 0.035 | . . . | . . . | . . . | V, Ti, Nb added as necessary | | |
| A 808 | . . . | . . . | 0.12 | 1.65 | 0.04 | 0.05 max or 0.010 max | 0.15-0.50 | . . . | . . . | . . . | 0.10 | 0.02-0.10 Nb, V + Nb = 0.15 max |
| A 812 | 65 | . . . | 0.23 | 1.40 | 0.035 | 0.04 | 0.15-0.50[i] | . . . | . . . | . . . | V + Nb = 0.02-0.15 | 0.05 Nb max |
| | 80 | . . . | 0.23 | 1.50 | 0.035 | 0.04 | 0.15-0.50 | 0.35 | . . . | . . . | V + Nb = 0.02-0.15 | 0.05 Nb max |
| A 841 | . . . | . . . | 0.20 | [j] | 0.030 | 0.030 | 0.15- | 0.25 | 0.25 | 0.35 | 0.06 | 0.08 Mo, 0.03 Nb, |

| ASTM specification | Type or grade | UNS designation | Heat compositional limits, %[(a)] | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | C | Mn | P | S | Si | Cr | Ni | Cu | V | Other |
| | | | | | | | 0.50 | | | | | 0.02 Al total |
| A 871 | . . . | . . . | 0.20 | 1.50 | 0.04 | 0.05 | 0.90 | 0.90 | 1.25 | 1.00 | 0.10 | 0.25 Mo,<br>0.15 Zr,<br>0.05 Nb,<br>0.05 Ti |

(a) If a single value is shown, it is a maximum unless otherwise stated.

(b) Values may vary, or minimum value may exist, depending on product size and mill form.

(c) Optional or when specified.

(d) May be purchased as type 1 (0.005-0.05 Nb), type 2 (0.01-0.15 V), type 3 (0.05 Nb, max, plus 0.02-0.15 V) or type 4 (0.015 N, max, plus V $\geq 4N$).

(e) If chromium or silicon are each 0.50% min, the copper minimum does not apply.

(f) May be substituted for all or part of V.

(g) Niobium plus vanadium, 0.02 to 0.15%.

(h) Nitrogen with vanadium content of 0.015% (max) with a minimum vanadium-to-nitrogen ratio of 4:1.

(i) When silicon-killed steel is specified.

(j) For plate under 40 mm (1.5 in.), manganese contents are 0.70 to 1.35% or up to 1.60% if carbon equivalents do not exceed 0.47%. For plate over 40 mm (1 to 5 in.), ASTM A 841 specifies manganese contents of 1.00 to 1.60%.

### *Alloy Steels*

Alloy steels constitute a category of ferrous materials that exhibit mechanical properties superior to plain carbon steels as the result of additions of such alloying elements as nickel, chromium, and molybdenum. Total alloy content can range from 2.07% up to levels just below that of stainless steels, which contain a minimum of approximately 11% Cr. For many alloy steels, the primary function of the alloying elements is to increase hardenability in order to optimize mechanical properties and toughness after heat treatment. In some cases, however, alloy additions are used to reduce environmental degradation under certain specified service conditions. Alloy steels can be classified according to:

- *Chemical composition*, such as nickel steels, nickel-chromium steels, molybdenum steels, chromium-molybdenum steels, and so on, as described in SAE-AISI designations and shown in Table 4

- *Heat treatment,* such as quenched and tempered, normalized and tempered, annealed, and so on

**Table 4 SAE-AISI system of designations for carbon and alloy steels**

| **Numerals and digits** | **Type of steel and nominal alloy content, %** |
|---|---|
| **Carbon steels** | |
| 10*xx* | Plain carbon (Mn 1.00 max) |
| 11*xx* | Resulfurized |
| 12*xx* | Resulfurized and rephosphorized |
| 15*xx* | Plain carbon (max Mn range: 1.00-1.65) |
| **Manganese steels** | |
| 13*xx* | Mn 1.75 |
| **Nickel steels** | |
| 23*xx* | Ni 3.50 |
| 25*xx* | Ni 5.00 |
| **Nickel-chromium steels** | |
| 31*xx* | Ni 1.25; Cr 0.65 and 0.80 |
| 32*xx* | Ni 1.75; Cr 1.07 |
| 33*xx* | Ni 3.50; Cr 1.50 and 1.57 |
| 34*xx* | Ni 3.00; Cr 0.77 |
| **Molybdenum steels** | |
| 40*xx* | Mo 0.20 and 0.25 |
| 44*xx* | Mo 0.40 and 0.52 |

| | |
|---|---|
| **Chromium-molybdenum steels** | |
| 41*xx* | Cr 0.50, 0.80, and 0.95; Mo 0.12, 0.20, 0.25, and 0.30 |
| **Nickel-chromium-molybdenum steels** | |
| 43*xx* | Ni 1.82; Cr 0.50 and 0.80; Mo 0.25 |
| 43BV*xx* | Ni 1.82; Cr 0.50; Mo 0.12 and 0.25; V 0.03 min |
| 47*xx* | Ni 1.05; Cr 0.45; Mo 0.20 and 0.35 |
| 81*xx* | Ni 0.30; Cr 0.40; Mo 0.12 |
| 86*xx* | Ni 0.55; Cr 0.50; Mo 0.20 |
| 87*xx* | Ni 0.55; Cr 0.50; Mo 0.25 |
| 88*xx* | Ni 0.55; Cr 0.50; Mo 0.35 |
| 93*xx* | Ni 3.25; Cr 1.20; Mo 0.12 |
| 94*xx* | Ni 0.45; Cr 0.40; Mo 0.12 |
| 97*xx* | Ni 0.55; Cr 0.20; Mo 0.20 |
| 98*xx* | Ni 1.00; Cr 0.80; Mo 0.25 |
| **Nickel-molybdenum steels** | |
| 46*xx* | Ni 0.85 and 1.82; Mo 0.20 and 0.25 |
| 48*xx* | Ni 3.50; Mo 0.25 |
| **Chromium steels** | |
| 50*xx* | Cr 0.27, 0.40, 0.50, and 0.65 |
| 51*xx* | Cr 0.80, 0.87, 0.92, 0.95, 1.00, and 1.05 |
| **Chromium (bearing) steels** | |

| | | |
|---|---|---|
| 50*xxx* | Cr 0.50 | C 1.00 min |
| 51*xxx* | Cr 1.02 | |
| 52*xxx* | Cr 1.45 | |
| **Chromium-vanadium steels** | | |
| 61*xx* | Cr 0.60, 0.80, and 0.95; V 0.10 and 0.15 min | |
| **Tungsten-chromium steel** | | |
| 72*xx* | W 1.75; Cr 0.75 | |
| **Silicon-manganese steels** | | |
| 92*xx* | Si 1.40 and 2.00; Mn 0.65, 0.82, and 0.85; Cr 0 and 0.65 | |
| **High-strength low-alloy steels** | | |
| 9*xx* | Various SAE grades | |
| **Boron steels** | | |
| *xx*B*xx* | B denotes boron steel | |
| **Leaded steels** | | |
| *xx*L*xx* | L denotes leaded steel | |

Note: The *xx* in the last two digits of these designations indicates that the carbon content (in hundredths of a percent) is to be inserted.

Because of the wide variety of chemical compositions possible and the fact that some steels are used in more than one heat-treated condition, some overlap exists among the alloy steel classifications, which include (1) low-carbon quenched and tempered (QT) steels, (2) medium-carbon ultrahigh-strength steels, (3) bearing steels, and (4) heat-resistant chromium-molybdenum steels.

**Low-carbon quenched and tempered steels** combine high yield strength (from 350 to 1035 MPa, or 50 to 150 ksi) and high tensile strength with good notch toughness, ductility, corrosion resistance, or weldability. The various steels have different combinations of these characteristics based on their intended applications. The chemical compositions of typical QT low-carbon steels are given in Table 5. Many of the steels are covered by ASTM specifications. However, a few steels, such as HY-80 and HY-100, are covered by military specifications. The steels listed are used primarily as plate. Some of these steels, as well as other similar steels, are produced as forgings or castings.

**Table 5 Chemical compositions for typical alloy steels**

| **Steel** | **Composition, wt%**[(a)] | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | **C** | **Si** | **Mn** | **P** | **S** | **Ni** | **Cr** | **Mo** | **Other** |
| **Low-carbon quenched and tempered steels** | | | | | | | | | |
| A 514/A 517 grade A | 0.15-0.21 | 0.40-0.80 | 0.80-1.10 | 0.035 | 0.04 | . . . | 0.50-0.80 | 0.18-0.28 | 0.05-0.15 Zr[(b)], 0.0025 B |
| A 514/A 517 grade F | 0.10-0.20 | 0.15-0.35 | 0.60-1.00 | 0.035 | 0.04 | 0.70-1.00 | 0.40-0.65 | 0.40-0.60 | 0.03-0.08 V, 0.15-0.50 Cu 0.0005-0.005 B |
| A 514/A 517 grade R | 0.15-0.20 | 0.20-0.35 | 0.85-1.15 | 0.035 | 0.04 | 0.90-1.10 | 0.35-0.65 | 0.15-0.25 | 0.03-0.08 V |
| A 533 type A | 0.25 | 0.15-0.40 | 1.15-1.50 | 0.035 | 0.04 | . . . | . . . | 0.45-0.60 | . . . |
| A 533 type C | 0.25 | 0.15-0.40 | 1.15-1.50 | 0.035 | 0.04 | 0.70-1.00 | . . . | 0.45-0.60 | . . . |
| HY-80 | 0.12-0.18 | 0.15-0.35 | 0.10-0.40 | 0.025 | 0.025 | 2.00-3.25 | 1.00-1.80 | 0.20-0.60 | 0.25 Cu, 0.03 V, 0.02 Ti |
| HY-100 | 0.12-0.20 | 0.15-0.35 | 0.10-0.40 | 0.025 | 0.025 | 2.25-3.50 | 1.00-1.80 | 0.20-0.60 | 0.25 Cu, 0.03 V, 0.02 Ti |
| **Medium-carbon ultrahigh-strength steels** | | | | | | | | | |
| 4130 | 0.28-0.33 | 0.20-0.35 | 0.40-0.60 | . . . | . . . | . . . | 0.80-1.10 | 0.15-0.25 | . . . |
| 4340 | 0.38-0.43 | 0.20-0.35 | 0.60-0.80 | . . . | . . . | 1.65-2.00 | 0.70-0.90 | 0.20-0.30 | . . . |
| 300M | 0.40-0.46 | 1.45-1.80 | 0.65-0.90 | . . . | . . . | 1.65-2.00 | 0.70-0.95 | 0.30-0.45 | 0.05 V min |
| D-6a | 0.42-0.48 | 0.15-0.30 | 0.60-0.90 | . . . | . . . | 0.40-0.70 | 0.90-1.20 | 0.90-1.10 | 0.05-0.10 V |
| **Carburizing bearing steels** | | | | | | | | | |
| 4118 | 0.18-0.23 | 0.15-0.30 | 0.70-0.90 | 0.035 | 0.040 | . . . | 0.40-0.60 | 0.08-0.18 | . . . |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 5120 | 0.17-0.22 | 0.15-0.30 | 0.70-0.90 | 0.035 | 0.040 | . . . | 0.70-0.90 | . . . | . . . |
| 3310 | 0.08-0.13 | 0.20-0.35 | 0.45-0.60 | 0.025 | 0.025 | 3.25-3.75 | 1.40-1.75 | . . . | . . . |
| **Through-hardened bearing steels** | | | | | | | | | |
| 52100 | 0.98-1.10 | 0.15-0.30 | 0.25-0.45 | 0.025 | 0.025 | . . . | 1.30-1.60 | . . . | . . . |
| A 485 grade 1 | 0.90-1.05 | 0.45-0.75 | 0.95-1.25 | 0.025 | 0.025 | 0.25 | 0.90-1.20 | 0.10 | 0.35 Cu |
| A 485 grade 3 | 0.95-1.10 | 0.15-0.35 | 0.65-0.90 | 0.025 | 0.025 | 0.25 | 1.10-1.50 | 0.20-0.30 | 0.35 Cu |
| **Chromium-molybdenum heat-resistant steels** | | | | | | | | | |
| $2\frac{1}{4}$ Cr-1Mo | 0.15 | 0.50 | 0.30-0.60 | 0.040 | 0.040 | . . . | 2.00-2.50 | 0.87-1.13 | . . . |
| 5Cr-$\frac{1}{2}$ Mo | 0.15 | 0.50 | 0.30-0.60 | 0.030 | 0.030 | . . . | 4.00-6.00 | 0.45-0.65 | . . . |
| 9Cr-1Mo | 0.15 | 0.50-1.00 | 0.30-0.60 | 0.030 | 0.030 | . . . | 8.00-10.00 | 0.90-1.10 | . . . |

(a) Single values represent the maximum allowable.

(b) Zirconium may be replaced by cerium. When cerium is added, the cerium/sulfur ratio should be approximately 1.5/1, based on heat analysis.

**Medium-carbon ultrahigh-strength steels** are structural steels with yield strengths that can exceed 1380 MPa (200 ksi). Table 5 lists typical compositions. Many of these steels are covered by SAE-AISI designations or are proprietary compositions. Product forms include billet, bar, rod, forgings, sheet, tubing, and welding wire.

**Bearing steels** used for ball and roller bearing applications are comprised of low-carbon (0.10 to 0.20% C) case-hardened steels and high-carbon (~1.0% C) through-hardened steels (Table 5). Many of these steels are covered by SAE-AISI designations.

**Chromium-molybdenum heat-resistant steels** contain 0.5 to 9% Cr and 0.5 to 1.0% Mo. The carbon content is usually below 0.20%. Table 5 lists typical compositions. The chromium provides improved oxidation and corrosion resistance, and the molybdenum increases strength at elevated temperatures. They are generally supplied in the normalized and tempered, quenched and tempered, or annealed condition. Chromium-molybdenum steels are widely used in the oil and gas industries and in fossil fuel and nuclear power plants. Product forms include forgings, tubing, pipe, castings, and plate.

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## Reference cited in this section

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# Cleaning of Steels

Cleaning is the process of removing objectionable matter from the surfaces of manufactured products. Drawing and stamping lubricants, cutting fluids, heat treatment scale and oxides, and fingerprints are typical of soils that must be removed.

Important reasons for adequate cleaning of components and products are as follows:

- As an intermediate step to facilitate manufacturing operations, like inspection and assembly
- To prepare surfaces for subsequent operations such as coating
- As a final finish, to improve performance, appearance, and salability

The cleaning and surface preparation of manufactured components and products are accomplished by many different processes. Some of the more common processes include a variety of chemical cleaning methods such as the application of solvents, aqueous cleaners, and acids by soaking or spraying; steam and flame cleaning methods; vapor degreasing; and ultrasonic cleaning. In addition, some of the finishing processes discussed in the following section of this article, for example, dry or wet blasting, are also used for cleaning and surface preparation. Additional information on each of the cleaning procedures described below can be found in the various articles contained in the Section on "Surface Cleaning" in this Volume.

In selecting a cleaning process for steels, many factors must be considered, including: (a) identification and characterization of the soil to be removed; (b) identification of the substrate to be cleaned and the importance of the condition of the surface or structure to the ultimate use of the part; (c) degree of cleanness required, which depends on subsequent operations such as phosphating, plating and painting; (d) capabilities of the available facilities; (e) impact of the process on the environment; and (f) overall cost of the process.

Types of soil may be broadly classified into six groups: (a) pigmented drawing compounds, (b) unpigmented oil and grease, (c) chips and cutting fluids, (d) polishing and buffing compounds, (e) rust and scale, and (f) miscellaneous surface contaminants, such as lapping compounds and residue from magnetic particle inspection.

Dried or oxidized greases, oils, and drawing compounds are very difficult to remove, and thus every effort should be made to clean the parts as soon after processing as possible.

**Removal of Pigmented Drawing Compounds.** All pigmented drawing lubricants are difficult to remove from metal parts. Consequently, many plants review all aspects of press forming operations to avoid the use of pigmented compounds. Table 6 indicates cleaning processes typically selected for removing pigmented compounds from drawn and stamped parts.

### Table 6 Selection guide for cleaning steel surfaces

Processes are listed in order of decreasing preference.

| Type of production | In-process cleaning | Preparation for painting | Preparation for phosphating | Preparation for plating |
|---|---|---|---|---|
| **Removal of pigmented drawing compounds**[(a)] | | | | |
| Occasional or | Hot emulsion hand slush, | Boiling alkaline, | Hot emulsion hand slush, | Hot alkaline soak, hot rinse (hand |

| | | | | |
|---|---|---|---|---|
| intermittent | spray emulsion in single stage, vapor slush degrease[(b)] | blow off, hand wipe<br>Vapor slush degrease, hand wipe<br>Acid clean[(c)] | spray emulsion in single stage, hot rinse, hand wipe | wipe, if possible), electrolytic alkaline, cold water rinse |
| Continuous high production | Conveyorized spray emulsion washer | Alkaline soak, hot rinse, alkaline spray, hot rinse | Alkaline or acid(d) soak, hot rinse, alkaline or acid(d) spray, hot rinse | Hot emulsion or alkaline soak, hot rinse, electrolytic alkaline, hot rinse |
| **Removal of unpigmented oils and greases** | | | | |
| Occasional or intermittent | Solvent wipe<br>Emulsion dip or spray<br>Vapor degrease<br>Cold solvent dip<br>Alkaline dip, rinse, dry (or dip in rust preventive) | Solvent wipe<br>Vapor degrease or phosphoric acid clean[(d)] | Solvent wipe<br>Emulsion dip or spray, rinse<br>Vapor degrease | Solvent wipe<br>Emulsion soak, barrel rinse, electrolytic alkaline rinse, hydrochloric acid dip, rinse |
| Continuous high production | Automatic vapor degrease<br>Emulsion, tumble, spray, rinse, dry | Automatic vapor degrease | Emulsion power spray, rinse<br>Vapor degrease<br>Acid clean[(c)] | Automatic vapor degrease, electrolytic alkaline rinse, hydrochloric acid dip, rinse[(e)] |
| **Removal of chips and cutting fluids** | | | | |
| Occasional or intermittent | Solvent wipe<br>Alkaline dip and emulsion surfactant<br>Stoddard solvent or trichlorethylene<br>Steam | Solvent wipe<br>Alkaline dip and emulsion surfactant<br>Solvent or vapor | Solvent wipe<br>Alkaline dip and emulsion surfactant[(f)]<br>Solvent or vapor | Solvent wipe<br>Alkaline dip, rinse, electrolytic alkaline[(g)], rinse, acid dip, rinse[(h)] |
| Continuous high production | Alkaline (dip or spray) and emulsion surfactant | Alkaline (dip or spray) and emulsion surfactant | Alkaline (dip or spray) and emulsion surfactant | Alkaline soak, rinse, electrolytic alkaline[(g)], rinse, acid dip and rinse[(h)] |
| **Removal of polishing and buffing compounds** | | | | |
| Occasional or intermittent | Seldom required | Solvent wipe<br>Surfactant alkaline (agitated soak), rinse<br>Emulsion soak, rinse | Solvent wipe<br>Surfactant alkaline (agitated soak), rinse<br>Emulsion soak, rinse | Solvent wipe<br>Surfactant alkaline (agitated soak), rinse electroclean[(i)] |
| Continuous high production | Seldom required | Surfactant alkaline spray, spray rinse<br>Agitated soak or spray, rinse[(j)] | Surfactant alkaline spray, spray rinse<br>Emulsion spray, rinse | Surfactant alkaline soak and spray, alkaline soak, spray and rinse, electrolytic alkaline[(i)], rinse, mild acid pickle, rinse |

(a) For complete removal of pigment, parts should be cleaned immediately after the forming operation, and all rinses should be by spraying where practical.

(b) Used only when pigment residue can be tolerated in subsequent operations.

(c) Phosphoric acid cleaner-coaters are often sprayed on the parts to clean the surface and leave a thin phosphate coating.

(d) Phosphoric acid for cleaning and iron phosphating. Proprietary products for high- and low-temperature applications are available.

(e) Some plating processes may require additional cleaning dips.

(f) Neutral emulsion or solvent should be used before manganese phosphating.

(g) Reverse-current cleaning may be necessary to remove chips from parts having deep recesses.

(h) For cyanide plating, acid dip and water rinse are followed by alkaline and water rinses.

(i) Other preferences: stable or diphase emulsion spray or soak, rinse, alkaline spray or soak, rinse, electroclean; or solvent presoak, alkaline soak or spray, electroclean.

(j) Third preference: emulsion spray rinse

**Removal of Unpigmented Oil and Grease.** Common shop oils and greases, such as unpigmented drawing lubricants, rust-preventive oils, and quenching and lubricating oils, can be effectively removed by several different cleaners. Table 6 lists cleaning methods frequently used for removing oils and greases.

**Removal of Chips and Cutting Fluids from Steel Parts.** Cutting and grinding fluids used for machining may be classified into three groups, as follows:

- Plain or sulfurized mineral and fatty oils (or combinations of the two), chlorinated mineral oils, and sulfurized chlorinated mineral oils
- Conventional or heavy-duty soluble oils with sulfur or other compounds added and soluble grinding oils with wetting agents
- Chemical cutting fluids, which are water-soluble and generally act as cleaners. They contain soaps, amines, sodium salts of sulfonated fatty alcohols, alkyl aromatic sodium salts of sulfonates, or other types of the soluble addition agents

Usually, all three types of fluids are easily removed, and the chips fall away during cleaning, unless the chips or the part become magnetic. Plain boiling water is often suitable for removing these soils, and in some plants, mild detergents are added to the water to increase its effectiveness. Steam is widely used for in-process cleaning, especially for large components. Table 6 indicates cleaning processes typically used for removing cutting fluids to meet specific production requirements.

**Removal of Polishing and Buffing Compounds.** Table 6 lists preferred and alternate methods for removing polishing and buffing compounds from sheet metal parts. However, some modification may be required for complete removal of all classes of these soils.

**Removal of Rust and Scale.** The seven basic methods used for removing rust and scale from ferrous mill products, forgings, castings and fabricated steel parts are:

- Abrasive blasting (dry or wet)
- Tumbling (dry or wet)
- Brushing
- Acid pickling
- Salt bath descaling
- Alkaline descaling
- Acid cleaning

The most important considerations in selecting one of the above methods are:

- Thickness of rust or scale
- Composition of metal
- Condition of metal (product form or heat treatment)
- Allowable metal loss
- Surface finish tolerances
- Shape and size of workpieces
- Production requirements
- Available equipment
- Cost
- Freedom from hydrogen embrittlement

Combinations of two or more of the available processes are frequently used to advantage.

**Cleaning Prior to Coating.** Chemical cleaning is the most widely used method of providing a suitable surface for subsequent finishing by phosphating, electroplating, organic coating, or other coating processes. Chemical cleaning usually depends upon the use of solvents or a chemical action between the cleaning material and the contaminant. Table 7 compares the most common of the basic chemical cleaning methods. The types of chemical cleaners generally used for removing contaminants from metal surfaces fall into the broad categories of solvent cleaners, solvent emulsion cleaners, alkaline cleaners, and acid cleaners.

**Table 7 Comparison of chemical cleaning methods**

| Factors | Emulsifiable solvent cleaning | Alkali cleaning, immersion or spray | Alkali electrocleaning | Acid pickling | Molten-salt descaling |
|---|---|---|---|---|---|
| Equipment | Same as for alkali cleaning without current | Still tanks or conveyorized spray washers of various sizes and capacities | Open steel tanks with dc current source, busbars, and control equipment | Appropriate corrosion-resistant tankage | Low-carbon steel tanks with high-temperature heat source |
| Cleaning medium | Mineral solvents mixed with suitable emulsifiers; used in water solution | Appropriate proprietary cleaners in water solution properly inhibited for sensitive metals | Same as for alkali cleaning without current | Various acids | Mixture of fused salts |
| Operating temperature | Depends on flashpoint of solvent. Usually room temperature to 60 °C (140 °F) | Room temperature to 100 °C (212 °F) | 50-95 °C (120-200 °F) | Room temperature to 80 °C (180 °F) | 205-510 °C (400-950 °F) |

| | | | | | |
|---|---|---|---|---|---|
| Health hazards | Safe when body contact is avoided. Venting may be required. | Safe when body contact is avoided. Venting may be required. | Safe when body contact is avoided. Venting may be required. | Safe with protective clothing, gloves, face shields, goggles, etc. Venting may be required. | Safe with protective clothing, gloves, face shields, goggles, etc. |
| Fire hazard | Temperature must not exceed flashpoint of solvent. | None | None | None | Slight |
| Type soil removed | Both organic and inorganic matter | Both organic and inorganic matter | Normally used for final cleaning prior to plating to remove slight contamination and to activate surface | Oxides, scale, rust, etc. | Scale, oxides, etc. |
| Effect on base metal | None | None when properly inhibited, but caustic alkali will attack aluminum and zinc. | None when properly inhibited | Very slight surface attack when properly controlled | Sometimes slight etch |
| Time required | 1 to 15 min | 1 to 30 min | $\frac{1}{2}$ to 3 min | 1 to 30 min | Varies from seconds to minutes, depending on the application |

Source: Ref 2

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### Reference cited in this section

2. Chemical Cleaning, in Vol 3, *Materials, Finishing and Coating, Tool and Manufacturing Engineers Handbook,* C. Wick and R.F. Veilleux, Ed., Society of Manufacturing Engineers, 1985, p 18-3

## Finishing of Steels

Of the many different processes used for finishing, some simply clean contaminants from surfaces. Others remove or form the surface material to produce the desired results. The finishing processes can be broadly classified into mechanical, thermal, and electrochemical methods, but some combine several methods. Each of these finishing categories will be briefly described below. The reader should also refer to the article "Classification and Selection of Finishing Processes" for additional information. Table 8 compares various finishing methods used for burr removal.

**Table 8 Advantages and limitations of various finishing processes**

| **Process** | **Advantages and typical applications** | **Possible limitations** |
|---|---|---|
| Abrasive flow | Removes hard-to-reach burrs. Polishes surfaces | Blind features not deburred |
| Abrasive blasting | Good for hard metals | Produces matte finish. Dust control required. Burr must be accessible |

| | | |
|---|---|---|
| Barrel tumbling | Low cost. Suitable for all materials | Edges must be exposed. Slow and not effective for interior surfaces and edges |
| Brushing and buffing | All accessible burrs and edges. Polishes surfaces | |
| Centrifugal barrel | Fast process. Suitable for all materials. Residual compressive stresses | |
| Electrochemical | Removes hard-to-reach burrs | Possible stray etching. Limited to conductive metals |
| Electropolishing | Good for thin burrs. Polishes surfaces | Possible pitting and streaking |
| Hand deburring | For hard-to-reach areas and small volume requirements. | Usually expensive and inconsistent. Burrs must be accessible |
| Spindle finishing | Fast process. For uniform shapes | Fixturing needed |
| Thermal energy | For thin burrs. Deburrs blind features | Covers part with oxide film. Burr area must be free of oil and water |
| Vibratory | Versatile, economical process. Many deburring and finishing applications | Not usually suitable for removing internal burrs in intersecting holes |

Source: Ref 3

### ***Mechanical Finishing***

The term "mechanical finishing" encompasses the technology of edge and surface conditioning of metal and nonmetal products for both cosmetic and functional purposes. Generation of smooth and specular surfaces to improve appearance of components is an essential part of the manufacturing cycle of most manufactured products, but functional finishing is still more important. Most mechanisms will run longer and more efficiently if component surfaces and edges are smooth. If an appropriate scratch pattern is generated, edges and surfaces may have much improved retention of lubricants, resulting in still smoother operation. Removal of stress raisers at sharp corners and generation of controlled radii on edges can substantially improve thermal and mechanical fatigue strength of highly stressed components. Removal of tensile stresses by improved surface integrity will reduce or eliminate their contribution to service failures. Moreover, generation of high compressive stresses, which can be achieved by several mechanical finishing processes, can significantly increase resistance to fatigue stresses and thus increase the service life of highly stressed parts. Improved edge and surface condition in passages through which gases or fluids flow reduces "drag" and thus increases flow rates.

Mechanical finishing is an essential part of the manufacturing cycle for most products. A high standard of mechanical finish will normally result in a better product that is also better looking. Proper attention to the technology of mechanical finishing will result in improved productivity as well as an improved product.

Mechanical finishing processes for processing steels may be classified as follows:

- Manual filing, scraping, and deburring
- Polishing, buffing, and brushing
- Abrasive and nonabrasive blasting
- Mass finishing
- Shot peening

- Honing and lapping
- Abrasive flow machining

**Polishing, Buffing, and Brushing.** Polishing is the mechanical finishing of a product using abrasives which are firmly adhered to a flexible backing, such as with an abrasive belt or with abrasives bonded to a flexible wheel or a flap wheel (while grinding is the use of abrasives firmly bonded to a rigid backing, as is the case with a grinding wheel). Polishing operations usually follow grinding and precede buffing.

Buffing refers to the finishing of a product by means of abrasive loosely adhering to a flexible backing, typically liquid or bar compounds applied to cloth wheels.

Brushing is the use of filament wheels for edge or surface conditioning of a product. Filaments are normally nonabrasive fibers or metal wires, but can be abrasive-laden filaments. Brushing may be done either wet or dry, and may employ compounds loosely applied.

Polishing processes are primarily abrasive processes, whereas in buffing and brushing a substantial part of the action may be plastic deformation of surfaces and edges.

Traditionally, polishing and buffing have been associated with decorative surface finishing operations and surface finishing prior to plating or painting. Modern automated polishing and buffing are more frequently used for improving functional edge and surface condition and are often used to improve product shape and tolerances (replacing some machining operations). Brushing is most often used for cleaning (removing scale, oxide films, rust, and old paint), although it also finds many applications in deburring and in edge and surface conditioning. More detailed information on polishing, buffing, and brushing can be found in the article "Finishing Methods Using Multipoint or Random Cutting Edges" in this Volume.

**Blasting processes,** both abrasive and nonabrasive, are based on the principle of propelling a series of particles (normally steel shot or grit for blasting steels) against a surface for the purpose of modifying the condition of that surface. In the vast majority of cases, the particles are propelled in a matrix of air or water to the work surface. The basic means of propelling the blasting material is with either air pressure or a centrifugal wheel. Equipment for blast cleaning and finishing is described in the article "Mechanical Cleaning Systems" in this Volume.

Blast finishing processes are used for removal of contaminants, effecting changes in surface condition, deburring, and peening.

***Removal of Contaminants.*** Major applications in this group are removal of sand from castings and removal of scale from forgings. Blasting is also the standard means of removing all scale from steel products and of cleaning paint, rust, oil and other undesirable coatings from part surfaces.

***Changes in Surface Condition.*** Blasting can be used to improve the mechanical bonding of most coatings--paints, galvanized coatings, elastomeric linings, and enamel coatings.

***Deburring.*** Blasting may be used to break off small burrs on some products; if the material is ductile, blasting may blunt burrs and sharp edges. The blasting process is not suitable for generating radii on edges and corners.

**Mass finishing** normally involves loading of components to be finished into a container together with some abrasive medium, water, and compound. Action is applied to the container to cause the medium to rub against the surfaces, edges, and corners of the components, or to cause the components to rub against each other, or both. This action may deburr, generate edge and corner radii, clean the parts by removing rust and scale, and modify the surface stress. The basic mass finishing processes include:

- Barrel finishing
- Vibratory finishing
- Centrifugal disk finishing
- Centrifugal barrel finishing

- Spindle finishing

Each of these processes is described in the article "Mass Finishing Methods" in this Volume. Table 9 compares the advantages and limitations of mass finishing processes.

**Table 9 Advantage and limitations of major mass finishing processes**

| Mass finishing process | Advantages | Limitations |
|---|---|---|
| Rotary barrel | Low initial, operating, and maintenance costs. Batch automation capability | Slow process. High operator skill needed. Large floor space required. No in-process inspection. Wet working area. Little-to-no work in part recesses |
| Vibratory tub | Faster than barrel. Can handle small to very large and very long parts. Open for in-process inspection. Full automation capability. Batch or continuous operation | Noisy. Slower than high-energy processes (centrifugal barrel and disk). External material handling generally needed |
| Vibratory bowl | Faster than barrel. Handles very small to large parts. Open for in-process inspection. Integral separation. Less noisy than vibratory tub. Generally lower initial cost and better media-parts mixing than vibratory tub. Economical for general-purpose work, heavy deburring, and continuous processing. Good automation capabilities. Batch or continuous operation | Cannot handle very long parts |
| Centrifugal barrel | Fast processing. Can handle precision and fragile parts. Produces smooth finishes. Batch automation capability. Versatile-can change from fine finishing to heavy stock removal. Improves fatigue strength. Low floor space needs | No in-process inspection. Complex to automate |
| Centrifugal disk | Fast processing. Open for in-process inspection. Batch automation capability. Versatile | Limited part sizes. External material handling |
| Spindle | Fast processing. No impingement of workpieces. Produces smooth finishes. Automation capability with robot reload | Parts must be fixtured. Limited part sizes and geometries (typically used for cylindrical parts). Less versatile than other processes |

Source: Ref 4

**Shot peening** is the cold working of a metal surface with a stream of spherical shot particles applied to the surface at high velocity under carefully controlled conditions. Shot peening is most effective in reducing fatigue failures in parts subject to cyclic loading. Failures originate in surface areas under repeated tensile loading, and cracks will propagate from a surface defect or other stress riser. Shot peening prevents these failures by creating compressive stress layers in the surfaces of parts. As a part is loaded, its critical surface area will not develop tensile stresses until the shot-peen-induced compressive stresses are first overcome, thus permitting an increase in the allowable stress level and hence in the service life of the part. The effect of shot peening in improving the surface integrity of the part is also important. No matter how carefully a part is manufactured, it will exhibit some surface imperfections. These flaws may be localized areas of tensile stresses or phase transformations from machining or grinding, as well as pits, scratches, and other surface defects. As peening cold works the part surface, it blends these surface imperfections and effectively eliminates them as stress concentration points. Table 10 shows the effect of shot peening on the fatigue strength of machined 4340 alloy steel.

**Table 10 Effect of shot peening on fatigue strength of 4340 steel**

| **Machining operation** | **Endurance limit in bending, $10^7$ cycles** | | **Gentle grinding, %** |
|---|---|---|---|
| | **MPa** | **ksi** | |
| Gentle surface ground | 703 | 102 | 100 |
| Gentle surface ground and shot peened | 772 | 112 | 110 |
| Abusive surface ground | 430 | 62 | 61 |
| Abusive surface ground and shot peened | 630 | 92 | 90 |
| Electropolished | 620 | 90 | 88 |
| Electropolished and shot peened | 660 | 96 | 94 |

Shot peening has long been used to improve the fatigue characteristics of leaf and coil springs (Fig. 1). Increases in fatigue life up to 800% are often obtained. The process is also used extensively on gears, driveshafts, crankshafts, torsion bars, axles, ball studs, high-strength fasteners, railroad wheels, and oil well drilling equipment. Often it is applied only at a critical area, such as a fillet radius.

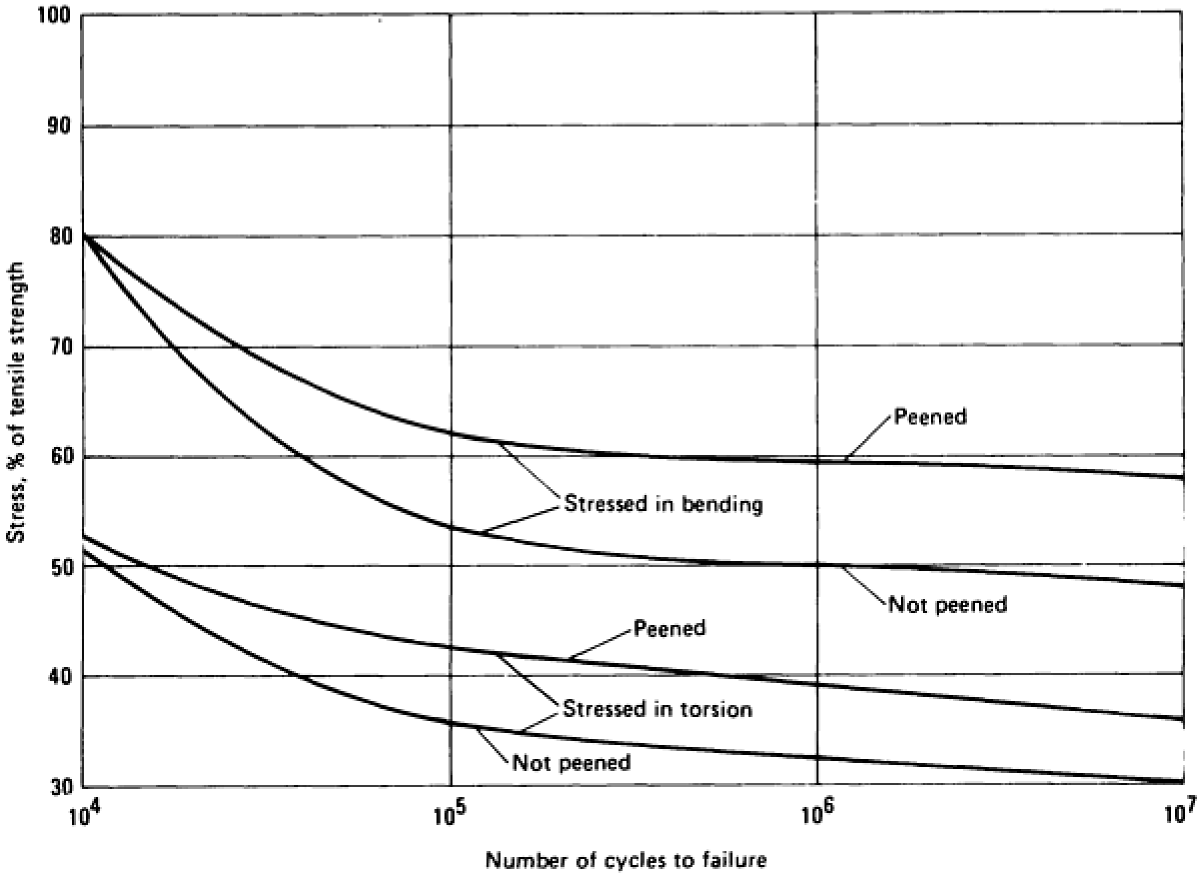

**Fig. 1 Fatique curves for peened and unpeened and steel spring wires**

Parts requiring shot peening should be clean, dry, and free of any scale. Any material on top of the base material may absorb the energy of the controlled peening process. Degreasing, descaling, or blast cleaning operations are often performed prior to shot peening to ensure proper and beneficial results. Additional information on this process can be found in the article "Shot Peening" in this Volume.

**Honing** is a controlled, low-speed sizing and surface-finishing process in which stock is removed by the shearing action to the bonded abrasive grains of a honing stone, or stick. Honing machines simultaneously apply several sticks (although one can be used) mounted on the periphery of a cylindrical body to the work surface. The usual purpose of honing is to produce uniform high accuracy and fine finish, and in the most common applications only a few thousandths of an inch of stock is removed although heavy stock removal up to 6.35 mm (0.250 in.) can also be cost effective.

The most frequent application of honing is for finishing inside cylindrical surfaces, but numerous outside surfaces also are honed. Gear teeth, valve components, and races for ball bearings and roller bearings are typical applications of external honing. Microhoning, also known as superfinishing or microfinishing, is closely related to honing. Microhoning uses finer grit (or grain) sizes (320 to 1200) than honing (60 to 600 grit). The primary distinction between honing and microhoning is that the tool rotates in honing, while in microhoning it is always the workpiece that rotates. Microhoning is a special honing operation in which the bonded abrasive stone is subjected to very light pressure and a short, high-frequency stroke.

Honing is generally used to produce surface finishes in the range of 0.80 to 0.20 μm (32 to 8 μin.) $R_a$ (roughness average), while microhoning can be cost effective in producing surface finishes of the order of 0.10 to 0.050 μm (4 to 2 μin.) $R_a$. Each method can produce even finer finishes, but productivity, as a result, suffers. Figure 2 compares typical ranges of surface finishes obtained by honing and microhoning to other common production finishing processes. More detailed information on honing can be found in the article "Honing" in *Machining,* Volume 16 of the *ASM Handbook.*

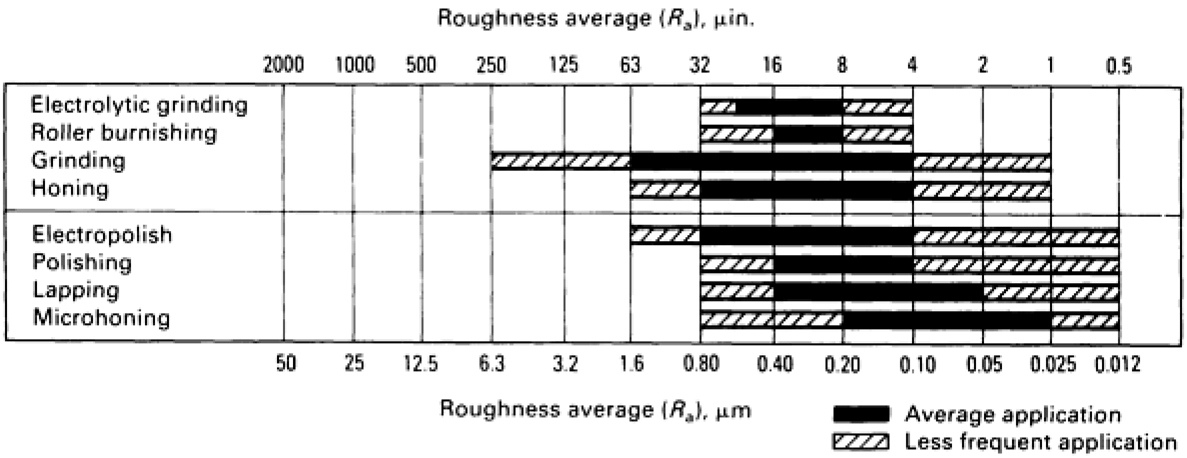

**Fig. 2 Typical ranges of surface finish from common production processes. Higher or lower values may be obtained under various conditions.**

**Lapping** is a low-velocity abrading process that removes controlled, very small amounts of material. It is accomplished with loose abrasive grains (usually retained in a viscous or liquid media, called the vehicle) between a tooling plate or wheel, called the lap, and the work surface to be finished. A typical setup for lapping flat steel products is shown in Fig. 3.

**Fig. 3 A 1220 mm (48 in.) planetary top plate drive dual-face lapping machine loaded with a variety of components having various configurations and thicknesses to demonstrate the processing capabilities of the equipment. Shown clockwise, starting with the bottom-most carriers, are hardened high-carbon steel shear blades; 102 by 102 mm (4 by 4 in.) photomask blanks used to project microcircuits onto electronic substrates; stainless steel sender bars, which will be etched into optical position indicators; valve plates machined from cutoff hot-rolled bar stock for use in hydraulic motors; and a hardened alloy steel rotary slitter blade.**

Lapping is generally a final finishing operation that results in four major refinements in the workpiece: (1) extreme accuracy of dimension, (2) correction of minor imperfections of shape, (3) refinement of surface finish, and (4) close fit between mating surfaces. The life of moving parts that are subject to wear can be greatly increased by eliminating the hills and valleys on workpiece surfaces and creating a maximum percentage of bearing area. Besides developing a workpiece that meets the surface finish requirements and is correct for geometrical and dimensional accuracy, there is no distortion, as lapping procedures do not require the use of magnetic chucks or other holding or clamping devices.

In normal lapping operations, less heat is generated than in most other finishing operations, thus minimizing the possibility of rehardened and decarburized areas on hardened or heat-treated parts. When both sides of a flat piece are lapped in the same operation (Fig. 3), extreme accuracy in flatness and parallelism can be accomplished; and by removing the same amount of stock from both sides of the part simultaneously, any inherent stresses in the piece are equally relieved. Typical applications for lapping include piston rings, crankshafts, ball bearings and bearing assemblies, and gears. More detailed information on lapping can be found in the article "Lapping" in *Machining,* Volume 16 of the *ASM Handbook.*

**Abrasive-flow machining** (AFM) is a process in which a semisolid abrasive media is forced, or extruded, through a workpiece passage. The media consist of a pliable polymer carrier and a concentration of abrasive grains such as silicon carbide. The viscosity of the carrier and the type, concentration, and size of the abrasive grains can be varied to achieve specific results.

By proper control of parameters and abrasive flow, the AFM process can perform a wide range of precision machining and finishing operations. These operations include deburring, edge radiusing, honing, polishing, and the removal of recast layers from workpiece surfaces. Important features of the process include selectivity, the capability of finishing inaccessible areas, and versatility.

Polishing with AFM can improve surface finishes of 0.75 to 7.5 μm (30 to 300 μin.) to one tenth or less of the original finishes. Material removal by the abrasion results in a dimensional change of about 25 to 35% more than the total roughness of the surface. For example, in reducing a surface finish of 2.5 μm (100 μin.) produced by electrical discharge machining to a finish of 0.25 μm (10 μin.) requires the removal of about 0.03 mm (0.001 in.) of stock. In most cases, stock removal can be held uniform throughout a passage with ±20%.

The finishing of dies (extruding, compacting, cold heading, upsetting, and others) is a major application of the AFM process. Advantages include reduced costs and longer die life. Costs are reduced by eliminating or minimizing the need for time-consuming hand polishing of the dies. Longer die life results from the directional finish produced by AFM and the improved uniformity and quality of the finished surfaces. Other components commonly finished by the AFM process include gears, bearing races and cages, and splined parts. More detailed information on AFM can be found in the article "Abrasive Flow Machining" in *Machining,* Volume 16 of the *ASM Handbook.*

### *Thermal and Electrochemical Finishing*

**Thermal Deburring.** Burrs and flash, both internal and external, are rapidly burned away using the thermal energy method (TEM). Parts to be processed are loaded in baskets or special fixtures and placed in a water-cooled furnace chamber. A fuel mixture of natural gas and oxygen is then injected into the chamber under pressure. The initial fire or heat is supplied by an ignition system in the form of a spark from an ignitor. The spark causes the combustible gas mixture to ignite, and all the fuel gas is consumed in approximately 2 ms to form a 3300 °C (6000 °F) heat wave.

The heat wave hits everything within the chamber. It hits the water-cooled walls of the chamber, the parent metal of the part or parts, and the burrs within blind holes, external edges, and intersecting holds (small or large) that cannot be reached by hand. The main body of the part becomes warm (usually under 150 °C, or 300 °F), while the flash or burrs (having less mass per surface area) heat up instantly and burst into flames. Heat created by the burning of fuel gas thus triggers the start of a second fire of the burr material itself. Because there is an abundance of oxygen in the initial fuel mixture, burrs will continue to burn until the heat is dispersed throughout the main body of the part.

Applications for the TEM include deburring of various steel castings and machined gears. For the gears, burrs are removed from the teeth and from tapped holes at the rate of 120 gears per hour. More detailed information on thermal deburring can be found in the article "Thermal Energy Method" in *Machining,* Volume 16 of the *ASM Handbook.*

**Electropolishing** is an electrochemical process for removing metal. Etching, deburring, smoothing, coloring, and machining are typical electropolishing processes. The removal of metal is done anodically in an acid or alkaline solution.

During the process, products of anodic metal dissolution react with the electrolyte to form a film at the metal surface. Two types of films have been observed: (a) a viscous liquid that is nearly saturated, or is supersaturated, with the dissolution products; and (b) anodically discharged gas, usually oxygen. Both types of films exist simultaneously in most commercial electropolishing solutions. The gas appears to be a blanket on the outside of the viscous film. Which type of film predominates depends on (a) the kind of metal, (b) the nature of the electrolyte, and (c) the surface condition prior to electropolishing (i.e., surface contamination, grain size, inclusions).

The most widely used electropolishing solutions for steels contain one or more of the concentrated inorganic acids--sulfuric, phosphoric, and chromic. Table 11 lists conditions for electropolishing alloy steels in acid electrolytes. Some of the steel products that undergo electropolishing are low-alloy (4130, 4140, and similar steels) automotive piston rings, crankpins, cotton-picker spindles, hand tools, gears, television chassis, and paper knives.

**Table 11 Conditions for electropolishing steels in acid electrolytes**

| Type of metal (and product) | Purpose of treatment | Bath volume | | Installed power | | Current density | | Polishing cycle, min | Daily production | | | Operators |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | Area | | |
| | | L | gal | A | V | A/dm$^2$ | A/ft$^2$ | | No. of parts | m$^2$ | ft$^2$ | |
| **Sulfuric-phosphoric acid electrolytes** | | | | | | | | | | | | |
| Carbon steels (job-shop work) | Brighten; deburr | 1500 | 400 | 1500 | 12 | 25-40 | 250-400 | Varies | Varies | . . . | . . . | 1 |
| 4140 steel | Prepare for chromium plate | 3200 | 850 | 4000 | 12 | 15 | 150 | 10 | 7000-10,000 | 45-75 | 500-800 | 3 |
| **Sulfuric-phosphoric-chromic acid electrolytes** | | | | | | | | | | | | |
| Carbon steel | Smooth; deburr | 1500 | 400 | . . . | . . . | 30 | 300 | 2 | 5000 | 90 | 1000 | 1 |
| 4130 steel (tools) | Bright finish | 950 | 250 | 1500 | 9 | 17.5 | 175 | 4 | 2000-5000 | . . . | . . . | 2 |

Steels are electropolished for one or more of the following purposes:

- Improve appearance and reflectivity
- Improve resistance to corrosion
- Prepare metals for plating, anodizing, or conversion coating
- Remove edge burrs produced by mechanical cutting tools
- Remove the stressed and disturbed layer of surface metal caused by the cutting, smearing, and tearing action of mechanical stock removal or of abrasive finishing

- Inspect for surface imperfections in cast, forged, or wrought metal
- Remove excess material as desired for milling metal parts

***Effect on Fatigue Strength.*** Removal of not more than 25 μm (1 mil) on the diameter of steel fatigue specimens by electropolishing can lower the endurance limit from 10 million cycles without failure to failure at 100,000 to 120,000 cycles at 520 MPa (75 ksi) (Ref 5). The decrease in diameter is not responsible for the loss. Grinding and hand finishing to the same undersize has no adverse effect.

Static stress-strain values on electropolished specimens showed little or no scatter, and when the electropolished surface was rubbed with used 000 emery paper, the original value for fatigue limit was obtained. The mild treatment indicates that any detrimental effect of an electropolished surface results from removal of a compressively stressed skin. It has been observed that wet blasting raised fatigue strength of electropolished specimens to the level attained by polishing mechanically.

The lower fatigue strength of electropolished specimens appears to be because of removal of, or inability to produce, compressive stress in metal surfaces. Thus, electropolishing is comparable in effect to a stress-relieving anneal. For example, mechanical polishing of a chromium-vanadium steel produced a compressive stress of 350 to 520 MPa (50 to 75 ksi) at a depth of 0.02 to 0.05 mm (0.008 to 0.002 in.) below the surface. The stress was relieved by heating at 500 °C (930 °F) for 2 h, which resulted in lowering the fatigue limit from approximately 580 to 560 MPa (85 to 80 ksi). Similar treatment of a low-carbon steel lowered fatigue limit from approximately 730 to 630 MPa (105 to 90 ksi). Electropolishing lowered fatigue limit comparably.

Fatigue strength is not always lower after electropolishing. In an alternating torsion test, a nickel-chromium-molybdenum steel heat treated to 1450 MPa (210 ksi) had 34% higher fatigue strength after electropolishing a ground surface. The same steel heat treated to a lower tensile strength showed lower fatigue strength after electropolishing.

Because fatigue data for electropolished specimens show considerably less scatter than for mechanically polished specimens, electropolishing tends to show true fatigue value characteristic of a particular metal and metallurgical condition. Thus, any irregularly stressed surface can be removed by electropolishing, and a uniform compressive stress can then be applied by controlled working, such as shot peening (Table 10), wet blasting, or mild abrasive polishing.

Removal by electropolishing of 100 μm (4 mils) of metal from the surface of mechanically polished low-alloy steel containing 0.44% C, 0.61% Mn, 2.48% Ni, 0.82% Cr, and 0.48% Mo that was heat treated to a tensile strength of 1100 MPa (160 ksi) changed the residual surface compressive stress of approximately 170 to 200 MPa (25 to 30 ksi) to a tensile stress of 0 to 34 MPa (0 to 5 ksi). The fatigue limit was lowered about 28 MPa (4 ksi). The stress gradient was approximately 140 to 200 MPa (20 to 30 ksi) in 0.100 mm (0.004 in.) in the mechanically polished surfaces. The residual surface stress in mechanically polished specimens differed by approximately 200 to 240 MPa (30 to 35 ksi) from that of electropolished specimens with comparable surface roughness; fatigue limits differed by approximately 580 to 550 MPa (85 to 80 ksi). Variability of fatigue strength after certain mechanical operations and after electropolishing is shown in Table 12.

**Table 12 Typical surface compression stress and fatigue strength of various carbon steels finished mechanically or by electropolishing**

| Finishing method | Fatigue strength, % of value for mechanical polishing | Depth of cold work | | Surface compressive stress | |
|---|---|---|---|---|---|
| | | mm | in. | MPa | ksi |
| Mechanical polishing | 100 | <0.050 | <0.002 | 620 | 90 |
| Electropolishing | 70-90 | None | None | None | None |

| | | | | | |
|---|---|---|---|---|---|
| Lathe turning | 65-90 | 0.50 | 0.02 | . . . | . . . |
| Milling | . . . | 0.18 | 0.007 | . . . | . . . |
| Grinding | 80-140 | ≤ .25 | ≤ .01 | 760 | 110 |
| Surface rolling | 115-190 | 1.00 | 0.04 | 900 | 130 |
| Shot peening | 85-155 | 0.50 | 0.02 | 1030 | 150 |

Source: Ref 5

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## Conversion Coatings

Phosphate or chromate conversion coatings are used to enhance the corrosion resistance of steels. By themselves, they provide slightly better corrosion resistance than bare steel; more often, they are used in conjunction with another coating system. Conversion coatings are applied after hot-dip galvanizing and provide good corrosion protection when topcoated with an organic coating system. More detailed information on conversion coatings can be found in the articles "Phosphate Coatings" and "Chromate Conversion Coatings" in this Volume.

### *Phosphate Coating*

Phosphate coating is the treatment of bare or galvanized steel with a dilute solution of phosphoric acid and other chemicals in which the surface of the metal, reacting chemically with the phosphoric acid medium, is converted to an integral, mildly protective layer of insoluble crystalline phosphate. Phosphate conversion coatings are applied to steel substrates to enhance corrosion resistance, increase paint adhesion, or both.

Phosphate coatings range in thickness from less than 3 to 50 μm (0.1 to 2 mils). Coating weight (grams per square meter of coated area), rather than coating thickness, has been adopted as the basis for expressing the amount of coating deposited.

**Types of Phosphate Coatings.** The three principal types of phosphate coatings in general use include:

- *Iron phosphate*--lightweight, amorphous phosphate coatings that do not contain significant amounts of divalent metal ions from solution. Coating weights range from 0.16 to 0.80 g/m$^2$ (15 to 70 mg/ft$^2$). Although iron phosphate coatings are applied to steel to provide receptive surfaces for bonding of fabrics, woods, and other materials, they are used chiefly as base coatings for subsequent painting.
- *Zinc phosphate*--medium-weight, crystalline phosphate coatings that contain divalent metal ions from the solution and/or the metal surface. Coating weights range from 1.4 to 4.0 g/m$^2$ (130 to 370 mg/ft$^2$). Zinc phosphate coatings can be used for any of the following applications of phosphating: (a) as a base for paint or oil; (b) as an aid to cold forming, tube drawing, or wiredrawing; (c) for increasing wear

resistance; or (d) for rustproofing.

- *Heavy phosphate* (manganese phosphates)--heavy coatings that contain divalent metal ions from solution and from the metal surface. Coating weights range from 7.5 to 30 g/m$^2$ (700 to 2800 mg/ft$^2$). Manganese phosphate coatings are applied to ferrous parts (bearings, gears, and internal-combustion engine parts, for example) for break-in and for prevention of galling. These coatings are usually dark gray. However, because almost all manganese phosphate coatings are used as an oil base and because the oil intensifies the coloring, manganese phosphate coatings are usually black in appearance.

The characteristics of these three phosphate coating types are summarized in Table 13.

**Table 13 Characteristics of phosphate coatings**

| **Characteristics** | **Type of coating** | | |
|---|---|---|---|
| | **Iron phosphate** | **Zinc phosphate** | **Heavy phosphate** |
| Coating weight | 0.16-0.80 g/m$^2$ (0.0005-0.0026 oz/ft$^2$) | 1.4-4.0 g/m$^2$ (0.0045-0.013 oz/ft$^2$) | 7.5-30 g/m$^2$ (0.025-0.1 oz/ft$^2$) |
| Types | Cleaner/coater<br>Standard<br>Organic phosphate | Standard<br>Nickel-modified<br>Low-zinc<br>Calcium-modified<br>Manganese-modified | Manganese phosphate<br>Zinc phosphate<br>Ferrous phosphate |
| Common accelerators | Nitrite/nitrate<br>Chlorate<br>Molybdate | Nitrite/nitrate<br>Chlorate<br>Nitrobenzene sulfonic acid | None<br>Chlorate<br>Nitrate<br>Nitroguanidine |
| Operating temperatures | Room -70 °C (160 °F) | Room -70 °C (160 °F) | 60-100 °C (140-212 °F) |
| Free acid, points | -2.0 to 2.0 | 0.5-3.0 | 3.6-9.0 |
| Total acid, points | 5-10 | 10-25 | 20-40+ |
| Prephosphate conditioners | None | Titanium phosphate<br>None | Manganese phosphate<br>Titanium phosphate<br>None |
| Primary use | Paint base for low-corrosion environments | Paint base for high-corrosion environments | Unpainted applications |
| Limitations | Low painted corrosion resistance; low | Poor unpainted corrosion resistance | Expensive, long |

| | | | |
|---|---|---|---|
| Materials needed for tanks | Low-carbon steel | Low-carbon steel, stainless steel, or plastic-lined steel | Stainless steel or low-carbon steel |

**Process Details.** The application of a phosphate coating as a base for subsequent painting normally comprises five successive operations: (a) cleaning, (b) rinsing, (c) phosphating (by immersion or spraying), (d) rinsing, and (e) chromic acid rinsing. Some of these operations may be omitted or combined, such as cleaning and coating in one operation. Additional operations may be required, depending on the surface condition of the parts to be phosphated or on the function of the phosphate coating. Parts exemplifying these exceptions are:

- Heavily scaled parts, which may require pickling before cleaning
- Parts with extremely heavy coatings of oil or drawing compounds, which may require rough cleaning before the normal cleaning operation
- Parts that are tempered in a controlled atmosphere before being phosphated, which may not require cleaning and rinsing before phosphating
- Parts that are phosphated and later oiled for antifriction purposes, which may have the chromic acid rinse omitted, because corrosion resistance is not required. Some rust-preventive oils negate the need for a chromic rinse while still providing excellent corrosion resistance
- Automotive parts when electrodeposition of a primer is involved. A deionized water rinse is required after the chromic acid rinse

### *Chromate Conversion Coatings*

Chromate conversion coatings are formed by a chemical or an electrochemical treatment of metals or metallic coatings in solutions containing hexavalent chromium ($Cr^{6+}$) and, usually, other components. The process results in the formation of an amorphous protective coating composed of the substrate, complex chromium compounds, and other components of the processing bath.

Chromate conversion coatings are applied primarily to enhance bare or painted corrosion resistance, to improve the adhesion of paint or other organic finishes, and to provide the metallic surface with a decorative finish. Chromate conversion coatings are most frequently applied by immersion or spraying, but other methods of application, such as brushing, roll coating, dip and squeegee, electrostatic spraying, or anodic deposition, are used in special cases.

**Processing Sequence.** Chromate coatings are applied by contacting the processed surfaces with a sequence of processing solutions. The processing baths are arranged in a series of tanks, and the surfaces to be processed are transferred through the sequence of stages by using manual, semiautomatic, or automatic control. The chromate coatings are usually applied to metal parts or to a continuous metal strip running at speeds to 5 m/s (1000 ft/min).

The basic processing sequence consists of the following six steps: cleaning, rinsing, conversion coating, rinsing, post-treatment rinsing or decorative color rinsing, and drying. In many applications, this sequence is expanded to accommodate pickling deoxidizing, dyeing, brightening, and other rinsing stages, or the sequence can be shortened when cleaning or post-treatment rinsing is not necessary. Some typical processing sequences are given in Table 14.

**Table 14 Typical process sequences for chromating of continuous galvanized strip**

| Step | Electrogalvanized strip | Step | Hot-dip galvanized strip |
|---|---|---|---|
| 1 | Electrogalvanizing | 1 | Hot-dip galvanizing |
| 2 | Rinsing: warm water, multiple stages, neutralizing (optional) | 2 | Surface conditioning: heat treatments |

| | | | |
|---|---|---|---|
| 3 | Conversion coating: chromate | 3 | Conversion coating: chromate |
| 4 | Rinsing: cold or warm water | 4 | Drying: warm air |
| 5 | Post-treatment: chromate (optional) | 5 | Oiling (optional) |
| 6 | Drying: warm air | | |
| 7 | Oiling or painting (optional) | | |

**Chromating Galvanized Steels.** Although zinc-coated steels provide better atmospheric-corrosion resistance than bare cold-rolled steel, the natural resistance of zinc surfaces to atmospheric corrosion remains low. Most articles coated with zinc by electroplating or hot-dipping are further protected. Chromating is widely used to provide corrosion protection and a decorative finish in bare applications; it can also be used as a pretreatment before painting. The chromate coatings are formed on zinc surfaces from acid solutions containing $Cr^{6+}$, usually other mineral acids, and accelerators. Chromate coatings on zinc can be categorized as clear, iridescent, and colored.

The largest area for the application of clear coatings is the passivation of hot-dip galvanized steel. Most unpainted zinc and zinc-aluminum coated steel sheet products used for roofs and walls of industrial and farm buildings are chromated on hot-dip galvanizing lines. These chemical treatments are applied in the coating weight range of 0.01 to 0.02 g $Cr/m^2$ (1 to 2 mg $Cr/ft^2$), with the upper limit usually defined by the color acceptable to the coated sheet users. On the strip line, coatings are applied by immersing or spraying the freshly prepared galvanized strip in chromating solutions for 1 to 3 s immediately before a set of squeegee rolls, which remove the excess solution from the strip. Broad ranges of chromium concentration and temperatures of 40 to 70 °C (100 to 160 °F) are used to achieve the desired coating weights. The corrosion protection provided by the chromate coatings increases with their color. Typical salt spray corrosion data are given in Table 15.

**Table 15 Typical salt spray data for chromate coatings on zinc-coated steel**

| Substrate | Type of chromate coating | Time to corrosion stain, h |
|---|---|---|
| Electroplated zinc | Untreated | <4 |
| | Clear | 24-48 |
| | Iridescent | 100-200 |
| | Olive drab | 100-400 |
| | Electrolytic | 1000 |
| Hot-dip zinc | Untreated | <4 |

Chromate coatings can be deposited electrolytically from baths containing $CrO_4^{2-}$, $PO_4^{3-}$, $F^-$, and other anions. The resulting coatings, which are gray to black in appearance, have superior corrosion resistance and hardness when compared to the conversion coatings (Table 15).

**Chromating Bare Steel.** Both chemical and electrochemical methods for chromating steel have been used. The chemical method requires high temperatures and prolonged contact times. No-rinse chromate treatments are used on continuous strip lines for paint base applications. They are applied using chemical compositions and wet film thicknesses to give coating weights in the 0.16 to 0.38 g/$m^2$ (15 to 35 mg/$ft^2$) range and provide excellent paint base properties. Electrolytically produced chromium/chromium oxide coatings, better known as tin-free steel, are extensively used in the metal-packaging industry.

## Hot-Dip Coating Processes

Hot-dip coating processes are used to apply coatings of zinc, aluminum, lead, tin, and some alloys of these metals to carbon steels. The hot-dip process consists of immersing the steel in a molten bath of the coating metal. Zinc coating (galvanizing) protects steel galvanically because the zinc is anodic to the steel base metal and therefore corrodes preferentially in most environments. Hot-dip galvanizing affords adequate atmospheric-corrosion protection to steel. Aluminum hot-dip coatings (aluminizing) provide carbon steels with resistance to both corrosion and heat. In many environments, aluminum protects steel galvanically in much the same way as zinc.

Zinc-aluminum and aluminum-zinc alloys are also applied to steel by hot dipping. Heating aluminized steel results in the formation of an iron-aluminum intermetallic compound that resists oxidation at temperatures up to about 800 °C (1500 °F). Aluminized steel is often used where heat resistance is required--for example, in automotive exhaust systems.

Hot-dip lead coatings are sometimes used on steel that will be exposed to sulfuric acid fumes or other aggressive chemical environments. Terne plate, a lead-tin alloy coating, gives more protection than pure lead coatings and is solderable.

### *Hot Dip Galvanizing*

Hot dip galvanizing is a process in which an adherent, protective coating of zinc and iron-zinc alloys is developed on the surfaces of iron and steel products by immersing them in a bath of molten zinc. Most zinc coated steel is processed by hot dip galvanizing. In general, steels with the following maximum alloying/impurity levels are best suited to galvanizing: 0.05% Si, 0.05% P, 0.25% C, and 1.3% Mn.

**Batch Galvanizing.** One method of hot dip galvanizing is the batch process, which is used for prefabricated steel items. This method involves cleaning the steel articles, applying a flux to the surfaces, and immersing them in a molten bath of zinc for varying time periods to develop a thick alloyed zinc coating.

The advantage to galvanizing after fabrication is that the zinc completely seals edges, overlaps, rivets, and welds; establishes liquid tightness; and prevents corrosion from starting. Iron and steel in all shapes and sizes can be coated with zinc by batch galvanizing. The process is simple, extremely versatile, and has been used to provide protection to articles ranging from small items, such as bolts, nuts, and miscellaneous hardware, to large items like structural beams for bridges or buildings. The virtually unrestricted size range of parts that can be galvanized and the ability to bolt or weld prefabricated sections after galvanizing enables almost any structure to be built from galvanized steel. Shape is not a restriction to batch galvanizing. Tubes, open vessels, drums, tanks, and complicated shapes such as large heat exchangers are readily galvanized on the inside and outside in one operation.

The thickness of the coating is controlled by the composition of the steel substrate and the immersion time. Part withdrawal rate and any postgalvanizing treatments also influence the coating thickness. Process details (zinc bath temperature, steel surface preparation, degree of wiping, shaking, or centrifuging, and rate of cooling) are described in the article "Batch Hot Dip Galvanized Coatings" in this Volume.

The zinc coating on batch galvanized parts is generally specified in ounces or grams per unit of surface area, measured in either square feet or square meters on a single surface or on one side of the part. With proper coating techniques, the coating weight can usually be controlled between 610 and 1220 g/$m^2$ (2 and 4 oz/$ft^2$), equivalent to a coating thickness of approximately 43 to 86 μm (1.7 to 3.4 mils) per side (Ref 6).

**Continuous Galvanizing.** Steel sheet and wire are coated by a continuous hot dip process; that is, they enter the coating bath in an unending strip. In theory, all continuous hot dip processes are similar in that the steel sheet or wire is subjected to successive cleaning, coating, and postcoating steps.

Typical cleaning steps may include alkaline cleaning or acid pickling (both of which may be electrolytic), oxidation (usually gaseous for sheet, but often in molten lead for wire), and reduction (gaseous). If a gaseous reduction is the final cleaning step, the steel must enter the molten coating bath directly without being exposed to air. When the final cleaning step is an acid pickle (this is usually the case for wire), the steel is then immersed in a liquid flux, which dissolves any remaining oxides, before entering the molten bath. Similarly, gaseous reduction can also be considered a flux treatment. All-gaseous cleaning is used on about 60% of the steel-coating lines. The remaining 40% is approximately half liquid cleaning/flux and half liquid cleaning/gaseous cleaning. Most wire-coating lines use the liquid/flux technique. More detailed information on surface cleaning and fluxing can be found in the article "Surface Preparation for Continuously Applied Coatings" in this Volume.

The clean steel is then immersed in the molten coating bath long enough to allow the coating metal to wet and react with the steel surface. As the coated sheet or wire emerges from the molten bath, it pulls coating metal up from the surface which can then be smoothed or wiped to the desired thickness by a variety of methods. Most sheet-coating lines use a gas-wiping technique in which a jet of steam, air, or gas (such as nitrogen) is directed against the emerging sheet.

The coated steel can be given any number of subsequent mechanical, thermal, or chemical post-treatments designed to impart specific properties. Typically, a coated sheet might be oiled or coated with a chromate solution to inhibit staining or superficial corrosion during storage and transit (see the previous discussion of chromate conversion coating in this article). Waxing would serve the same purpose on wire and would facilitate handling during subsequent processing.

Hot-dipped galvanized coatings are applied by highly mechanized mass production methods at speeds of over 90 m/min (300 ft/min). Several designs of galvanizing lines have been developed for commercial use by the steel suppliers. Most steel suppliers can produce galvanized coils (sheets) in widths of 250 to 1830 mm (10 to 72 in.) and thicknesses of 0.43 to 4.2 mm (17 to 165 mils). Typical applications for mill coated sheets are roofing and siding panels, guardrails, appliance cabinets, automotive body parts, and ductwork.

Coating weights applied by continuous galvanizing vary from 150 to 840 g/m$^2$ (0.5 to 2.75 oz/ft$^2$) (Ref 7). The zinc coating may be on one side of the sheet only, of equal weight on both sides of the sheet, or differentially applied (one side has a thicker coating than the other side). Process details are given in the article "Continuous Hot Dip Coatings" in this Volume.

**Nature of the Hot Dip Galvanized Coating.** Figure 4 shows a photomicrograph of a typical hot dip galvanized coating consisting of a series of layers. These layers are also identified in Table 16. Starting from the base steel at the bottom of the section, each successive layer contains a higher proportion of zinc until the outer layer, which is relatively pure zinc, is reached. Therefore, there is no real line of demarcation between the iron and the zinc; instead, there is a gradual transition through the series of iron-zinc intermetallics, which provide a powerful bond between the base metal and the coating.

**Table 16 Properties of alloy layers of hot dip galvanized steels**

| Layer | Alloy | Iron, % | Melting point | | Crystal structure | Diamond pyramid microhardness | Alloy characteristics |
|---|---|---|---|---|---|---|---|
| | | | °C | °F | | | |
| Eta (η) | Zinc | 0.03 | 419 | 787 | Hexagonal | 70-72 | Soft, ductile |
| Zeta (ζ) | $FeZn_{13}$ | 5.7-6.3 | 530 | 986 | Monoclinic | 175-185 | Hard, brittle |
| Delta (δ) | $FeZn_7$ | 7.0-11.0 | 530-670 | 986-1238 | Hexagonal | 240-300 | Ductile |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Gamma (Γ) | $Fe_3Zn_{10}$ | 20.0-27.0 | 670-780 | 1238-1436 | Cubic | . . . | Thin, hard, brittle |
| Steel base metal | Iron | . . . | 1510 | 2750 | Cubic | 150-175 | . . . |

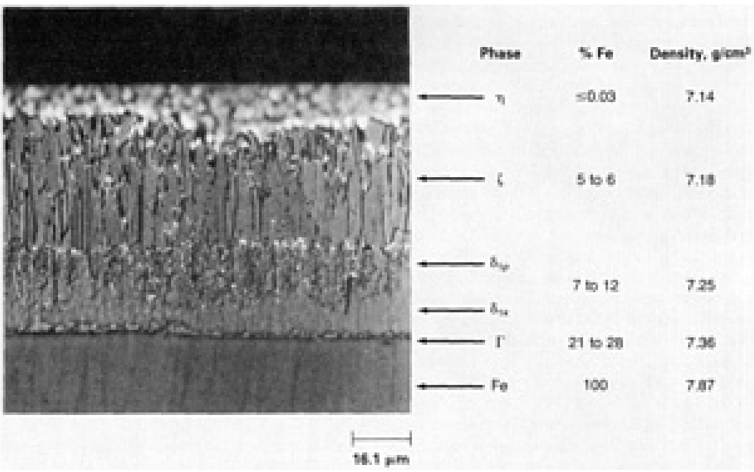

**Fig. 4 Typical hot dip galvanized coating. Note the gradual transition from layer to layer, which results in a strong bond between base metal and coating.**

**Hardness and Abrasion Resistance.** The layers that compose the galvanized coating, being discrete zinc-iron alloys, vary in hardness. The free zinc layer (η) is relatively soft, but the alloy layers are very hard, harder even than ordinary structural steels. Typical values for the microhardness and other properties of the various alloy layers are given in Table 16.

The alloy layers are from four to six times more resistant to abrasion than pure zinc. Galvanized coatings exhibit better abrasion resistance compared to paints with the same coating thickness and can be effectively used where excessive abrasive wear is expected, for example, floor gratings, stairs, conveyors, and storage bins.

**Adhesion and Impact Resistance.** Unlike other coatings, which are mechanically or chemically bonded to the steel, the galvanized coating is metallurgically bonded to and integral with the steel, making conventional measures of bond strength inappropriate for this coating. As a result of the metallurgical bond, the galvanized coating is very adherent.

The structure of the galvanized coating, particularly the relative thicknesses of the δ and ζ layers (Table 16), is primarily influenced by the steel chemistry and, to a lesser extent, by the galvanizing temperature and the duration of immersion. Coating structure has the greatest effect on the impact resistance of the coating. A high relative proportion of ζ phase in the iron-zinc alloy may result in localized flaking if the coating is subjected to heavy impact or excessive twisting or bending. Semikilled steels with silicon contents of 0.05 to 0.12% are the most susceptible to coating brittleness and less adherent coatings.

**Corrosion Protection Mechanism.** Galvanized coatings protect steel in corrosion service in two ways: barrier protection and cathodic protection. Barrier protection is provided by the galvanized coating and is further enhanced by the formation of a thin, tightly adherent layer of zinc corrosion products on the coating surface. Upon initial weathering of a freshly galvanized surface, ZnO is formed, and it is converted to $ZnOH_2$ in the presence of moisture. Further reaction with $CO_2$ in the air results in the formation of basic $ZnCO_3$, which is relatively insoluble and impedes further corrosion. The gray patina normally associated with weathered galvanized coatings is the result of this thin layer of basic $ZnCO_3$.

Cathodic protection is provided to the steel by the fact that zinc is anodic to steel in most environments. Minor discontinuities or small areas of exposed steel resulting from drilled holes or cut edges are protected from corrosion by the sacrificial protection afforded by zinc. The corrosion products that result from this action provide further protection.

**Atmospheric Exposure.** Zinc, steel, and hot dip galvanized coatings have been the subject of long-term atmospheric studies conducted throughout the world (Ref 8, 9). From these studies, the behavior of these materials in a specific atmospheric environment can be reasonably estimated. An exact determination of corrosion behavior is complicated by several factors: the frequency and duration of exposure to moisture (rain, sleet, snow, and dew), the type and concentration of corrosive pollutants, the prevailing wind direction and velocity, and exposure to sea spray or windborne abrasives. All atmospheres contain some type of corrosive agent, and the concentration of these agents, as well as the frequency and duration of moisture contact, determines the corrosion rate of galvanized coatings.

Figure 5 shows the results of outdoor atmospheric-exposure tests designed to measure the protective life of galvanized coatings in various atmospheric environments. The sites were selected as representative of various broad environmental classifications: heavy industrial, moderate industrial (urban), suburban, rural, and marine. Within these broad classifications, the following factors are most significant in influencing the rate of corrosion of the galvanized coating.

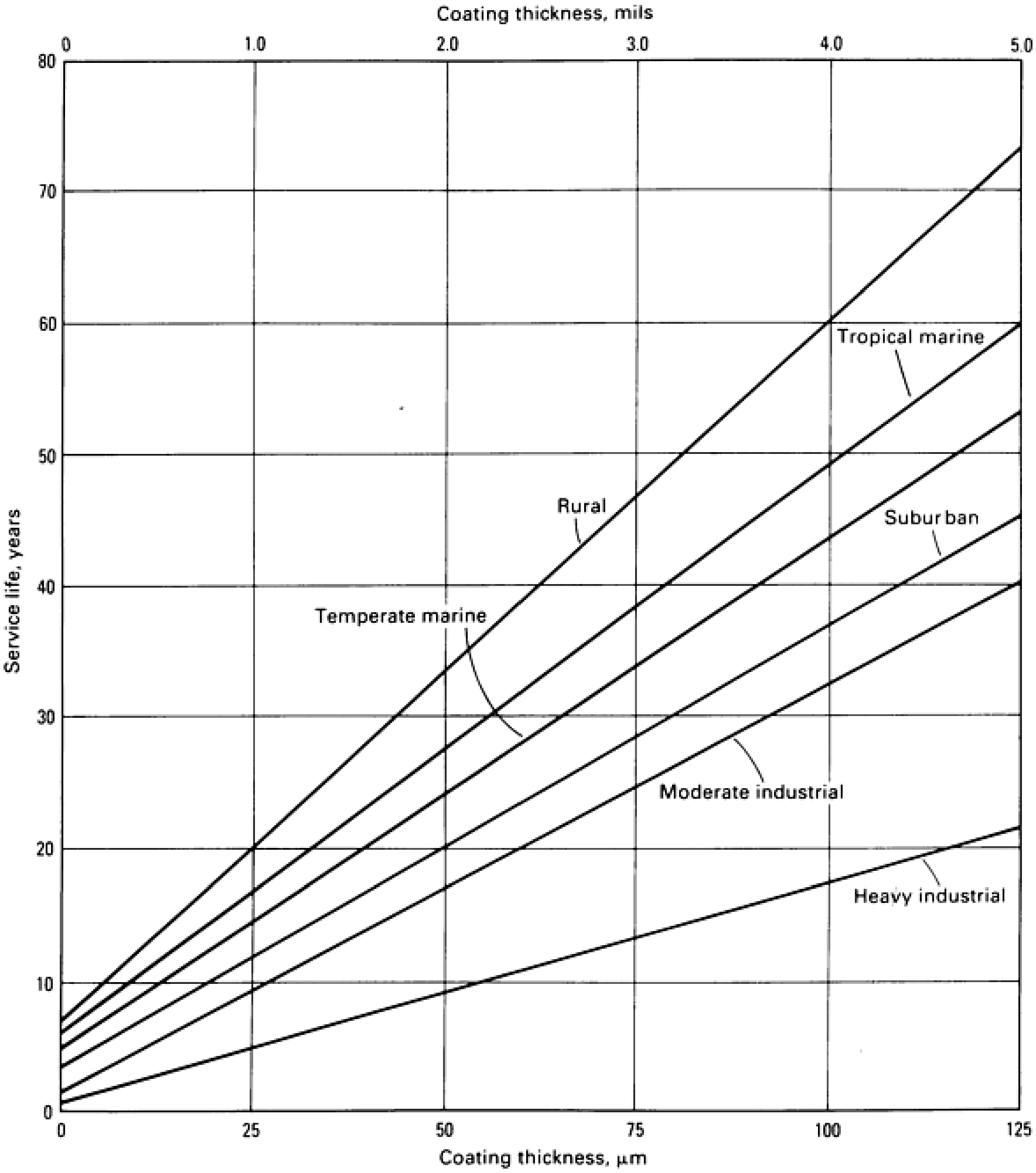

**Fig. 5 Service life versus coating thickness for hot dip galvanized steel in various atmospheres. Source: Ref 8**

***Industrial and Urban Environments.*** Corrosive conditions are most pronounced in areas with highly developed industrial complexes that release sulfurous gases and corrosive fumes and mists to the atmosphere. These corrodents react with the normally impervious basic $ZnCO_3$ film to produce $ZnSO_4$ and other soluble zinc salts that, in the presence of moisture, are washed from the surface. This exposes fresh zinc to the atmosphere, and another corrosion cycle begins.

***Rural and Suburban.*** The corrosion rate of zinc in these areas is relatively slow compared to that in industrial settings. Once the original weathering occurs, there is little in the atmosphere to convert the basic zinc salts to water-soluble compounds.

***Marine Atmospheres.*** The corrosion rate of zinc and galvanized steel in marine atmospheres is influenced by several factors. Zinc forms a soluble corrosion product, zinc chloride ($ZnCl_2$), in marine atmospheres; therefore, the corrosion rate is influenced by salt spray, sea breezes, topography, and proximity to the coastline. For example, one investigation found that the corrosion rate for zinc exposed 25 m (80 ft) from the ocean was three times that for zinc exposed 250 m (800 ft) from the ocean (Ref 9).

The corrosion product formed in a given type of atmosphere (industrial, marine, and so on) determines the corrosion rate of zinc in that atmosphere. Results from exposures in a variety of atmospheres show that zinc is 20 to 30 times more resistant to corrosion than is steel (Table 17).

**Table 17 Weight losses of steel and zinc in various locations**

Results are from 2-year atmospheric exposures.

| Location | Weight loss, g | | |
|---|---|---|---|
| | Zinc | Steel | Steel/zinc loss ratio |
| Norman Wells, N.W.T., Canada | 0.07 | 0.73 | 10.4 |
| Phoenix, AZ | 0.13 | 2.23 | 17.2 |
| Saskatoon, Sask., Canada | 0.13 | 2.77 | 21.3 |
| Esquimalt, Vancouver Is., Canada | 0.21 | 6.50 | 31.0 |
| Fort Amidor Pier, Panama C.Z. | 0.28 | 7.10 | 25.4 |
| Ottawa, Ontario, Canada | 0.49 | 9.60 | 19.6 |
| Miraflores, Panama C.Z. | 0.50 | 20.90 | 41.8 |
| Cape Kennedy, 0.8 km (0.5 mile) from ocean | 0.50 | 42.0 | 84.0 |
| State College, PA | 0.51 | 11.17 | 21.9 |
| Morenci, MI | 0.53 | 7.03 | 13.3 |
| Middletown, OH | 0.54 | 14 | 25.9 |

| | | | |
|---|---|---|---|
| Potter County, PA | 0.55 | 10 | 18.2 |
| Bethlehem, PA | 0.57 | 18.30 | 32.1 |
| Detroit, MI | 0.58 | 7.03 | 12.1 |
| Point Reyes, CA | 0.67 | 244.0 | 364.2 |
| Trail, B.C., Canada | 0.70 | 16.90 | 24.1 |
| Durham, NH | 0.70 | 13.30 | 19.0 |
| Halifax, NS (York Redoubt) | 0.70 | 12.97 | 18.5 |
| South Bend, PA | 0.78 | 16.20 | 20.8 |
| East Chicago, IN | 0.79 | 41.10 | 52.0 |
| Brazos River, TX | 0.81 | 45.40 | 56.0 |
| Monroeville, PA | 0.84 | 23.80 | 28.3 |
| Daytona Beach, FL | 0.88 | 144.0 | 163.6 |
| Kure Beach, NC (244 m, or 800 ft), site | 0.89 | 71.0 | 79.8 |
| Columbus, OH | 0.95 | 16.00 | 16.8 |
| Montreal, Quebec, Canada | 1.05 | 11.44 | 10.9 |
| Pittsburgh, PA | 1.14 | 14.90 | 13.1 |
| Waterbury, CN | 1.12 | 11.00 | 9.8 |
| Limon Bay, Panama C.Z. | 1.17 | 30.30 | 25.9 |
| Cleveland, OH | 1.21 | 19.0 | 15.7 |
| Newark, NJ | 1.63 | 24.7 | 15.2 |
| Cape Kennedy, 55 m (180 ft) from ocean | | | |

| | | | |
|---|---|---|---|
| Ground level | 1.83 | 215.0 | 117.5 |
| 9 m (30 ft) elevation | 1.77 | 80.2 | 45.3 |
| 18 m (60 ft) elevation | 1.94 | 64.0 | 33.0 |
| Bayonne, NJ | 2.11 | 37.70 | 17.9 |
| Kure Beach, NC (25 m, or 80 ft) site | 2.80 | 260.0 | 92.9 |
| Halifax, NS (Federal Building) (25m, or 80 ft) | 3.27 | 55.30 | 16.9 |
| Galeta Point, Panama C.Z. | 6.80 | 336.0 | 49.4 |

**Seawater and Salt Spray Performance.** Table 18 gives the approximate corrosion rates of zinc in various waters, and Fig. 6 illustrates the expected service life of galvanized coatings in areas exposed to salt spray influences. Sea salts are mainly NaCl, with small amounts of calcium, magnesium, and manganese salts. Typical pH is about 8. Compared to other metals and alloys, galvanized coatings provide considerably more protection to steel than many other metals and alloys, even though the anticipated coating life is shorter in seawater and salt spray exposures than a number of other environments.

**Table 18 Corrosion of zinc in various waters**

| **Water type** | **Approximate material loss** | |
|---|---|---|
| | **µm/yr** | **mils/yr** |
| Seawater | | |
| Global oceans, average | 15-25 | 0.6-1.0 |
| North Sea | 12 | 0.5 |
| Baltic Sea and Gulf of Bothnia | 10 | 0.4 |
| Freshwater | | |
| Hard | 2.5-5 | 0.1-0.2 |
| Soft river water | 20 | 0.8 |
| Soft tap water | 5-10 | 0.2-0.4 |

| | | |
|---|---|---|
| Distilled water | 50-200 | 2.0-8.0 |

Source: Ref 10

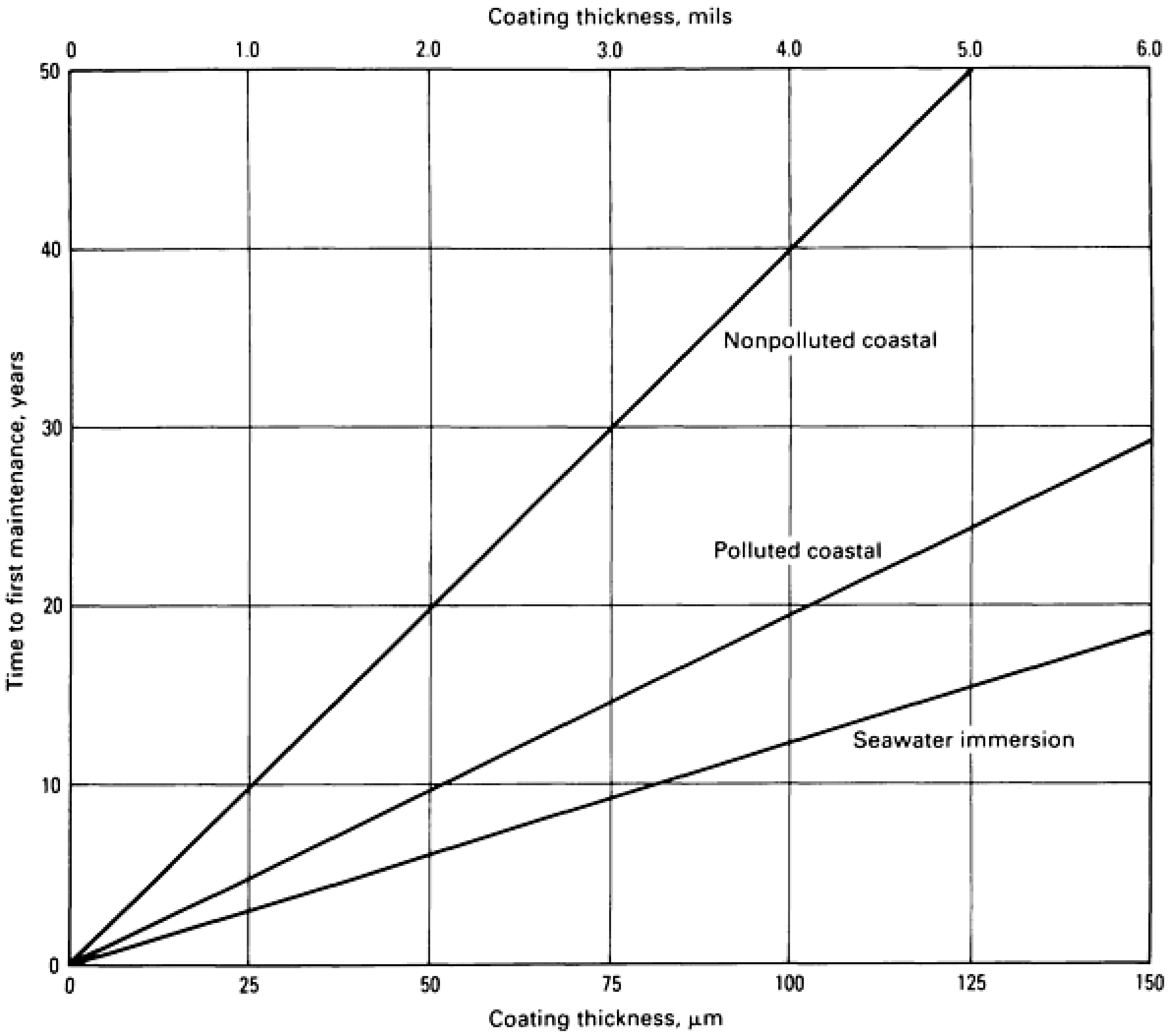

**Fig. 6 Time to first maintenance versus coating thickness for hot dip galvanized coatings in seawater immersion and sea spray exposures. Source: Ref 11**

**Freshwater Performance.** The corrosion protection mechanism of zinc in freshwater is similar to that in atmospheric exposures. The corrosion rate depends on the ability of the coating to develop a protective layer of adherent basic zinc salts. This layer denies access to the coating by oxygen and slows the rate of attack. The ability of the water to form scale depends on a number of variables, such as the pH of the water, hardness, total alkalinity, and total dissolved solids. Table 19 demonstrates the effects of various water chemistries on the relative corrosion rates of zinc.

**Table 19 Corrosion of zinc in different types of water**

| **Water type** | **Attacking substances** | **Passivating substances** | **Properties of corrosion products** | | **Relative corrosion rate** |
|---|---|---|---|---|---|
| | | | **Solubility** | **Adhesion** | |

| | | | | | |
|---|---|---|---|---|---|
| Hard water | Oxygen, $CO_2$ | Calcium, magnesium | Very low | Very good | Very low |
| Seawater | Oxygen, $CO_2$, $Cl^-$ | Calcium, magnesium | Low | Very good | Moderate |
| Soft with free air supply | Oxygen, $CO_2$ | . . . | High | Good | High |
| Soft or distilled with poor air supply | Oxygen | . . . | Very high | Very poor | Very high |

Source: Ref 10

***Water Temperature.*** The corrosion rate of zinc in water, and therefore that of the galvanized coating, increases with temperature to between 65 and 70 °C (150 and 160 °F), at which point the rate begins to decrease (Fig. 7). At temperatures near 70 °C (160 °F), a reversal in potential may occur where zinc coatings become cathodic to iron. Low oxygen and high bicarbonate contents favor reversal, but the presence of oxygen, sulfates, and chlorates tends to maintain the natural anodic state of the zinc.

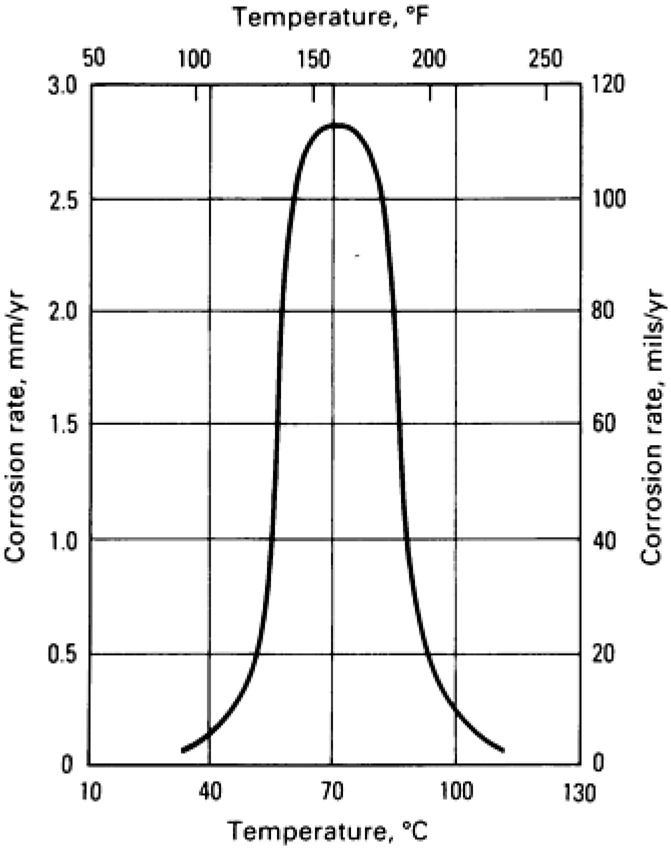

**Fig. 7 Influence of water temperature on the corrosion rate of zinc in distilled, aerated water. Source: Ref 12**

***Water pH.*** Zinc is an amphoteric metal with the capacity to passivate by means of protective layers. The corrosion rate of zinc decreases with increasing pH and reaches a minimum at 12.0 to 12.5. Most waters are in the pH range of 6 to 8. The scale-forming ability of the water and the concentration of dissolved ions in the water are more important influences on the corrosion rate than pH in this practical exposure range.

**Performance in Soils.** The corrosion rate and performance of galvanized steels in soils are a function of the type of soil in which the steel is located. Soils can vary considerably in composition and can contain bound and unbound salts, organic compounds, products of weathering, bacteria and other microorganisms, dissolved gases (such as hydrogen, oxygen, and methane), acids, and alkalies. Soils vary in permeability, depending on the soil structure. Although the concentration of oxygen is lower in soils than in air, the $CO_2$ concentration is higher. Variation among soils is high, and corrosion conditions are complicated.

In general, soils in coarse, open textures are often aerated, and the performance of galvanized steel would be expected to be similar to that in air. In soils with fine textures and high water-holding capacities, such as clay and silt-bearing soils, corrosion rates are likely to be higher. Soil resistivity is recognized as a reliable method of predicting the corrosivity of soils. High-resistivity (poor conducting) soil would be less corrosive than low-resistivity (good conducting) soil. Dry soils are poor conductors and are the least corrosive to zinc.

**Painting Galvanized Steel.** Galvanized coatings, when used without further treatment, offer the most economical corrosion protection for steel in many environments. The galvanized coating makes an excellent base on which to develop a paint system. Painting of galvanized steel is desirable for aesthetics, as camouflage, as warning or identification markings, to prevent bimetallic corrosion, or when the anticipated environment is particularly severe.

In corrosive atmospheres, a duplex system of galvanized steel top coated with paint has several advantages that make it an excellent system for corrosion prevention:

- The life of the galvanized coating is extended by the paint coating
- The sacrificial and barrier properties of the zinc coating are used if a break occurs in the paint film
- Undercutting of damaged paint coatings, a major cause of failure of paints on steel, does not occur with a zinc substrate
- Surface preparation of a weathered zinc surface for maintenance painting is easier than that for rusted steel

The galvanized coating prevents rusting of steel by acting as a barrier against the environment and by sacrificially corroding to provide cathodic protection. Painting the galvanized coating extends the service life of the underlying zinc because the barrier property of the paint delays the reaction of zinc with the environment. If a crack or other void occurs in the paint and exposes the galvanized coating, the zinc corrosion products formed tend to fill and seal the void; this delays further reaction.

When painted steel is exposed to the environment, rust forms at the steel/paint interface. Because rust occupies a volume several times that of the steel, the expansion resulting from rusting leads to rupture of the steel/paint bond. Further, rust is porous; it accumulates moisture and other reactants, and this increases the rate of attack on the steel. The result is undercutting, flaking, and blistering of the paint film, leading to failure of the paint coating (Fig. 8). Zinc corrosion products occupy a volume only slightly greater (20 to 25%) than zinc; this reduces the expansive forces and conditions that lead to paint failure.

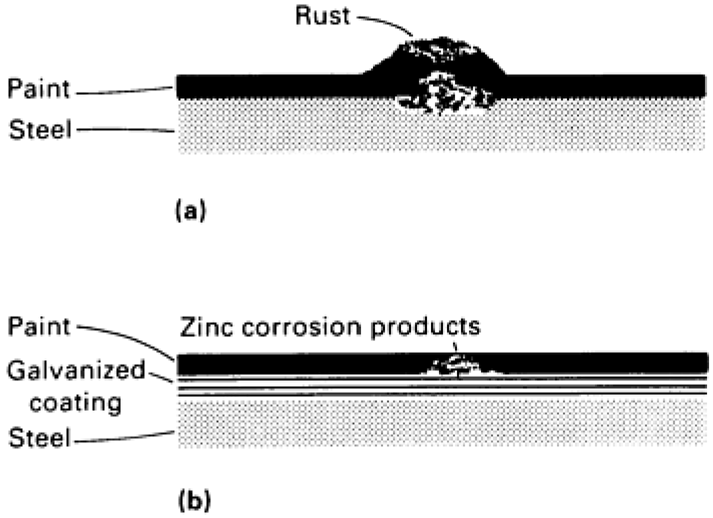

**Fig. 8 Illustration of the mechanism of corrosion for painted steel (a) and painted galvanized steel (b). (a) A void in the paint results in rusting of the steel, which undercuts the paint coating and results in further coating degradation. (b) A void in the coating of a painted galvanized steel is sealed with zinc corrosion products; this avoids the undercutting seen in (a) and prevents further deterioration of the painted coating.**

A coating system consisting of painted galvanized steel provides a protective service life up to 1.5× that predicted by adding the expected life times of the paint and the galvanized coating in a severe atmosphere (Ref 13). This is demonstrated in Table 20. The synergistic improvement is even greater for mild environments (Ref 14, 15).

**Table 20 Synergistic protective effect of galvanized steel/paint systems in atmospheric exposure**

| Type of Atmosphere | Galvanized steel | | | Paint | | | Galvanized plus paint | | |
|---|---|---|---|---|---|---|---|---|---|
| | Thickness | | Service life(a), years | Thickness | | Service life(a), years | Thickness | | Service life(a), years |
| | µm | mils | | µm | mils | | µm | mils | |
| Heavy industrial | 50 | 2 | 10 | 100 | 4 | 3 | 150 | 6 | 19 |
| | 75 | 3 | 14 | 150 | 6 | 5 | 225 | 9 | 29 |
| | 100 | 4 | 19 | 100 | 4 | 3 | 200 | 8 | 33 |
| | 100 | 4 | 19 | 150 | 6 | 5 | 250 | 10 | 36 |
| Metropolitan (urban) | 50 | 2 | 19 | 100 | 4 | 4 | 150 | 6 | 34 |
| | 75 | 3 | 29 | 150 | 6 | 6 | 225 | 9 | 52 |
| | 100 | 4 | 39 | 100 | 4 | 4 | 200 | 8 | 64 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 100 | 4 | 39 | 150 | 6 | 6 | 250 | 10 | 67 |
| Marine | 50 | 2 | 20 | 100 | 4 | 4 | 150 | 6 | 36 |
| | 100 | 4 | 40 | 100 | 4 | 4 | 200 | 8 | 66 |
| | 100 | 4 | 40 | 150 | 6 | 6 | 250 | 10 | 69 |

Source: Ref 14

(a) Service life is defined as time to about 5% red rust.

***Paint adhesion*** is the primary concern in painting galvanized steel. The surface of the zinc is nonporous and does not allow mechanical adhesion of the paint. Surface contaminants, such as oils, waxes, or postgalvanizing treatments, also effect adhesion. A fresh zinc surface is reactive to certain paint ingredients, such as fatty acids; this can produce zinc soaps and disrupt the zinc-paint bond.

Galvanized coatings can be successfully painted immediately after galvanizing or after extended weathering. The deliberate use of weathering is not recommended, because weathering may not be uniform, the time required is long (6 to 17 months), hygroscopic impurities can form that may be difficult to remove, and there is exposure to atmospheric pollutants.

Chemical etchants, such as acids or copper sulfate, should not be used for surface preparation. The action of these chemicals is difficult to control, the resulting surface may be nonuniform, and the galvanized coating could be damaged if allowed to remain in extended contact with the chemicals. Long-term adhesion will suffer with this type of treatment, although initial adhesion may be obtained.

Mechanical roughening of the zinc surface through the use of a light blast can provide a good surface for painting. However, careful control of the blast pressure and flow rate must be exercised to avoid excessive removal of the galvanized coating.

Initial adhesion of the paint can be achieved through the use of a pretreatment primer to provide an adequate base for further coating. Long-term adhesion is obtained by the selection of a top coat that is compatible with the primer and galvanized steel. Additional information on various paints can be found in the sections "Organic Coatings" and "Painting With Zinc-Rich Paints" in this article.

### *Hot Dip Aluminum Coatings*

Although zinc is well established as a coating material, aluminum is gaining in popularity. Aluminum-coated steel products are used successfully in corrosive and oxidizing environments in which the temperature ranges from that of outdoor exposure to 1150 °C (2100 °F). Aluminum coatings protect steel from attack by forming a very resistant barrier between the corrosive atmosphere and the steel. The aluminum oxide that forms on the aluminum surface is highly resistant to a wide range of environments.

The process of applying a hot-dipped aluminum coating to steel substrates is also referred to as aluminizing. As in hot dip galvanizing, aluminizing can be carried out by batch or continuous processes. Additional information on batch and continuous hot dip aluminum coating processes can be found in Ref 16 and 17.

**The batch aluminizing process** consists of cleaning, heating, fluxing, and coating. Organic soils can be removed from the parts to be coated by alkaline cleaning and water rinsing. Steel parts are then descaled by abrasive blasting or acid pickling, followed by rinsing and drying.

Fluxing dissolves any oxide film left on the part surface after cleaning and is carried out in either molten-salt baths or aqueous solutions prior to hot dipping. The salt bath is usually maintained at approximately 600 °C (1100 °F) and the parts are immersed in the bath from 30 s to several minutes. Immediately after fluxing, the parts are immersed in the molten-aluminum bath at 700 °C (1300 °F).

Temperature control of the molten aluminum is important in order to control the coating thickness. Temperatures that are too high increase the thickness of the intermetallic layer and decrease the thickness of the pure aluminum coating. Immersion time must also be closely controlled. Coating thickness is also affected by substrate composition and aluminum coating bath composition.

Parts that can be aluminum hot dipped include fasteners, poppet valves, and blades and nozzle vanes for gas turbines. Parts with small threads are not considered practical, nor are parts that may nest during the coating process.

**Continuous Aluminizing.** The aluminum dip coating of continuous steel strip, sheet, or tubing is produced on continuous in-line equipment similar to that used for galvanizing. The process consists of surface preparation, heat treatment, and immersion coating with aluminum. Surface preparation may take place in an oxidizing furnace or in a nonoxidizing preheater; if an oxidizing furnace is used, the surface oxides are reduced in a suitable atmosphere. The immersion time, the temperature of the steel before and after immersion, and the temperature of the molten aluminum must be controlled to prevent the formation of an excess of iron-aluminum interfacial alloy. More detailed information on processing of continuous hot-dipped aluminum coatings can be found in the articles "Surface Preparation for Continuously Applied Coatings" and "Continuous Hot Dip Coatings" in this Volume.

**Microstructure of Aluminum Coatings.** Two types of aluminum coatings are commercially significant. Type 2 uses commercially pure aluminum for the coating, and Type 1 uses an aluminum alloy containing 5 to 11% Si. The microstructure of the Type 2 coating shows a layer of aluminum, often with scattered iron-aluminum intermetallic particles, bonded to the steel substrate by an iron-aluminum intermetallic layer (Fig. 9). This intermetallic layer forms a distinctive serrated boundary with the steel and is generally identified as $Fe_2Al_5$, although some investigations have found additional iron-aluminum compounds (Ref 18).

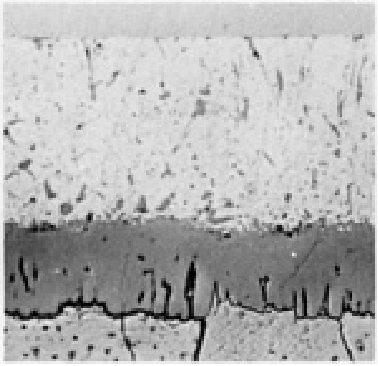

**Fig. 9 Microstructure of type 2 aluminum coating on steel. This coating forms a layer of essentially pure aluminum (top) with scattered gray particles of aluminum-iron; the light gray center layer is aluminum-iron, and the bottom layer is the base steel. 1000×**

When silicon is added to form a Type 1 coating, a different microstructure results. The intermetallic layer becomes narrower and smoother (Fig. 10), resulting in increased coating ductility relative to the Type 2 coating. With increasing silicon additions, the coating bath temperature can also be lowered, and the growth of the intermetallic layer is further inhibited.

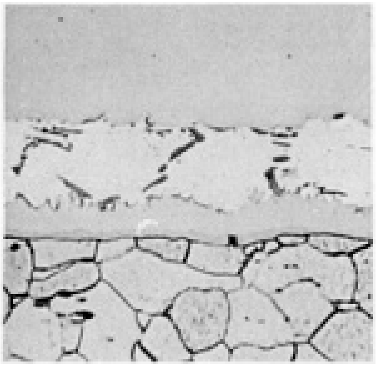

**Fig. 10 Microstructure of type 1 aluminum coating on steel. From top: a nickel filler, aluminum-silicon alloy, aluminum-silicon-iron alloy, and steel base metal. 1000×**

Beryllium, copper, and some other elements have also been found to retard the growth of the intermetallic layer. Additions of these and other elements to the steel itself can also retard the growth of the alloy layer. The way in which these elements reduce the growth is not understood, although silicon appears to act after being incorporated into the intermetallic layer itself (Ref 19).

**Atmospheric Corrosion Resistance.** Numerous tests have shown that Type 1 and Type 2 aluminum coatings provide excellent atmospheric corrosion protection for steel. The major difference between the two coatings is the darkening and pinpoint rust formation that occur very early on Type 1 coatings. Weight loss measurements show that overall corrosion losses are nearly identical for both coatings (Ref 20). However, because of this appearance factor, the major use for Type 1 coatings is for high-temperature resistance, especially in automotive exhaust components. Typical atmospheric corrosion data for Type 2 aluminum-coated steel are given in Table 21. Galvanized steel data are included for comparison purposes. On the basis of this and similar investigations, a Type 2 aluminum coating will provide substantially longer life than a galvanized coating of equivalent thickness.

**Table 21 Coating thickness losses for galvanized steel and type 2 aluminized steel in atmospheric exposure**

| Years exposed | Middletown, OH | | | | Kure Beach, NC | | | |
|---|---|---|---|---|---|---|---|---|
| | G90[(a)] | | Type 2 | | G90 | | Type 2 | |
| | µm | mils | µm | mils | µm | mils | µm | mils |
| 1 | 2.6 | 0.1 | 0.5 | 0.02 | 7.0 | 0.28 | 1.4 | 0.04 |
| 2 | 5.2 | 0.2 | 0.7 | 0.028 | 8.6 | 0.34 | 2.4 | 0.09 |
| 4 | 9.3 | 0.37 | 1.2 | 0.047 | 12.7 | 0.5 | 3.8 | 0.15 |
| 6 | 14.5 | 0.57 | 3.1 | 0.12 | 16.2 | 0.64 | 4.5 | 0.18 |
| 10 | 24.4 | 0.96 | 2.9 | 0.11 | 23.5 | 0.93 | 6.0 | 0.24 |

Source: Ref 20

(a) G90 galvanized steel has a coating weight of 0.90 oz/ft$^2$ (270 g/m$^2$).

In 1961, the American Society for Testing and Materials (ASTM) exposed aluminum-coated wire (all hot dip coated wire is made with a Type 1 coating) and galvanized wire at marine, industrial, and rural atmosphere test sites. Results from unfabricated wire show that (Ref 21):

- Aluminum coatings are rust free 1.3 to 2.2 times longer than zinc coatings of the same thickness (43 $\mu$m) in industrial and marine atmospheres
- Zinc coatings are rust free longer at the rural test site, an unexpected result that is possibly explained by the nonuniformity of the aluminum coating. Fabricated wire products made from precoated wire showed virtually no difference between aluminum and zinc coatings

***Corrosion Mechanism.*** Because contact with oxygen results in the formation of a protective aluminum oxide layer, other components of the atmosphere must be responsible for the corrosion of the aluminum coating. Careful analysis of the corrosion products formed on aluminum coatings in industrial and marine atmospheres has shown that the predominant product is an amorphous, hydrated aluminum sulfate. This suggests that $SO_2$ is an important factor in atmospheric corrosion. This sulfate compound also appears to be more protective than the sulfates found on zinc coatings, which is consistent with observed corrosion behavior.

**Aqueous Corrosion Resistance.** Aluminum-coated steel has not generally been used in situations requiring aqueous corrosion resistance. There are no counterparts to galvanized water tanks, galvanized pipe, or galvanized pails. However, since 1979 the Type 2 aluminum coating has been used in the manufacture of corrugated steel pipe.

***Corrosion in Natural Waters.*** Numerical data on the corrosion resistance of aluminum coatings are few because of the lack of use. Behavior is usually inferred from aluminum alloy data, but this could be inappropriate because of differences in structure and composition. Nonetheless, studies on aluminum alloys have shown that the air-formed aluminum oxide is destroyed after immersion (Ref 22). Corrosion resistance then depends on the oxide being re-formed from dissolved oxygen quicker than the aluminum is attacked by other ions, such as chlorides ($Cl^-$), nitrates ($NO_3^-$), or sulfates ($SO_4^{2-}$). With the protective aluminum oxide layer in place, the normal mode of failure is pitting, not general dissolution.

In general, soft waters are the least aggressive toward aluminum. The oxide is regarded as stable from pH 5 to 9. However, specific ions can change this range of stability. There is also some evidence that pitting may increase as the pH varies from neutral, but increasing the flow rate, especially at the more extreme pH values, can alleviate pitting. Small concentrations of copper and some other heavy metals can also lead to accelerated pitting. Pitting and corrosion have been observed in less than 3 years on aluminum-coated roofing panels exposed to stagnant water (Ref 23). On the other hand, when under a constant flow of relatively soft neutral pH water, corrugated steel pipe made from Type 2 aluminum-coated steel gives excellent service (Ref 24).

***Corrosion in Seawater.*** Unlike aluminum alloys, aluminum-coated steel is not used in seawater. Corrosion rates are too high to provide economical use except as part of a more complex protection system. Typical thickness loss after 1 year of immersion in seawater has been reported to be 198 μm (7.8 mils) for Type 1 and 38 μm (1.5 mils) for Type 2 aluminum-coated sheets (Ref 20).

**Corrosion in Soils.** As with aqueous environments, aluminum-coated steel does not have a history of use in soils. Behavior would be expected to depend on pH, resistivity, and especially the chemistry of the soil. The mode of failure should be pitting.

**Elevated-Temperature Exposure.** Successful application of aluminum-coated steel for resistance to oxidation and corrosion at elevated temperatures depends on the physical and mechanical properties of the alloy chemical bond between the aluminum and the steel. It is important that the hot strength of the steel be suitable for the stress and temperatures encountered. Low-carbon HSLA steels alloyed with titanium or niobium offer improved high-temperature creep resistance when used as substrates for aluminum coatings.

Aluminum coatings that contain from 5 to 11% Si minimize the thickness of the iron-aluminum alloy bond and improve formability. Undiffused, such coatings retain excellent heat reflectivity at temperatures to 480 °C (900 °F).

Above 480 °C (900 °F), further alloying occurs between the aluminum coating and steel base. Because the rate of alloying is dependent on time and temperature, all coating converts to aluminum-iron-silicon alloy with sufficient time at temperature. The refractory alloy formed is extremely heat-resistant and resistant to spalling up to 680 °C (1250 °F). Spalling at service temperatures above 680 °C (1250 °F) can be overcome by the use of heat-resistant aluminized steel that contains sufficient titanium to stabilize carbon and nitrogen as well as maintain excess titanium in solution (Ref 25).

Table 22 lists applications for steels that have been prepared by batch hot dipping in aluminum and then heat-treated to diffuse the aluminum into the steel. This treatment eliminates spalling and provides an impervious protective coating during high-temperature service.

**Table 22 Applications of diffused aluminum hot dip coatings for resistance to oxidation and corrosion at 455 to 980 °C (850 to 1800 °F)**

| Product and base metal | Type of service |
|---|---|
| **Heat treating equipment** | |
| Burner pipes, 5Cr-0.5Mo | Oxidation, 870 °C (1600 °F) |
| Fixtures, low-carbon and medium-alloy steels | Carburizing, carbonitriding |
| Flue stacks, low-carbon steel | Oxidation, sulfur corrosion |
| Furnace insulation supports, low-carbon and medium-alloy steels | Oxidation, 540-650 °C (1000-1200 °F) |
| Pyrometer protection tubes, 310 and 316 stainless steel, low-carbon steel | Oxidation, 980 °C (1800 °F) |
| **Heat exchanger components** | |
| Boiler soot blowers, 1Cr-0.5Mo | Oxidation, sulfur attack |
| Boiler tubing, 2Cr-05.Mo | Oxidation, 540-595 °C (1000-1100 °F) |
| Cylinder barrel, air-cooled engine, Nitralloy | Oxidation to 480 °C (900 °F) |
| Preheater tubing, 1Cr-0.5Mo | Oxidation, 650 °C (1200 °F) |
| Tubing, low-carbon steel, 1.5Cr-0.5Mo | Hydrogen sulfide gases |
| **Fasteners** | |

| | |
|---|---|
| Steel fasteners for chemical piping and boilers | Oxidation to 480 °C (900 °F) |
| High-temperature fasteners | Oxidation to 760 °C (1400 °F) |
| Studs, 4140, for chemical and oil refineries | Oxidation and ease of removal after service at 480 °C (900 °F) |
| **Miscellaneous equipment** | |
| Chemical reactor tubing, low-carbon steel | Carbonization, iron contamination |
| Chimney caps, low-carbon steel | Oxidation and corrosion |
| Recuperator tubing, 2.5Cr-0.5Mo | Oxidation and sulfidation |
| Refinery tubing, 304 stainless steel, 2.25Cr-1Mo | Oxidation and sulfidation |
| Sulfuric acid converters, 5Cr-0.5Mo | Sulfur dioxide corrosion, 705 °C (1300 °F) |

The use of aluminum-coated plain carbon steel for complicated heat-treating fixtures subjected to temperatures lower than 870 °C (1600 °F) may decrease overall fixture cost in comparison to fixtures made of the highly alloyed austenitic steels normally used for this application. Figure 11 shows the effects of coating thickness and operating temperature on oxidation resistance for coated and uncoated heat-treating fixtures made of 1020 steel.

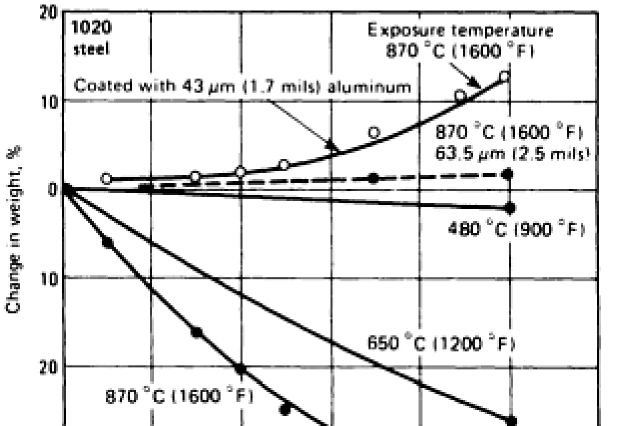

**Fig. 11 Effects of coating thickness and exposure temperature on oxidation of coated and uncoated steel. Oxidation at 480 to 870 °C (900 to 1600 °F). Steel 6.4 mm ($\frac{1}{4}$ in.) thick was completely oxidized after 700 h at 870 °C (1600 °F).**

Compared to solid stainless steel, aluminum-coated carbon steel offers greater resistance to attack by hydrogen sulfide. One set of test data indicated that, at 595 °C (1110 °F), aluminized carbon steels offer more than 100 times the resistance of 18-8 stainless steel to pure hydrogen sulfide. Other data have shown them to be 25 times more resistant than straight chromium steel.

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## Hot Dip Aluminum-Zinc Coatings

Many attempts have been made to improve the corrosion resistance of both galvanized and aluminum coatings through alloying. Although combinations of these two elements with each other were known to provide an attractive degree of corrosion resistance, hot dip coatings did not become feasible until the discovery that silicon inhibits the rapid alloying reaction with steel (Ref 26). The 55Al-Zn coating was first available commercially in 1972. This composition was selected from a systematic investigation of aluminum-zinc alloys, with up to 70% Al providing the best combination of galvanic protection and low corrosion rate. Current use varies from metal roofing, for which it is the major coated steel used, to automotive components, appliances, and, most recently, corrugated steel pipe.

Aluminum-zinc alloy coatings of steel sheet and wire are applied on continuous hot dip coating lines with in-line gas cleaning and heat treating of the steel substrate. With a nominal composition of 55% Al, 43.4% Zn, and 1.6% Si, the coating provides the durability and high temperature resistance of aluminum coatings with the sacrificial protection characteristics of zinc coatings. Silicon is added to the coating bath to control growth of an intermetallic layer. Steel sheet and wire products coated with 55% aluminum-zinc alloy are especially useful in applications requiring superior atmospheric corrosion resistance, cut edge protection, and/or high-temperature oxidation resistance. Processing details for aluminum-zinc coatings are given in Ref 16.

**Microstructure of 55Al-Zn Coating.** The 55Al-Zn coating has a two-phase structure of cored aluminum-rich dendrites and a zinc-rich interdendritic constituent (Fig. 12). This overlay is bonded to the steel substrate by a thin intermetallic layer whose composition is 48% Al, 24% Fe, 14% Zn, and 11% Si. X-ray diffraction suggests a structure similar to $Al_{13}Fe_4$. In addition, silicon particles are often found in the interdendritic region. By volume, the coating is approximately 80% Al + Si and 20% Zn. The effect of cooling rate during solidification is manifested in the spacing between the dendritic arms. Faster cooling (used commercially) results in finer spacing, which improves corrosion resistance.

**Fig. 12 Microstructure of an aluminum-zinc coated sheet**

**Protection by Aluminum-Zinc Alloy Coatings.** The 55Al-Zn coating provides both barrier and galvanic protection. Because the zinc-rich constituent is intimately distributed throughout the coating, it will be in contact with exposed steel at any break in the coating and at cut edges. Although less galvanic protection is available than with pure galvanized coatings, the alloy coating lasts longer because the overall corrosion rate is controlled by the aluminum-rich phase, which corrodes much more slowly than zinc.

**Atmospheric Corrosion Resistance.** Samples of 55Al-Zn-coated steel have been tested in atmospheric exposure for over 20 years. Figure 13 shows thickness loss with time for the first 13 years of exposure in four different atmospheres. Compared to galvanized panels exposed at the same time, the 55Al-Zn coating provides two to six times the corrosion resistance (based on equal coating thicknesses). Although these results were based on pilot line samples, subsequent testing of commercial 55Al-Zn sheet steel for 10 years shows a slightly greater advantage over galvanized steel (Ref 28).

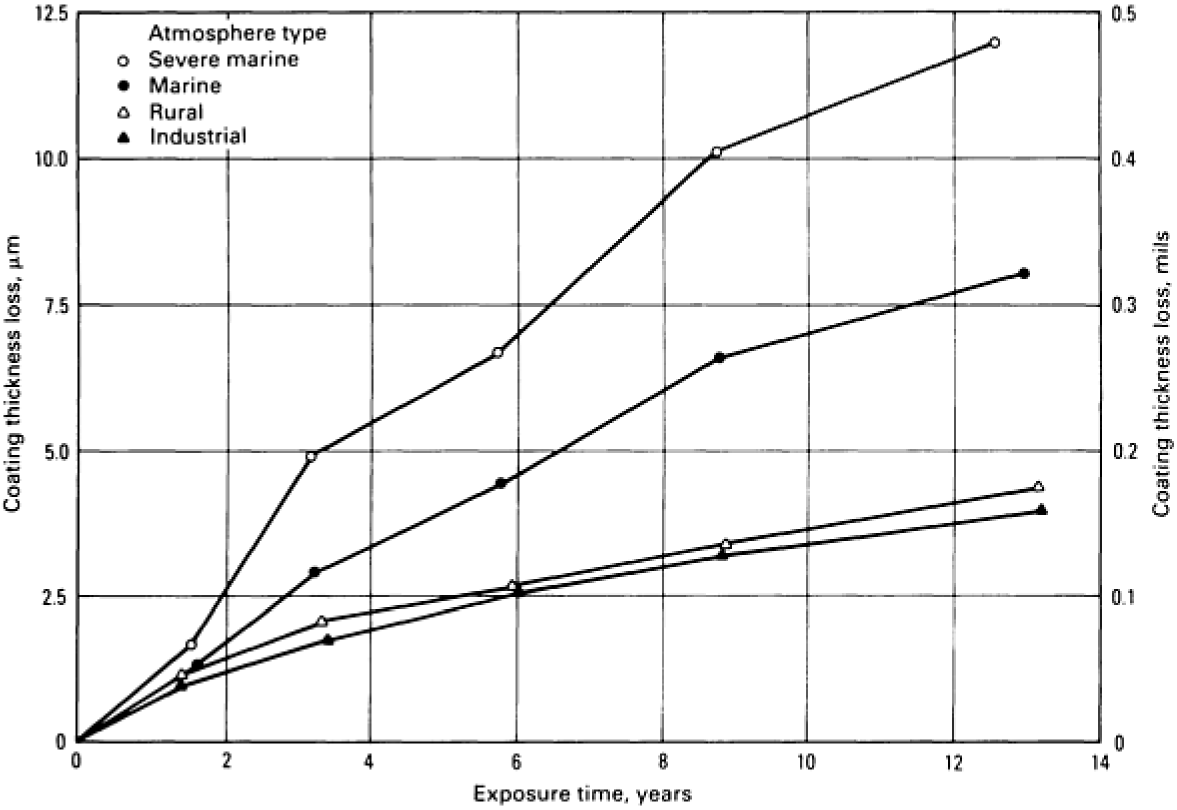


**Fig. 13 Coating thickness loss of 55Al-Zn-coated steel in four atmospheres. Source: Ref 27**

***Corrosion Mechanism.*** The zinc-rich constituent of the coating has been observed to corrode preferentially. As these regions are removed, their space is taken by corrosion products that become mechanically locked into the interdendritic spaces. These corrosion products are mostly amorphous aluminum or hydrated aluminum-zinc sulfates--similar to the corrosion products found on the coating surface of aluminum and 55Al-Zn coatings. These sulfates are adherent and may help explain the improved durability of the aluminum-zinc coating. Support for this mechanism is also obtained from aqueous corrosion studies in which the corrosion potential is observed to change that of a galvanized coating upon immersion to a value approaching that of aluminum after subsequent corrosion (Ref 29).

**Aqueous Corrosion Resistance.** The 55Al-Zn coating is finding increased use in applications demanding resistance to aqueous corrosion, especially where wet/dry cycles are obtained.

***Corrosion in Natural Waters.*** As with other coatings, the corrosion of 55Al-Zn coating would be expected to vary with the specific properties of the water. It is not known how water hardness will affect corrosion, but in distilled water (very soft) and distilled water containing 85 mg/L of $Cl^-$ ion, the 55Al-Zn coating is much more resistant than a galvanized coating (Table 23). In similar tests, 55Al-Zn and galvanized panels were immersed for 90 days in distilled water containing 45 ppm of $SO_4^{2-}$ and 10 ppm of $Cl^-$ at pH values from 3 to 11 (Ref 31). The pH was maintained through sulfuric acid ($H_2SO_4$) or sodium hydroxide (NaOH) additions. As Table 24 demonstrates, the 55Al-Zn retains more coating than the galvanized at all pH values, especially within the 5 to 9 range most characteristic of natural waters.

**Table 23 Average coating thickness loss of galvanized and 55Al-Zn-coated steel after 56 days of immersion**

| Material | Thickness loss | |
|---|---|---|
| | Distilled water | 85 mg/L NaCl |

|  | µm | mils | µm | mils |
|---|---|---|---|---|
| Galvanized | 1.06 | 0.042 | 1.26 | 0.049 |
| 55Al-Zn | 0.015 | 0.0005 | 0.133 | 0.005 |

Source: Ref 30

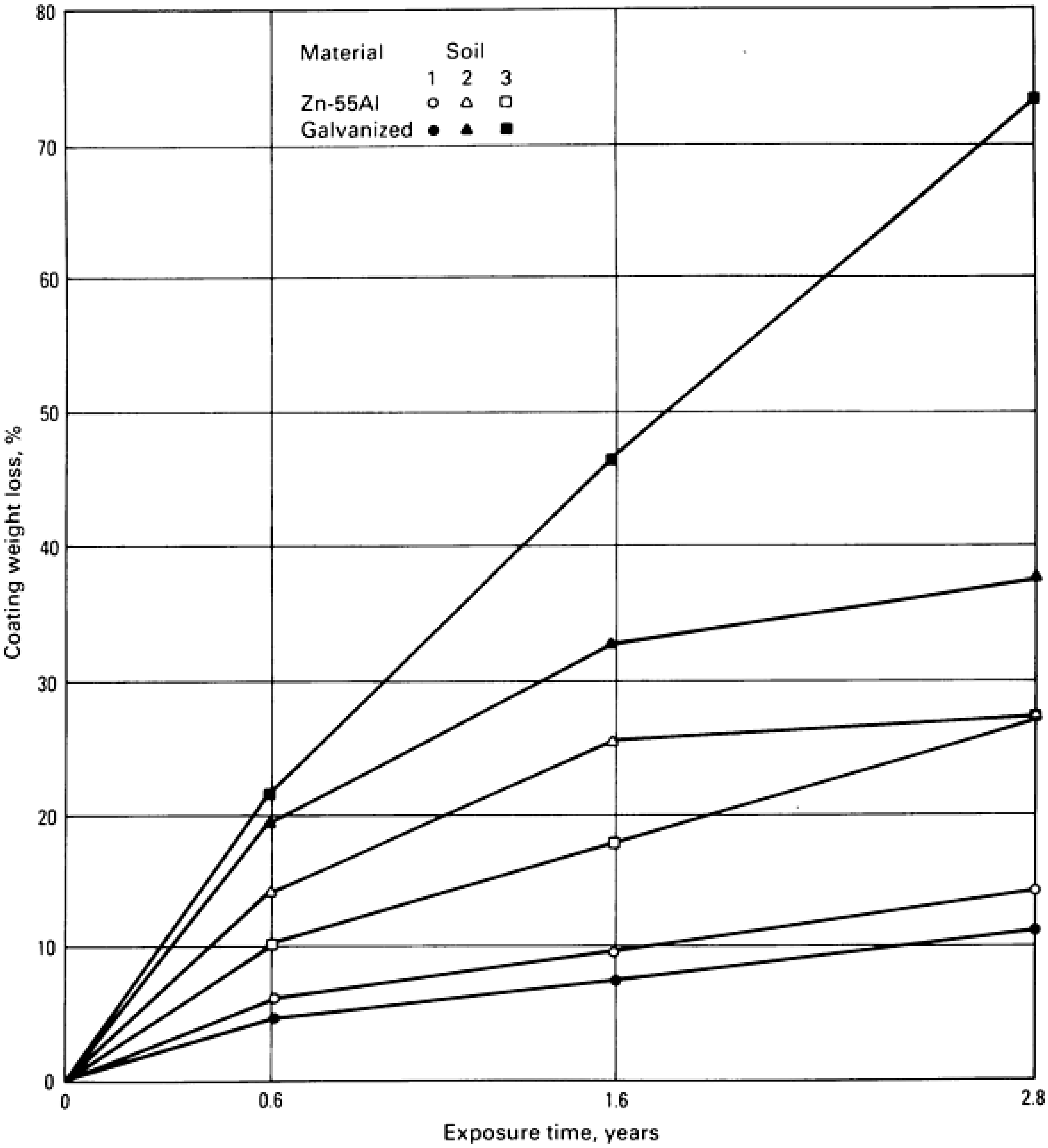
**Table 24 Coating weight losses of galvanized and 55Al-Zn-coated steels after a 90-day immersion in water of various pHs**

| pH | Coating weight loss, % |  |
|---|---|---|
|  | Galvanized | 55Al-Zn |
| 3 | 32 | 31 |
| 5 | 45 | 2 |
| 7 | 41 | 4 |
| 9 | 40 | 8 |
| 11 | 33 | 26 |

The longest service history of exposure to natural water for the 55Al-Zn coating is obtained from corrugated steel pipe installed between October, 1973, and October, 1974 (Ref 32). Water chemistry, pH, and resistivity varied widely from site to site and sometimes changed considerably with time. Erosion and abrasion caused additional wear factors.

Overall, 55Al-Zn applied at a coating weight of 180 g/m$^2$ (0.6 oz/ft$^2$) provides greater durability than a 600 g/m$^2$ (2 oz/ft$^2$) galvanized coating. Continued monitoring of these sites suggests an average of 10 years of additional life for the 55Al-Zn coating in the pipe inverts, the point of severest corrosion and wear.

**Corrosion in Soils.** There are few performance data for the 55Al-Zn coating in soil. The corrugated steel pipe exposures described previously provide the longest history of soil exposure, but because most culverts fail from the inside, exterior soil corrosion was not monitored closely in these tests. Some data are available from laboratory tests in which 16-gage coated steel panels were buried in test soils and monitored for coating loss (Ref 32). Figure 14 shows coating loss and the soil characteristics. These data suggest that the 55Al-Zn coating should provide corrosion resistance in soil similar to that of a galvanized coating.



| Soil number | Description | pH | Resistivity, Ω· cm |
|---|---|---|---|
| 1 | Native shale, clay: wet to dry | 4 | 76,000 |
| 2 | Native shale with chloride and sulfate salts: wet and dry | 5 | 35,000 |
| 3 | Native shale, clay, and bentonite with chloride and sulfate salts: wet | 6 | 1,700 |

**Fig. 14 Corrosion of galvanized steel and 55Al-Zn-coated steel in three soils. Soil characteristics are also given.**

**Source: Ref 32**

## *Hot Dip Lead Alloy (Terne) Coatings*

Long terne steel sheet is carbon steel sheet that has been coated by bath or continuous hot dip processes with terne metal (lead with 3 to 15% Sn). This coated sheet is duller in appearance than conventional tin-coated sheet; this accounts for the name terne, which means dull or tarnished in French. The smooth, dull coating gives the sheet corrosion resistance, formability, excellent solderability, and paintability. The term long terne is used to describe terne-coated sheet, whereas short terne is used for terne-coated plate.

**Applications.** Because of its unusual properties, long terne sheet has been adapted to a wide variety of applications. Its principal use is in automotive gasoline tanks. Its excellent solderability and special corrosion resistance make the product well-suited for this application. Other typical applications include:

- Automotive parts such as air conditioners, air filters, cylinder head covers, distributor tubes, oil filters, oil pans, radiator parts, and valve rocker arm covers
- Caskets
- Electronic chassis and parts for radios, tape recorders, and television sets
- File drawer tracks
- Fire doors and frames
- Furnace and heating equipment parts
- Railroad switch lamps
- Small fuel tanks for lawn mowers, power saws, tractors, and outboard motors

**Forming.** Long terne sheet is often produced in accordance with ASTM A 308. For applications requiring good formability, the coating is applied over commercial quality, drawing quality, or drawing quality special killed low-carbon steel sheet. The terne coating acts as a lubricant and facilitates forming, and the strong bond of the terne metal allows it to be formed along with the base metal. When higher strength is required, the coating can be applied over low-carbon steel sheet of structural (physical) quality, although this will result in some loss in ductility. The mechanical properties of long terne sheet are essentially the same as those of hot dip galvanized or aluminized steel sheet.

**Corrosion Characteristics.** Lead has excellent corrosion resistance, and terne metal is principally lead, with 3 to 15% tin added to react with the steel to form a tight intermetallic bond. However, because lead does not offer galvanic protection to the steel basis metal, care must be exercised to avoid scratches and pores in the coating. Small openings can be sealed by corrosion products of iron, lead, and oxygen, but larger ones can corrode in an environment unfavorable to the steel base metal.

**Joining.** Long terne sheet can be readily soldered with noncorrosive fluxes using normal procedures because the sheet is already presoldered. This makes it a good choice for applications in which ease of solderability is important, such as television and radio chassis and gasoline tanks. It also can be readily welded by either resistance seam welding or spot welding; however, when the coating is subjected to high temperatures, significant concentrations of lead fumes can be released. Therefore, the U.S. Occupational Safety and Health Administration and similar state agencies have issued standards that must be followed when welding, cutting, or brazing metals containing lead or metals coated with lead or lead alloys.

**Painting and Handling Considerations.** Long terne sheet has excellent paint adherence, which allows it to be painted using conventional systems; however, it is not usually painted. When painting is done, no prior special surface treatment or primer is necessary, except for the removal of ordinary dirt, oil, and grease. Oiled sheet, however, should be thoroughly cleaned to remove the oil. Alternatively, a wash primer treatment or a paint that will tolerate a slight residue of manufacturing oil can be used.

Long terne sheet normally is furnished dry and requires no special handling. It should be stored indoors in a warm, dry place. Unprotected outdoor storage of coils or bundles can result in white or gray staining of the terne coating. Also, if pores are present in the terne coating, rust staining can occur.

**Nickel terne** coated steel includes an electrolytic flash coating of nickel (1 to 1.5 g/m$^2$) underneath a conventional lead-tin coating for enhanced corrosion resistance. Applications are similar to the conventional long terne coatings described above.

**Composite Coatings.** A variation of long terne coated steel employs a subsequent prepainted organic coating on each surface for some fuel tanks. The outer surface has a zinc-rich organic coating to provide added exterior corrosion protection, while the inner surface has an aluminum-rich organic coating to augment the lead-tin coatings resistance to gasoline, and low concentrations of methanol- and ethanol-containing fuels.

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## Electrogalvanizing

The development of continuous electrogalvanizing lines added another dimension to zinc-coated steel, that is, very thin, formable coatings ideally suited to deep drawing or painting. Zinc is electrodeposited on a variety of mill products by the steel industry: sheet, wire, and, in some cases, pipe. Electrogalvanizing at the mill produces a thin, uniform coat of pure zinc with excellent adherence. The coating is smooth, readily prepared for painting by phosphatizing, and free of the spangle that is characteristic of some other zinc coatings.

Electrogalvanized steel is produced by electrodepositing an adhering zinc film on the surface of sheet steel or wire. These coatings are not as thick as those produced by hot dip galvanizing and are mainly used as a base for paint. Processing details applicable to electrogalvanizing can be found in the article "Continuous Electrodeposited Coatings" in this Volume.

The coating produced on strip coils or sheets has a coating weight in the range of less than about 18 to 60 g/m$^2$ (0.06 to 0.2 oz/ft$^2$), or 1.3 to 4.3 μm (0.05 to 0.17 mil) thick on each side. A small amount carries considerably less--approximately 7.6 g/m$^2$ (0.025 oz/ft$^2$), or 0.5 μm (0.21 mil) on each side.

Zinc is usually electrodeposited on steel wire in the range of 90 to 915 g/m $^2$ (0.3 to 3 oz/ft$^2$). The diameter of plated wire (including wire that is cold drawn after plating) usually ranges from 0.23 to 4.9 mm (0.009 to 0.192 in.). Steel carbon contents range from 0.08 to 0.85%. Tensile strengths range from 345 to 2070 MPa (50 to 300 ksi). Heat-treated and coated wire can be cold drawn to approximately 95% reduction in area, depending on chemical composition, heat treatment, and diameter.

**Nature of the Electrogalvanized Coating.** The pure zinc coating deposited is highly ductile. Because of its excellent adhesion, electrogalvanized steel strip and wire have good working properties, and the coating remains intact after severe deformation.

Electrodeposited zinc coatings are simpler in structure than hot dip galvanized coatings. They are composed of pure zinc and have a homogeneous structure. Surfaces have a smooth texture whose appearance can be varied by additives and special treatments in the plating bath. They can be used where a fine finish is needed.

Electrogalvanizing provides adequate protection for many types of mild exposures. These coatings are frequently treated with chromate conversion solutions to improve appearance, reduce staining, and retard the formation of white corrosion products under high-humidity conditions.

**Advantages and Limitations.** In electrogalvanizing, steel strip or wire is continuously fed through suitable entry equipment, a series of washes and rinses, and a plating bath. Either an acid sulfate zinc or cyanide zinc bath is used as the plating bath. Both produce even, adhering zinc deposits. Although brighteners are not used for electrogalvanizing, grain refiners are usually added to help produce a fine, tightknit zinc surface on the steel.

Zinc electrodeposits are considered to have the best adhesion of any metallic coating. Good adhesion depends on very close physical conformity of the coating with the base metal. Therefore, particular care must be taken during initial cleaning. Electrodeposition affords a continuous process for applying zinc coatings to parts that cannot be hot dipped. They are especially useful where a high processing temperature could damage a part.

**Applications.** Electrogalvanized sheets are produced in various tempers suitable for simple bending or forming, for curving, and for rolling into cylinders without fluting. Spot welding is easily accomplished if care is taken.

Electrogalvanized steel is easily prepared to receive decorative finishes. Much of it is produced with a phosphate treatment or an organic coating. The phosphate treatment provides an adequate surface for a good bond with organic finishing materials. Organic coating applied over electrozinc thus treated maintains good adhesion in adverse conditions, such as sudden changes in temperature and high humidity. Phosphated electrogalvanized steel is used for parts subject to atmospheric corrosion or salt spray and for parts that will be lacquered or painted. Phosphate treatment increases corrosion resistance markedly, particularly in atmospheres with a high sulfur content.

Electrogalvanized sheet is used for manufacturing water cooler housings, exterior panels of ranges, freezers, dryers, washers, air conditioners, and other major appliances. It is used for deep-drawn parts for kitchen cabinets, refrigerators, and allied products instead of plain cold rolled sheet because zinc holds better in the dies and reduces breakage significantly. Bakery goods and other merchandizing display cases, stud systems for steel building construction, acoustical ceiling members, and television antennas are also made of electrogalvanized steel.

Sheets for automotive applications can be electrogalvanized on one side only. The galvanized side protects against corrosion, and the bare side can take the baked enamel finish required by the outer automobile surface.

Electrogalvanized wire is especially useful in applications in which the wire must be bent, twisted, or wrapped around its own diameter. When formed, the coating does not crack, peel, or flake. Many chain link fences are made from zinc-electrocoated wire because it is not rough and therefore is safe to handle. The wire is used for conveyor belts, twisted wire brushes, chains, baskets, kitchen utensils, staples, cages, bobby pins, clotheslines, and telephone and transmission wire.

## Electroplating

Electroplated coatings are applied to steel for corrosion resistance, appearance, solderability, or other special requirements. A wide variety of materials are electroplated on steel, including nickel, chromium, zinc, cadmium, and tin. Multilayer coatings can also be applied by electroplating; an example is the copper-nickel-chromium plating system used for bright automotive trim. This section will review some of the more widely used electroplating processes for steels. More detailed information on each of the processes described below can be found in the articles contained in the Section entitled "Plating and Electroplating" in this Volume.

### *Surface Preparation for Electroplating*

Preparation for plating is one of the most critical of all cleaning operations, because maximum adhesion of the plated coating to the substrate is the major requirement for quality work. Maximum adhesion depends on both the elimination of surface contaminants in order to induce a metallurgical bond whenever possible and the generation of a completely active surface to initiate plating on all areas. In addition to pickling or other descaling operations, adequate cleaning requires multistage cycles, usually comprised of the following steps: (a) precleaning with a solvent to remove most of the soil; (b) intermediate cleaning with alkaline cleaners; (c) electrocleaning to remove the last traces of solids and other contaminants that are especially adherent; (d) acid treatment and surface conditioning to remove light oxide films formed during previous cleaning processes and to microetch the surface; and (e) electrolytic (anodic) desmutting to remove any smut formed during acid pickling of heat treated high-carbon steel parts. Low-carbon steels do not require this desmutting step. Anodic electrocleaning also offers oxidation or conditioning of scale. The oxidized or softened scale is easily removed in subsequent acid pickling. The types of cleaning usually employed in the above steps are:

- *Precleaning:* cold solvent, vapor degreasing, emulsifiable solvent, solvent emulsion spray, or alkaline spray with or without solvent emulsion
- *Intermediate alkaline cleaning:* soak cleaning with 30 to 90 g/L (4 to 12 oz/gal) of cleaner at 80 °C (180 °F) to boiling, spray cleaning with 4 to 15 g/L (0.5 to 2 oz/gal) at 65 to 80 °C (150 to 180 °F), and barrel cleaning with 7.5 to 45 g/L (1 to 6 oz/gal) at temperatures below 80 °C (180 °F)
- *Electrocleaning:* cathodic, anodic, or periodic-reverse
- *Acid treatment:* practice is highly specific for the metal being processed
- *Anodic desmutting:* necessary to remove carbon smut

The ASTM recommended practice for cleaning steels with carbon contents less than 0.35% C is ASTM B 183 (Ref 33); ASTM B 242 covers surface preparation of steels with carbon contents of $\geq$0.35% C (Ref 34). Additional information on cleaning carbon and alloy steels prior to electroplating can also be found in the article "Classification and Selection of Cleaning Processes" in this Volume.

### *Nickel Plating*

Electrodeposits of nickel exhibit a wide variety of properties, depending on composition of the plating bath and operating conditions. They may be classified according to application or appearance as general-purpose, black, and bright. More detailed information on plating bath chemistries and processing parameters can be found in the article "Nickel Plating"in this Volume.

**Plating Baths.** General-purpose nickel deposits, produced by Watts, sulfamate and fluoborate baths, are essentially sulfur-free. They are used primarily to protect steels against corrosive attack in rural, marine, and industrial atmospheres.

Black nickel deposits are used primarily for decorative effect and to provide nonreflecting surfaces. Black nickel deposits are produced by sulfate or chloride baths containing zinc ($Zn^{2+}$) and thiocyanate ($CNS^-$) ions.

Bright nickel plating baths are modifications of the Watts nickel solution and contain organic or combined organic and inorganic brightening agents; these additions serve to produce a high degree of brightness, leveling reflectivity, and hardness. A wide variety of additives are used, usually in highly specific combinations. Their function is to produce as brilliant and ductile a deposit as possible over a wide range of current densities and operating conditions. Some of these additives are consumed very slowly during electrolysis; others are consumed more rapidly.

**Applications and Properties.** Nickel plating is widely used for decorative purposes. Bright nickel plate--especially in combination with a lower layer of sulfur-free, semibright nickel and a much thinner upper layer of chromium--is very widely used over steel to provide a bright and corrosion-resistant finish with a nontarnishing and wear-resistant surface. Typical applications are decorative trim for automotive and consumer products. For best corrosion resistance, the chromium deposit should be microdiscontinuous (microcracked or microporous).

Nickel deposits are also used for nondecorative purposes to improve or modify surface properties such as corrosion resistance, hardness, wear, and magnetic characteristics. For example, in the automotive industry, nickel coatings, generally greater than 125 μm (5 mils) thick, are deposited on pistons, cylinder walls, ball studs, transmission thrust washers, and different pinion cross-shafts to improve wear resistance. The most widely used solution for plating nickel for wear applications is the Watts solution. Its main components are nickel sulfate, nickel chloride, and boric acid. Organic addition agents in the plating solution can increase the hardness and wear resistance mainly by decreasing the grain size. Nickel usually is deposited with a tensile internal stress. Some sulfur compounds can cause the stress to become compressive, but also make the deposit more brittle, especially under elevated-temperature conditions. The nickel sulfamate plating solution produces low-stress deposits. It is possible to codeposit such metals as tungsten and molybdenum with nickel, even though they cannot be plated alone in aqueous solutions. Inclusion of hard particles or those of solid lubricants can also improve the wear or friction properties of electroplated nickel.

Improved wear resistance resulting from the incorporation of SiC particles is shown in Fig. 15. In the test on which the data of Fig. 15 are based, a plated block was pressed against a lubricated steel ring. Further improvement that was due to phosphide precipitates in heat-treated Ni-P-SiC coatings is also seen in this figure.

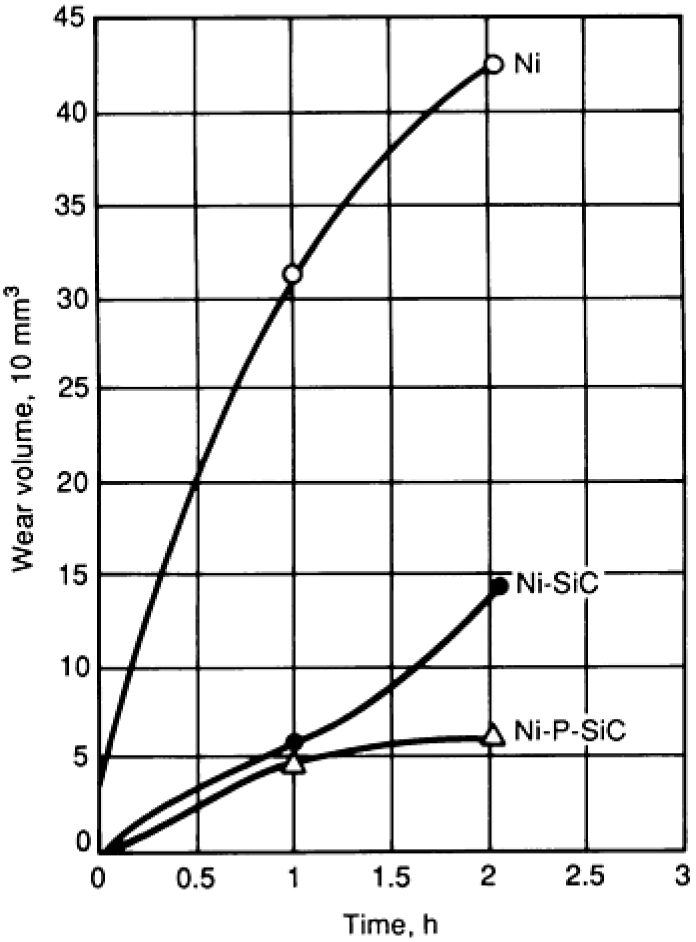

**Fig. 15 Effects of codeposited SiC particles and phosphide precipitates on wear of electrodeposited nickel heat treated for 1 h at 400 °C (750 °F). Source: Ref 35**

The hardness of nickel deposits can vary from about 150 to 500 on the Vickers scale. The hardness depends on the plating conditions, that is, current density, solution pH and temperature, and composition. Pulse plating can increase the hardness.

The coefficient of friction and wear rates of electroplated nickel are generally greater than those of chromium or electroless nickel deposits (Fig. 16).

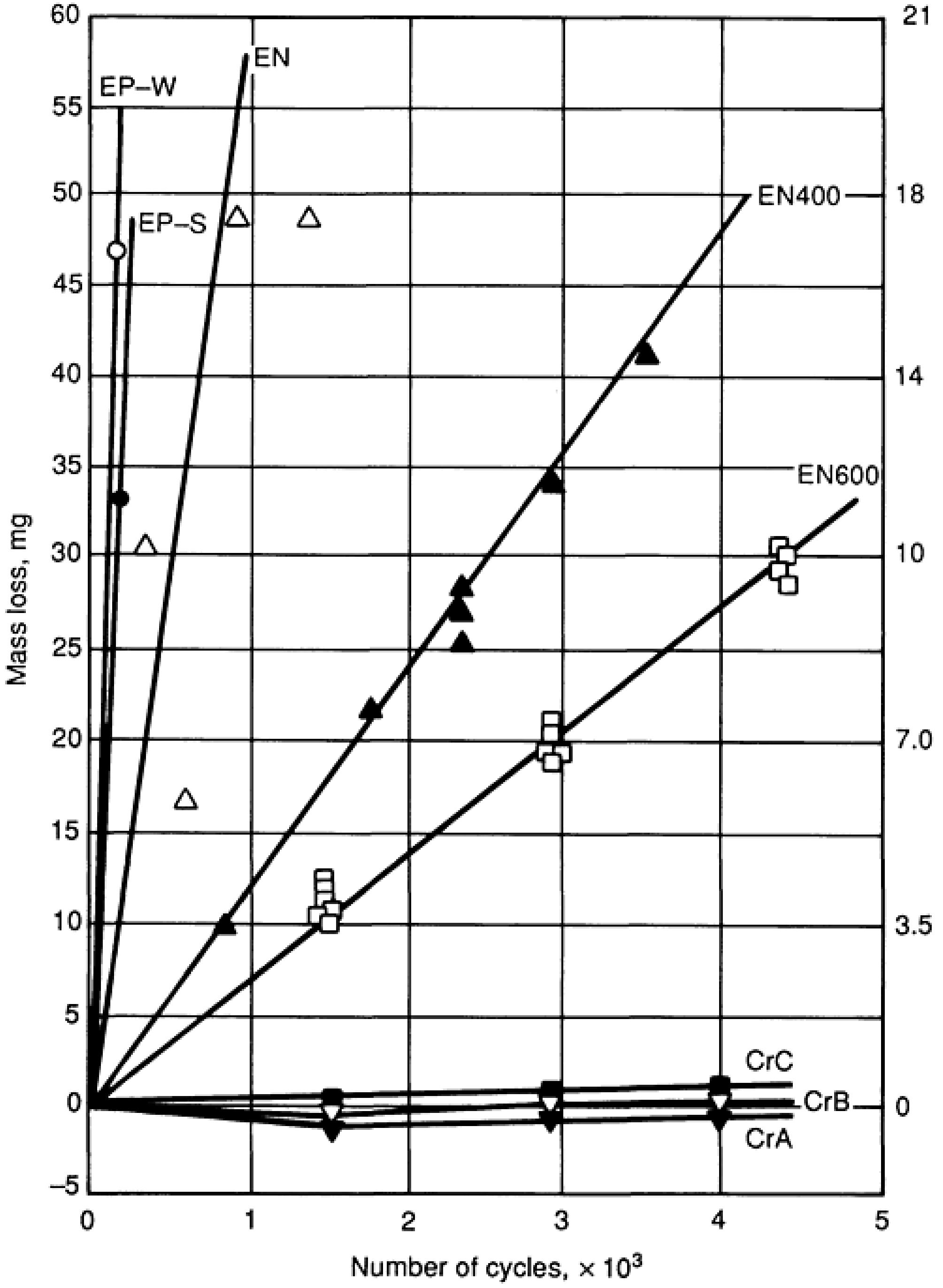

**Fig. 16 Effect of number of cycles on wear loss of plated pin versus steel blocks in a Falex test for three chromium deposits (CrA, CrB, and CrC), heat treated electroless nickel deposits (EN400 and EN600), a non-heat-treated electroless nickel deposit (EN), and two electroplated nickel deposits from a sulfamate solution (EP-S) and a Watts solution (EP-W). Source: Ref 36**

Depending on the substrate and the end use of the plated product, nickel may be applied directly to the substrate or over another metal coating such as copper and/or chromium. Because of their importance in the automotive industry, nickel-chromium (with or without a copper underlayer) coatings have been subjected to many changes and exhaustive testing over a long span of years. Figure 17 shows a history of the development and use of nickel-chromium coatings. Significant developments in this history were the determination that the basic corrosion resistance of these systems is controlled by the thickness and composition of the nickel layer, the invention of the leveling copper and nickel plating processes, the development of semibright and bright nickel plating, the emergence of crack-free and microcracked chromium, and the evolution of duplex and triplex (multilayer) nickel-chromium systems.

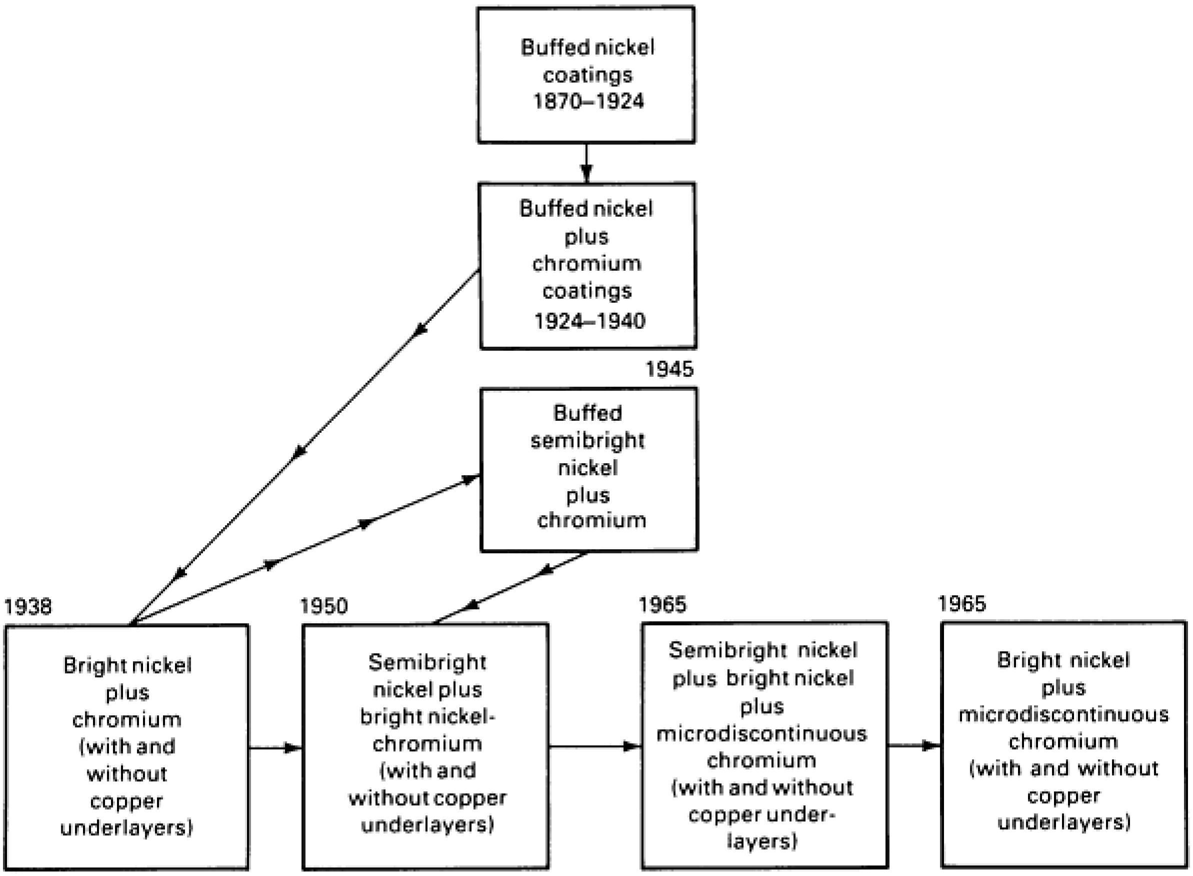

**Fig. 17 History of the development of nickel and nickel-chromium coatings showing time of introduction and periods of use. Source: Ref 37**

In nickel-chromium systems, the chromium layer is very thin--of the order of only 0.25 μm (0.01 mil). However, the corrosion resistance of chromium plate depends not so much on its thickness as on its physical state. Crack-free, or nonporous, chromium is excellent, but does not remain crack-free in service. A small number of cracks are detrimental, but the presence of many fine microcracks may be beneficial (Ref 38). Microcracked chromium deposits cause the galvanic-corrosion action to be spread over a very wide area and therefore do not suffer from localized corrosion. Microcracked chromium, in combination with duplex or triplex nickel, is the most durable of these coatings. The results of marine exposure for 36 months on variations of these coatings on steel are shown in Fig. 18. Recommended minimum thicknesses and typical applications of bright nickel-chromium coatings are listed in Table 25.

**Table 25 Recommended minimum thicknesses and typical applications for electrodeposited bright nickel-chromium coatings on steel, iron, or zinc die-cast substrates**

| Service conditions | Classification[(a)] | | Minimum thickness | | | | Typical applications |
|---|---|---|---|---|---|---|---|
| | | | Nickel | | Chromium | | |
| | Nickel | Chromium | μm | mils | μm | mils | |
| Mild (normally warm, dry, indoor atmospheres; minimum | b | r | 10 | 0.4 | 0.1 | 0.004 | Household appliances, interior auto hardware, hair dryers, fans, inexpensive cooking utensils, |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| wear or abrasion) | p | r | 10 | 0.4 | 0.1 | 0.004 | coat and luggage racks, standing ashtrays, interior trash receptacles, inexpensive light fixtures |
| | d | r | 10 | 0.4 | 0.1 | 0.004 | |
| | b | mc | 10 | 0.4 | 0.8 | 0.03 | |
| | p | mc | 10 | 0.4 | 0.8 | 0.03 | |
| | d | mc | 10 | 0.4 | 0.8 | 0.03 | |
| | b | mp | 10 | 0.4 | 0.3 | 0.012 | |
| | p | mp | 10 | 0.4 | 0.3 | 0.012 | |
| | d | mp | 10 | 0.4 | 0.3 | 0.012 | |
| Moderate (indoor exposure where condensation may occur, as in kitchens or bathrooms) | b | r | 20 | 0.8 | 0.3 | 0.012 | Steel and iron: stove tops, oven liners, home, office, and school furniture; bar stools, golf club shafts. Zinc alloys: bathroom accessories, cabinet hardware |
| | p | r | 20 | 0.8 | 0.3 | 0.012 | |
| | d | r | 20 | 0.8 | 0.3 | 0.012 | |
| | b | mc | 15 | 0.6 | 0.8 | 0.03 | |
| | p | mc | 15 | 0.6 | 0.8 | 0.03 | |
| | d | mc | 15 | 0.6 | 0.8 | 0.03 | |
| | b | mp | 15 | 0.6 | 0.3 | 0.012 | |
| | p | mp | 15 | 0.6 | 0.3 | 0.012 | |
| | d | mp | 15 | 0.6 | 0.3 | 0.012 | |
| Severe (occasional or frequent wetting by rain or dew; possible exposure to cleaners and saline solutions) | d | r | 30 | 1.2 | 0.3 | 0.012 | Patio, porch, and lawn furniture; bicycles; scooters; wagons; hospital furniture; fixtures; cabinets |
| | d | mc | 20 | 0.8 | 0.8 | 0.03 | |
| | d | mp | 25 | 1.0 | 0.3 | 0.012 | |
| | p | r | 40 | 1.6 | 0.3 | 0.012 | |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| | p | mc | 30 | 1.2 | 0.8 | 0.03 | |
| | p | mp | 30 | 1.2 | 0.3 | 0.012 | |
| Very severe (damage from wear or abrasion likely in addition to corrosive media) | d | r | 40 | 1.6 | 0.3 | 0.012 | Auto bumpers, grilles, hubcaps, and lower body trim; light housings |
| | d | mc | 30 | 1.2 | 0.8 | 0.03 | |
| | d | mp | 30 | 1.2 | 0.3 | 0.012 | |

Source: Ref 39

(a) Nickel classifications: b, fully bright; p, dull or semibright; d, double layer or triple layer nickel coating, with the bottom layer containing less than 0.005% S and the top layer more than 0.04% S. If there are three layers, the middle layer should contain more sulfur than the top layer. Chromium classifications: r, regular (conventional) chromium; mc, microcracked chromium having more than 750 cracks/in.: mp, microporous chromium containing a minimum of 64,500 pores/in.$^2$ that are visible to the unaided eye.

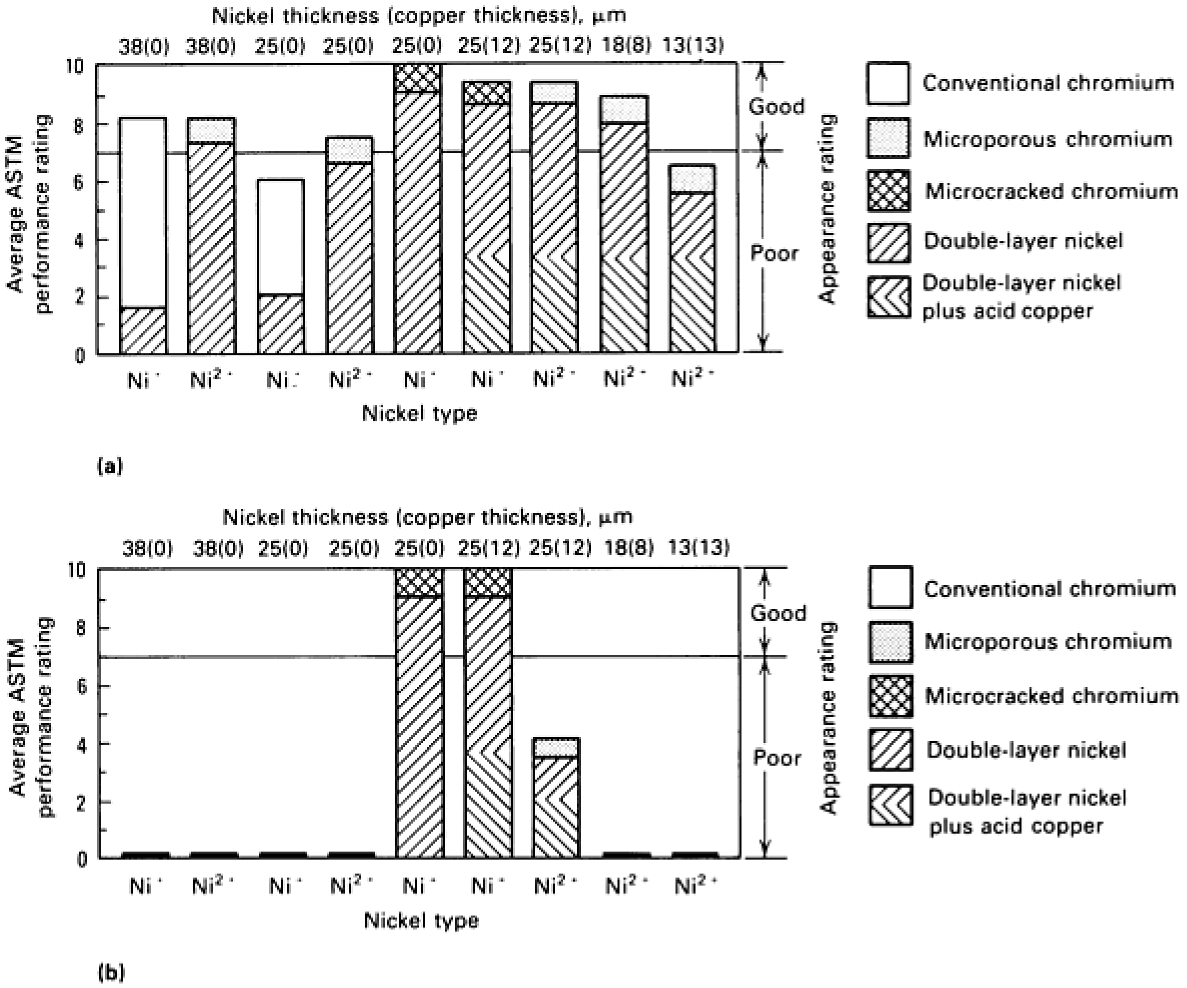

**Fig. 18 Performance in a marine atmosphere of various types of nickel-chromium and copper-nickel-chromium coatings on flat (a) and contoured (b) steel panels. ASTM performance rating: 10, best; 0, worst. Test duration: 36 months. Source: Ref 37**

## *Electroless Nickel Plating*

Electroless nickel plating is used to deposit nickel without the use of an electric current. The coating is deposited by an autocatalytic chemical reduction of nickel ions by hydrophosphite, aminoborane, or borohydride compounds. Details of the process can be found in the article "Electroless Nickel Plating" in this Volume. When sodium hypophosphite is the reducing agent, the deposit generally contains between 3 and 11% P. The boron contents of electroless nickel range from 0.2 to 4 wt% and from 4 to 7 wt% when the reducing agents are an aminoborane and sodium borohydride, respectively.

Electroless nickel is an engineering coating, normally used because of excellent corrosion and wear resistance. Because of these properties, electroless nickel coatings have found many applications, including those in petroleum, chemicals, printing, mining, aerospace, nuclear, and automotive industries.

Electroless nickel can be heat treated to hardnesses comparable to those of electrodeposited chromium. The maximum hardness can be attained in 1 h at about 400 °C (750 °F) or 10 h at 260 °C (500 °F). The hardness of as-plated nickel-phosphorus alloys varies from 500 to 650 on the Vickers scale. As-plated nickel-boron deposits are generally harder than the nickel-phosphorus ones. The ability of electroless nickel deposits to maintain their hardness under elevated-temperature service conditions increases with increasing phosphorus or boron content, but decreases rapidly above 385 °C (725 °F). Nickel-boron coatings tend to better withstand wear at elevated temperatures and are therefore more widely used under these conditions.

Wear rates of electroless nickel are summarized in Fig. 16. As this figure indicates, the wear loss of heat treated electroless deposits is lower than either electroplated nickel or non-heat-treated electroless deposits.

Coefficients of friction of electroless nickel in the as-deposited condition (EN) and heat treated at 400 °C (750 °F) (EN400) and at 600 °C (1110 °F) (EN600) are compared in Table 26 to the three chromium alloys depicted in Fig. 16. Additional information on the friction and wear characteristics of electroless nickel deposits can be found in Ref 36.

**Table 26 Coefficients of friction of chromium versus electroless nickel**

| Coating | Coefficients of friction | |
|---|---|---|
| | Counterface diamond | Counterface plain carbon steel |
| CrA | 0.040 | 0.88 |
| CrB | 0.035 | 0.82 |
| CrC | 0.030 | 0.81 |
| EN | 0.180 | 0.96 |
| EN400 | 0.300 | 0.95 |
| EN600 | 0.060 | 0.90 |

Source: Ref 36

## *Chromium Plating*

**Plating Baths.** Most chromium plating is done from hexavalent chromic acid ($CrO_3$) baths, but trivalent systems are gaining in popularity. Hexavalent chromium plating baths consist of chromic acid and small amounts of a sulfate catalyst ($SO_4^{2-}$). Recently, mixed catalyst baths containing fluoride compounds in addition to chromic acid and sulfate have been employed. Proprietary self-regulating baths control the concentration of the catalyst automatically. Bath formulations and process controls are discussed in the articles "Industrial (Hard) Chromium Plating" and "Decorative Chromium Plating" in this Volume.

**Applications and Properties.** As implied above, chromium plating is divided into decorative and hard coatings. Decorative coatings are applied over a base deposit of nickel or copper plus nickel to provide color and tarnish resistance. Coating thicknesses are usually less than 1 μm (0.04 mil). Decorative chromium coatings are most often found on automobiles, furniture, and kitchen appliances.

Hard chromium coatings are generally deposited directly on the base material without a nickel undercoat in thicknesses ranging from 1 to 500 μm (0.04 to 20 mils). Hard coatings provide resistance to wear, heat, abrasion, and/or corrosion. Typical applications for hard coatings include hydraulic pistons and cylinders, piston rings, wearing parts in business machines, aircraft engine parts, yarn and thread guides for textiles, plastics molds, and various parts of nuclear reactors where galling is a particular concern.

Microcracks are present in most electroplated hard chromium deposits. Figure 19 shows a typical microcrack structure. The density of the microcracks in chromium deposits varies from 0 to more than 1200 cracks/cm (3000 cracks/in.), depending on bath chemistry, current density, and temperature. The number of microcracks increases with the concentration of the catalyst in the plating bath. The depth of a microcrack is less than about 8 μm (0.3 mil) on a deposit that is 130 μm (5 mils) thick with crack counts of about 800 cracks/cm (2000 cracks/in.).

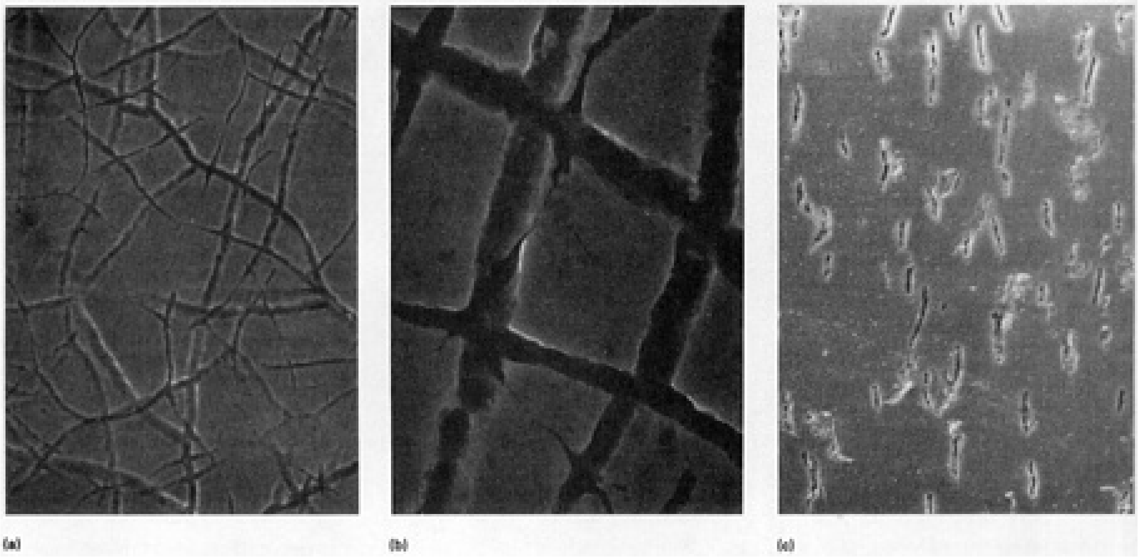

**Fig. 19 Photomicrographs of chromium deposits (plated in a high-efficiency etch-free bath) after etching. (a) and (b) Deposit plated at 78 A/dm$^2$ (5 A/in.$^2$) and at 55 °C (130 °F). (a) 540×. (b) 2300×. (c) Cross section of a chromium deposit plated at 93 A/dm$^2$ (6 A/in.$^2$) and at 58 °C (135 °F). The specimen was polished before etching. 880×. Both deposits contain 800 microcracks/cm (2000 microcracks/in.).**

Electroplated hard chromium is chemically resistant to most compounds and offers excellent corrosion protection in various environments. Electroplated chromium for atmospheric corrosion applications should be between 20 and 25 μm (0.8 and 1 mil) thick. For corrosion resistance in chemical exposures, electroplated chromium should be 50 to 75 μm (2 to 3 mils) thick. A detailed review on the corrosion resistance of electroplated chromium can be found in Ref 40.

The hardness of hard chromium varies from about 900 to 1100 on the Knoop and Vickers hardness scales. These values are considerably higher than the hardness of bulk chromium. Deposits from trivalent solutions are softer than those that are plated from hexavalent chromium solutions. However, after heat treating at about 700 °C (1290 °F), a hardness comparable to that of hard chromium can be achieved (Ref 41).

Chromium deposits are characterized by high internal tensile stresses that can reach 1000 MPa (145 ksi). These stresses can reduce the fatigue properties of coated components. Hydrogen is also codeposited with chromium and can diffuse into components, causing hydrogen embrittlement. Heat treatments are typically required to relieve the stresses and hydrogen effects, but can reduce the hardness.

The coefficients of friction of hard chromium against hard materials are generally the lowest of any electrochemically deposited coatings. The actual values vary considerably, depending on the test method, the mating surfaces of the materials, and the degree of lubrication. Some values of static and sliding coefficients of friction are listed in Table 27. In general, hard chromium has a lower wear rate than either electroplated or electroless nickel, which are the two competing materials. Wear rates are compared in Fig. 16.

**Table 27 Coefficients of friction for hard chromium electrodeposits**

| Couple | Static coefficient | Sliding coefficient |
|---|---|---|
| Chromium-plated steel versus itself | 0.14 | 0.12 |
| Chromium-plated steel versus steel | 0.15 | 0.13 |

| | | |
|---|---|---|
| Steel versus steel | 0.30 | 0.20 |

Source: Ref 42

### *Zinc Plating (Ref 43)*

**Plating Baths.** Zinc is deposited from three different baths: the conventional cyanide bath, the acid chloride bath, and the alkaline noncyanide (or zincate) bath. Compositions and processing conditions for these plating baths are described in the article "Zinc Plating" in this Volume. Cyanide baths offer the ease of control and normally trouble-free plating. However, the cost and toxicity associated with cyanide baths have prompted platers to install low-cyanide solutions or cyanide-free baths.

Chloride zinc baths have been available since the late 1960s. The original baths were chelated or based on complexing agents such as ammonium chloride. Today, state-of-the-art chloride baths use potassium or ammonium chloride. The advantages of the chloride systems include brilliant deposits, high cathode efficiency, low electric power consumption, and a nontoxic, easily treated electrolyte. The disadvantages are poor throwing power, a higher initial equipment investment, and higher brightener costs compared to the alkaline processes.

Alkaline noncyanide electrolytes consist of zinc and sodium hydroxide. In the absence of cyanide, proprietary sequestering agents are sometimes used to yield grain refinement. Alkaline noncyanide electrolytes are simple and low cost. The solutions and rinse waters are easily treated, and metal hydroxide sludges are reduced owing to low zinc content in the bath. These baths, however, offer the lowest cathode efficiency, and the deposits may be yellowish in color. Blistering is common at higher thicknesses and may be related to the greater hydrogen occlusion.

**Applications and Properties.** Zinc is plated over steel on a wide variety of parts where sacrificial corrosion resistance is required. The conventional zinc coating is dull gray in color with a matte finish, but whiter and more lustrous deposits can be produced by the use of proprietary addition agents. Zinc plate is almost always passivated with a chromate coating for added corrosion protection. The effects of chromate conversion coatings on the corrosion resistance of electrodeposited zinc are listed in Table 28. Coating thickness ranges from 5 to 25 μm (0.2 to 1 mil), depending on the particular application.

**Table 28 Recommended minimum thicknesses and typical applications for zinc and cadmium coatings electrodeposited on iron and steel**

| **Service conditions** | **Coating thickness** | | **Chromate finish** | **Time to white corrosion in salt spray, h** | **Typical applications** |
|---|---|---|---|---|---|
| | **μm** | **mils** | | | |
| **Electrodeposited zinc** | | | | | |
| Mild (indoor atmosphere: minimum wear and abrasion) | 5 | 0.2 | None | . . . | Screws, nuts and bolts, buttons, wire goods, fasteners |
| | | | Clear | 12-24 | |
| | | | Iridescent | 24-72 | |
| | | | Olive drab | 72-100 | |
| Moderate (mostly dry, indoor atmosphere; occasional condensation, wear, and abrasion) | 8 | 0.3 | None | . . . | Tools, zipper pulls, shelves, machine parts |

| | | | | | |
|---|---|---|---|---|---|
| occasional condensation, wear, and abrasion) | | | Clear | 12-24 | |
| | | | Iridescent | 24-72 | |
| | | | Olive drab | 72-100 | |
| Severe (exposure to condensation; infrequent wetting by rain; and cleaners) | 13 | 0.5 | None | . . . | Tubular furniture, window screens, window fittings, builders' hardware, military hardware, appliance parts, bicycle parts |
| | | | Clear | 12-24 | |
| | | | Iridescent | 24-72 | |
| | | | Olive drab | 72-100 | |
| Very severe (exposure to bold atmospheric conditions; frequent exposure to moisture, cleaners, and saline solutions; likely damage by abrasion or wear) | 25 | 1 | None | . . . | Plumbing fixtures, pole line hardware |
| **Electrodeposited cadmium** | | | | | |
| Mild (see above) | 5 | 0.2 | None | . . . | Springs, lock washers, fasteners, tools, electronic and electrical components |
| | | | Clear | 12-24 | |
| | | | Iridescent | 24-72 | |
| | | | Olive drab | 72-100 | |
| Moderate (see above) | 8 | 0.3 | None | . . . | Television and radio chassis, threaded parts, screws, bolts, radio parts, instruments |
| | | | Clear | 12-24 | |
| | | | Iridescent | 24-72 | |
| | | | Olive drab | 72-100 | |
| Severe (see above) | 13 | 0.5 | None | . . . | Appliance parts, military hardware, electronic parts for tropical service |
| | | | Clear | 12-24 | |
| | | | Iridescent | 24-72 | |

| | | | | | |
|---|---|---|---|---|---|
| | | | Olive drab | 72-100 | |
| Very severe (see above)(b) | 25 | 1 | None | . . . | . . . |
| | | | Clear | 24 | |
| | | | Iridescent | 24-72 | |
| | | | Olive drab | 72-100 | |

Source: Ref 39

(a) Thickness specified is after chromate conversion coating, if used.

(b) There are some applications for cadmium coatings in this environment; however, these are normally satisfied by hot-dipped or sprayed coatings.

The formation of white corrosion products in marine environments makes zinc less desirable than cadmium; but because it is less toxic and less expensive and its electrolytes are more easily waste treated, zinc has replaced cadmium in many applications. Zinc coatings are also superior to cadmium coatings in industrial environments. Common applications for zinc plating include fasteners, wire goods, tools, and sheet metal parts.

### *Cadmium Plating (Ref 43)*

**Plating Baths.** Cadmium is primarily plated from a cyanide electrolyte. Acid cadmium baths are also used to a limited extent, and are fluoborate, sulfate, or chloride in nature. The acid-type baths are more desirable if hydrogen embrittlement is a problem, and their waste treatment is simplified. However, the cyanide baths are easier to control than the acid baths. Typical cadmium plating compositions are described in the article "Cadmium Plating" in this Volume.

**Applications and Properties.** Cadmium provides galvanic protection when deposited on steel. The government is by far the largest specifier of cadmium, for military applications. As shown in Table 28, deposit thicknesses range from 5 to 25 μm (0.2 to 1 mil), depending on the degree of exposure to corrosion, and wear. As with zinc electroplates, chromate conversion coatings improve the corrosion resistance of cadmium electrodeposits. Cadmium is generally preferred for the protection of steel in marine environments whereas zinc is preferred in industrial environments. The coefficient of friction of cadmium is less than that of zinc; therefore, cadmium is preferred for fastening hardware and connectors that have to be taken on and off repeatedly. Typical applications include springs, lock washers, fasteners, electronic and electrical parts, washing machine parts, and military hardware. Because it is toxic, cadmium plating should never be used on parts that will come in contact with food or beverages.

**Avoiding Hydrogen Embrittlement.** Cadmium deposited from a cyanide solution is more likely to produce hydrogen embrittlement than any other commonly plated metal. Heat treated high-strength steels, particularly those plated and used at 35 HRC and above, are susceptible to hydrogen embrittlement.

Although the thickness of the plated deposit appears to have no direct bearing on hydrogen embrittlement, it is always more difficult to release the hydrogen (by baking) from heavy deposits. By adhering to the following procedures, hydrogen embrittlement can be minimized:

- Use mechanical cleaning methods, such as brushing, blasting, and tumbling
- Wherever possible, avoid the use of strong acid pickling solutions and extended exposure to acid pickling

- If pickling is essential to the preparation of medium-strength and high-strength steel parts, bake the parts at 175 to 205 °C (350 to 400 °F) for 3 h after pickling and before plating
- In plating, use the higher current densities to produce a more porous deposit; 7 A/dm$^2$ (70 A/ft$^2$) in a cyanide bath without brighteners has been satisfactory for steel at 46 HRC
- After plating, bake parts at 175 to 205 °C (350 to 400 °F) for 3 to 24 h. The shorter baking periods are generally adequate for parts with a tensile strength below about 1520 MPa (220 ksi); longer baking periods are recommended for steel of tensile strength above about 1520 MPa (220 ksi) or lower strength parts if sharp notches or threads exist. Parts greater than 25 mm (1 in.) thickness should also be baked for 24 h. The elapsed time between plating and baking must never exceed 8 h, and baking should be carried out as soon as possible, preferably within 4 h
- Plate parts to a thickness of about 5 μm (0.2 mil), bake for 3 h at 195 °C (385 °F), activate in cyanide, and then complete the plating to required final thickness

## ***Tinplate***

The term *tinplate* refers to a low-carbon steel strip product coated on both sides with a thin layer of tin. Electrolytic tinplate can be produced with either equal or unequal amounts of tin on the two surfaces of the steel base metal. Nominal coating thicknesses for equally coated tinplate range from 0.38 to 1.5 μm (15 to 60 μin.) on each surface. The thicker coating on tinplate with unequal coatings (differential tinplate) rarely exceed 2.0 μm (80 μin.). Tinplate is produced in thicknesses from 0.15 to 0.60 mm (0.006 to 0.024 in.). For almost 200 years, tinplate has been the primary material used to make containers (tin cans) for the long-term storage of food. More than 90% of the tinplate manufactured worldwide is used to make food cans, and nearly all food cans are made of tinplate.

Modern tinplate is much more sophisticated than a simple coating of tin on steel. To achieve the demanding deep-drawing properties necessary for the production of can bodies for two-piece can manufacture, the steel base for tinplate is often continuously cast using the most current technology. Inclusions or other defects in the steel may otherwise cause breakage in the can-body drawing operation. Because the economics of canmaking depend on high-speed operation using a continuous coiled strip, such breakage cannot be tolerated due to the lost production time; therefore, the steel must be as clean as possible.

In preparing the base steel, the metal is processed to strip form, the final step being a cold reduction that brings the strip to a thickness that is typically from 0.15 to 0.50 mm (6 to 20 mils). Next, the strip is annealed and then temper rolled to obtain the desired mechanical properties. At the final stage of temper rolling, textured rolls can be used to produce a special surface finish for particular applications. A cold reduction in place of temper rolling yields a product that is termed double reduced.

The coiled steel is now ready for the tinplate line. It is first welded to the end of the previous coil to form a continuous strip for processing. The strip passes through cleaning and pickling sections to prepare it for plating, then immediately through the plating cells, where up to 11.2 g/m$^2$ (1 g/ft$^2$) of tin is deposited. Tin may be plated from either alkaline electrolytes (stannate) or acid electrolytes (sulfate, fluoborate). Plating bath compositions and operating conditions are described in the article "Tin Plating" in this Volume.

The production steps that typically follow plating create additional layers in the tinplate structure that significantly affect corrosion properties. Upon exiting the plating cells, the tinplate has a matte surface that is usually reflowed by momentarily melting the tin coating in a resistance or induction heating unit. In doing so, a thin layer of tin-iron intermetallic compound is formed at the tin/steel interface. Next, an extremely thin passivation film based on chromium oxide is created by immersion or spraying of chromic acid ($H_2CrO_4$) on the tinplate surface or by passing the tinplate through a solution of $Na_2Cr_2O_7$, with or without the simultaneous application of electrical current. Finally, a very thin, uniform layer of lubricant, usually either dioctyl sebecate or acetyl tributyl citrate, is electrostatically applied.

Therefore, as supplied to the canmaker, the typical tinplate product consists of five layers, the innermost being a steel sheet about 200 to 300 μm (7.8 to 11.7 mils) thick. This steel is covered on each side with perhaps 0.08 μm (0.004 mil) of tin-iron intermetallic compound. The next layer is free tin that is perhaps 0.3 μm (0.012 mil) thick, with a passivation film of about 0.002 μm (0.00008 mil) and an oil film also about 0.002 μm (0.00008 mil) thick. All five layers affect corrosion behavior. Reference 44 is an excellent source of information on the corrosion characteristics of tinplate.

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## Metal Cladding

Carbon steels can be bonded to more corrosion-resistant materials, such as copper and stainless steels, by a variety of techniques. The resulting lamellar composite material has specific properties not obtainable in a single material.

**The principal cladding techniques** include hot roll bonding, cold roll bonding, explosive bonding, centrifugal casting, brazing, and weld cladding, although adhesive bonding, extrusion, and hot isostatic pressing have also been used to produce clad metals. With casting, brazing, and welding methods, one of the metals to be joined is molten when a metal-to-metal bond is achieved. With hot/cold roll bonding and explosive bonding processes, the bond is achieved by forcing clean oxide-free metal surfaces into intimate contact; this causes a sharing of electrons between the metals. Gaseous impurities diffuse into the metals, and nondiffusible impurities consolidate by spheroidization. These non-melting techniques involve some form of deformation to break up surface oxides, to create metal-to-metal contact, and to heat in order to accelerate diffusion. The techniques differ in the amount of deformation and heat used to form the bond and in the method of bringing the metals into intimate contact. More detailed information on metal cladding techniques can be found in Ref 45, 46, and 47.

**Noble metal clad systems** are materials having a relatively inexpensive carbon steel base metal covered with a corrosion-resistant metal. Clad metals of this type are typically used in the form of strip, plate, and tubing. The noble metal cladding ranges from commonly used stainless steels, such as type 304, to high-nickel alloys, such as Inconel 625. These clad metals find various applications in the marine, chemical-processing, power, and pollution control industries. Specific uses include heat exchangers, reaction and pressure vessels, furnace tubes, tubes and tube elements for boilers, scrubbers, and other systems involved in the production of chemicals.

**Transition Metal Systems.** A clad transition metal system provides an interface between two incompatible metals. It not only reduces galvanic corrosion where dissimilar metals are joined but also allows welding techniques to be used when direct joining is not possible.

The principle of a clad transition metal is illustrated in Fig. 20. In this example, aluminum is joined to low-carbon steel through a steel-clad aluminum transition metal. Steel and aluminum form brittle intermetallic compounds and are difficult to weld directly. The transition metal insert allows steel to be welded to steel and aluminum to aluminum; the actual bond between the steel and the aluminum occurs in the clad transition. In addition, the dissimilar-metal crevice is eliminated, which reduces susceptibility to galvanic corrosion.

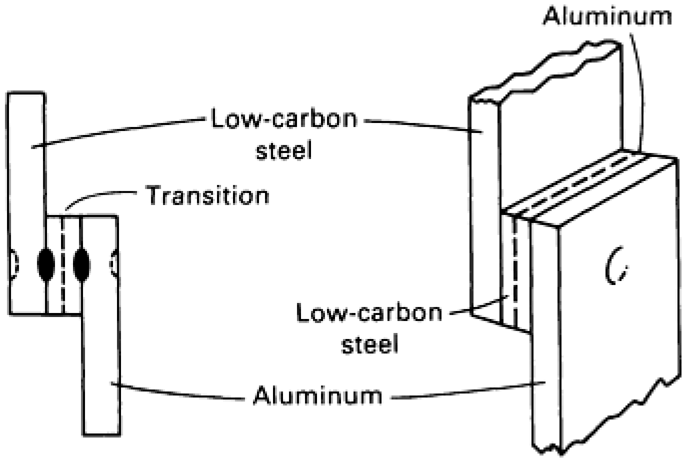

**Fig. 20 Illustration of a steel-clad aluminum transition insert used for joining aluminum to carbon steel**

**Complex Multilayer Systems.** In many cases, materials are exposed to dual environments; that is, one side is exposed to one corrosive medium, and the other side is exposed to a different one. A single material may not be able to meet this requirement, or a critical material may be required in large quantity.

Clad metals provide an ideal solution to the materials problem of dual environments. For example, in automobile windshield wiper sockets (Fig. 21), wear resistance is required on the mating surface, atmospheric-corrosion resistance is required on the external surface, and high strength is incorporated into the design. Multilayer phosphor-bronze-clad, steel-clad copper is used in this application. The phosphor bronze provides the required bearing surface, copper provides atmospheric-corrosion resistance, and steel provides the required strength.

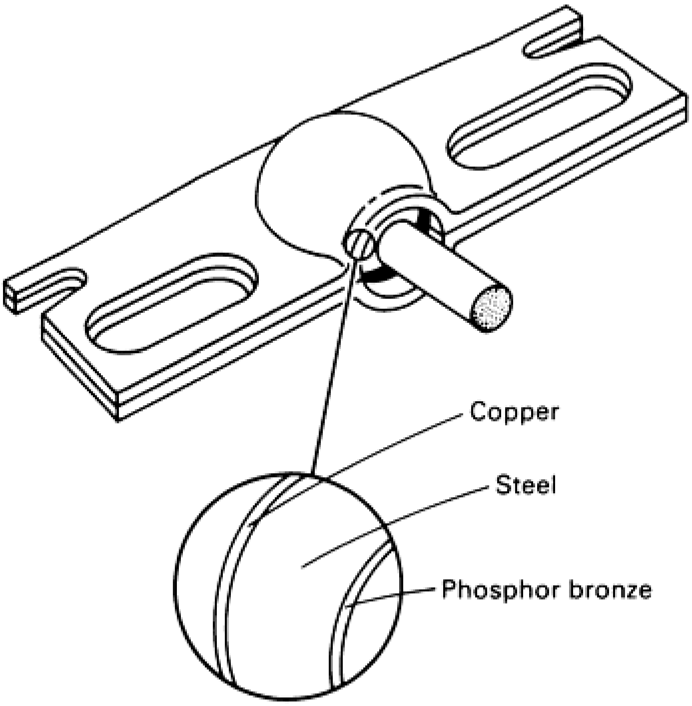

**Fig. 21 Clad metal windshield wiper socket, which consists of copper-clad, steel-clad phosphor bronze**

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## Organic Coatings

Paint is applied to a steel sheet or a part for one or both of the following reasons: enhancement of the aesthetic value of the product and/or preservation of structural integrity. The former goal is a consideration for the designer and will receive no further discussion in this section. The latter goal, however, will be discussed as it applies to prepainted steel.

This section will describe how paints deter corrosion, the prepainting process, the primary differences between prepaint paint formulations and postpaint formulations, considerations about part design, and selection criteria for the appropriate paint system. More detailed information on organic coating materials can be found in Ref 48 and the articles "Painting" and "Elastomeric Coatings and Linings" in this Volume.

**How Paint Films Deter Corrosion.** In the presence of water and oxygen, iron corrodes to form iron oxides and hydroxides. The corrosion rate is accelerated when electrolytic solutes, such as the chloride or sulfate salts of alkali metals, are present. Of course, temperature also increases the corrosion rate, and where possible, decreasing the service temperature will increase the service life of the part. However, because little can usually be done to change service temperature, the exclusion of one or more of the principal reactants (oxygen, water, or electrolytes) from the steel surface will help deter corrosion. Such exclusion of reactants is the purpose of the paint film.

There are primarily three methods of protection: barrier, passivation, and galvanic. In barrier protection, the paint film retards the diffusion of water, oxygen, or salts to the steel substrate. It has been demonstrated that the flow of water and oxygen through the film is rapid; therefore, the contribution of the coating to lowering the corrosion rate is the addition of a high electrolytic resistance (Ref 49). Flake-shaped pigment particles that leaf (overlap) can increase the path length a reactant must traverse before reaching the surface; this increases the effectiveness of the barrier film. Some aluminum and stainless steel pigments protect in this fashion. The reactivity of the steel surface can be decreased when the paint film contains passivating pigments such as chromate salts. As described below in the section on "Painting With Zinc-Rich Paints," paints are also often pigmented with zinc for both barrier and galvanic protection. The zinc loading must be sufficiently high for interparticle contact, a condition that requires that the critical pigment volume be exceeded; that is, the pigment particles are not completely wetted by the paint vehicle. Although some galvanic protection is afforded, most of the protection is provided by the barrier formed by zinc corrosion products (Ref 50).

**Prepaint Processing.** Much of the painted steel used today is prepainted in coil form (coil coated) before shipment to fabricators. Modern, high-speed paint lines can process bare or coated steel strip, and can be used to apply a wide variety of organic coatings.

After decoiling, the first step in the prepaint process is to clean the steel strip with an alkaline detergent. The steel strip is then brushed with an abrasive roll to remove mill oils and grime and to reduce the level of an amorphous form of surface carbon indigenous to steel strip processing. High levels of surface carbon lower corrosion resistance (Ref 51). Cleaning is usually more effective on flat strip than on a formed part. Next, the strip is rinsed and pretreated to improve paint adhesion and to reduce corrosion. A prepaint treatment may consist of phosphate coating or an organic pretreatment known as wash primer or etch primer. Such pretreatments are described in the article "Painting" in this Volume. Following pretreatment, a paint is then applied and cured in an oven. Depending on the paint formulation and the paint line, the dwell time in the oven is generally between 20 and 50 s. A second coat may then be applied and cured.

**Differences Between Prepaint and Postpaint.** In formulating a paint designed for a prepaint application, the forming step must be considered. Aside from steel consideration, successful forming of the part will depend on the flexibility and the abrasion resistance of the coating. The paint film must be flexible enough to withstand the strains induced from bending without crazing, which may compromise corrosion resistance. In addition, in the forming stages, the bend radii are often more severe than in the final part.

The coating must also withstand the abrasive forces of handling and forming. For a given coating type, the harder the coating, the more abrasion resistant the coating will be. Unfortunately, flexibility and hardness are inversely related; that is, the more flexible the coating, the softer the coating.

A method for overcoming the problems associated with coating flexibility is covered in the discussion on part design considerations in this section. Flexibility and hardness are considerations only for the end use of postpainted parts, while forming and handling are also factors of concern in the formulation of a paint designed for precoating a steel strip.

The final dried paint thickness, or dry-film thickness, on a prepainted steel strip is usually no more than 0.25 mm (1 mil). Plastisols and organosols are the major exceptions. Therefore, the prepaint dry-film thickness is much less than the typical dry-film thickness on a postpainted part. However, because of the method of application, the film is more evenly distributed; this results in significantly fewer areas of low dry-film thickness and the elimination of many of the appearance defects observed on finished postpainted parts. Many areas on postpainted parts will receive little or no paint because of the part shape. The formulations for prepaints are engineered to account for the lower dry-film thicknesses.

**Part Design Considerations.** When designing a part to be fabricated from prepainted steel, the maximum bend radius, the forming equipment, and the joining method must be considered. As mentioned earlier, the maximum bend radius is often smaller than that specified on the blueprint of the part. This radius should be as generous as the structural and decorative criteria will allow. In considering the part shape, the avoidance of catchment areas, where possible, will decrease failures due to corrosion.

The forming equipment should be well maintained to avoid marring the surface. Where possible, roll forming is preferable to stamping. In cases in which hard finishes in conjunction with tight radii (high flexibility) are required, the prepainted strip can be warm formed. In warm forming, the paint is heated into or above its glass transition temperature range. In this temperature range, the paint is softer and more flexible, thus allowing tighter radii to be achieved during forming. After cooling, the paint becomes harder and more abrasion resistant.

Lastly, the part may require joining. Welding and mechanical fastening damage the paint film. Therefore, it is necessary to touch up the scars to restore corrosion resistance. Adhesive bonding eliminates the need for touch up of these damage areas. Taking these factors into account, prepainted steel has been successfully fabricated into finished or semifinished (requiring a post finish coat operation) parts in many automotive, appliances, or office furniture manufacturing plants. Prepainted parts have been produced on lines designed for their use and on existing lines, sometimes with no modification to the line.

**Selection Guideline.** As an aid to understanding the evaluation process, Table 29 compares various common coatings in several categories of performance. Changes in pigmentation and resin source for the vehicle can influence the rating by a factor of one or more. Table 29 is merely a guideline to the performance of these coatings. Comments from technical personnel at a paint company should be sought before making any decision on paint selection.

### Table 29 Relative hardness rankings of various coatings in different performance categories

Category key: A, hardness; B, flexibility; C, humidity resistance; D, corrosion resistance to industrial atmospheres; E, salt spray; F, exterior durability, pigmented film; G, exterior durability, clear film; H, paint cure temperature, in °C (°F); I, cost guide. Ratings key: 1, excellent; 2, good; 3, fair; 4, poor; H, high cost; M, moderate cost; L, low cost

| **Type** | **A** | **B** | **C** | **D** | **E** | **F** | **G** | **H** | **I** |
|---|---|---|---|---|---|---|---|---|---|
| Silicone acrylic | 1 | 3 | 2 | 2 | 2 | 2 | 1 | 230 (450) | H |
| Thermoset acrylic | 2 | 2 | 1 | 2 | 1 | 2 | 2 | 220 (430) | M |
| Amine-alkyd | 2 | 3 | 2 | 2 | 3 | 2 | 3 | 170 (340) | L |
| Silicone alkyd | 2 | 3 | 2 | 2 | 2 | 1 | 2 | 215 (420) | H |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Vinyl-alkyd | 2 | 2 | 1 | 2 | 2 | 3 | 3 | 170 (340) | M |
| Straight epoxy | 1 | 2 | 1 | 1 | 1 | 4 | 4 | 205 (400) | H |
| Epoxy-ester | 2 | 2 | 1 | 2 | 1 | 4 | 4 | 205 (400) | M |
| Organosol | 2 | 1 | 1 | 1 | 1 | 2 | 3 | 175 (350) | L |
| Plastisol | 3 | 1 | 1 | 1 | 1 | 2 | 3 | 175 (350) | L |
| Polyester (oil-free) | 1 | 2 | 1 | 2 | 1 | 2 | 3 | 205 (400) | M |
| Silicone polyester | 2 | 2 | 1 | 2 | 1 | 1 | 2 | 230 (450) | H |
| Polyvinyl fluoride | 2 | 1 | 1 | 1 | 1 | 1 | 1 | 230 (450) | H |
| Polyvinyl idene fluoride | 2 | 1 | 1 | 1 | 1 | 1 | 1 | 230 (450) | H |
| Solution vinyl | 2 | 1 | 1 | 2 | 1 | 2 | 3 | 150 (300) | M |

The columns in Table 29 are self-explanatory, with the exception of those involving exterior durability and salt spray. Exterior durability is the resistance to weathering, particularly the resistance to ultraviolet light. Ultraviolet light causes some coatings to chalk. Proper pigmentation will prevent this phenomenon for some coatings, and this can be determined by comparing the columns for pigmented and clear films.

Salt spray is not a predictor of service life and coatings cannot be compared for end use on this basis. However, salt spray does detect coating defects and can be put to good use for detecting induced flaws by comparing results for flat panels with those of panels with coating defects induced, for example, by forming or abrasion.

The first step in the evaluation is the selection of a steel mill and/or paint company that is willing and able to help evaluate the needs of the final product. These needs can be categorized as either preservice or service. The preservice conditions involve forming, handling, and joining. The service conditions are those to which the customer exposes the product: humidity, temperature, corrosive agents, sunlight, and abrasion. Of course, the preservice conditions can affect the service life of the final product, and these effects should be evaluated.

The next step is the experimental design. The test program compares candidate materials to the current product, if possible. Evaluation in actual service conditions is often not possible because of time limitations. Therefore, accelerated and laboratory tests are needed (see the article "Corrosion Testing" in this Volume). From these results, acceptable candidates are identified and are included in the next level of tests. A set of suitable parts is identified for testing the candidates. After the parts are fabricated, they are inspected to determine whether coating damage occurred and whether corrosion resistance was compromised. In general, one material will not be superior in all aspects. Therefore, the desirable properties must be prioritized.

**Advantages of Prepainted Steels.** Although the above evaluation sequence may seem formidable, many manufacturers have found the use of prepainted steel to be productive and economical. The use of prepainted steel reduces or eliminates the problems of the waste treatment of the emissions from paint lines. The postpainting line is often the slow step in the process, and using prepainted steel increases output. Although the material cost of prepainted steel is higher than the bare metal, the final part cost is lower because of increased productivity and the reduction of other costs, such as emissions control. Although prepainted steel cannot replace postpainted steel in every application, prepainted steel has demonstrated its productive and economic advantages.

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## Painting With Zinc-Rich Paints

Zinc-rich coatings, often called zinc-rich primers, are a unique class of cross-linked coatings that provide galvanic protection to a ferrous substrate. As the name implies, the binder is highly loaded with a metallic zinc dust pigment. After the coating is applied to a thoroughly cleaned substrate, the binder holds the metallic zinc particles in contact with the steel and with each other. Thus, metal-to-metal contact of two dissimilar metals is made, resulting in a galvanic cell. In this couple, zinc becomes the anode and sacrifices itself to protect the underlying cathodic steel.

The major advantage of corrosion protection using zinc-rich coatings is that localized pitting corrosion and subfilm corrosion are eliminated, even at voids, pinholes, scratches, and abrasions in the coating system. This cannot be said of any other type of protective coating, and it is this protective capability that makes zinc-rich coatings unique and widely used.

This advantage, however, comes with certain disadvantages. The underlying steel substrate must be cleaned of all rust, old paint, and other contaminants that may interfere with metal-to-metal contact. Thus, the degree of surface preparation must be quite thorough: blast cleaning should produce a Commercial Blast Cleaning minimum and, for immersion service, a White or Near-White surface. The Steel Structures Painting Council (SSPC), NACE, and other organizations issue standards for the surface preparation of metals for organic coatings: these are discussed in more detail in Ref 48 and also mentioned below.

### *Zinc Dust/Zinc Oxide Coatings*

Zinc dust/zinc oxide paints, also known as metallic zinc paints, contain a pigmentation of approximately 80% zinc dust, 20% ZnO, and approximately 80% pigment by weight. These paints offer excellent rust-inhibitive properties, adhesion, film distensibility, and abrasion resistance. Because they adhere tightly to zinc and other metals, they are ideal for prime and finish coat applications and may be used as a primary first coat even over partially rusted surfaces.

Zinc dust/zinc oxide paints are used for the protection of many types of steel structures under a variety of service conditions. They are particularly well suited to use on galvanized steel; are highly satisfactory for priming steel for atmospheric and underwater exposure; and can be used on many outdoor structures, such as bridges, water tanks, and dams, where rusting must be prevented.

In accordance with Federal Specification TT-P-641 which covers primer paints and zinc dust/zinc oxides for galvanized surfaces, there are three types of zinc dust/zinc oxide paints:

- *Type I:* zinc dust/zinc oxide linseed oil for outdoor exposure, recommended as a primer or finish coat for broad, general use, especially when there is widespread rusting of the steel surfaces; should be air dried only
- *Type II:* zinc dust/zinc oxide alkyd resin paint, a heat-resistant paint sometimes sold as a stack paint, may also be used for outdoor exposures where rust is not severe; quick drying; can be air dried or baked at temperatures to 150 °C (300 °F)
- *Type III:* zinc dust/zinc oxide phenolic resin paint; used for water immersion and other severe moisture conditions; may be air dried or baked at temperatures to 150 °C (300 °F)

These paints, when properly formulated and prepared, can be applied by brushing, dipping, or spraying. Although the presence of ZnO prevents rapid or hard settling, adequate agitation of the paint in the dip tank is necessary to ensure the coating homogeneity necessary for maximum metal protection. Pressure equipment should be used when spraying, and the distance between the paint reservoir and the spray gun should be as short as possible to ensure the proper rate of feed to the nozzle. Again, some agitation of the paint in the reservoir is recommended.

Zinc dust/zinc oxide paints possess high covering power and can hide backgrounds of almost any color when spread at the rate of approximately 20 $m^2$/L (800 $ft^2$/gal). However, because the protection afforded by a paint coating is directly related to its thickness, the necessary protection cannot be guaranteed unless the dry film is thick enough for the specific environmental conditions. Therefore, care must be taken to avoid spreading the paints too thin. The natural blue-gray color of zinc dust/zinc oxide paints provides an aesthetic appearance, but if another color is desired, red, buff (orange-yellow), and green can be obtained by varying the pigment.

To prepare surfaces for zinc dust/zinc oxide paints, rust (or scale) and any accumulation of leaves, dirt or other foreign materials should be removed. This may be accomplished on large structures by sandblasting and on small structures or areas with a deck or wire brush.

### *Zinc-Rich Coatings*

In recent years, a number of paints have been developed that will deposit a film of metallic zinc having many properties in common with zinc coatings applied by hot-dip galvanizing, electroplating, thermal spraying, and mechanical plating. Such paint films will protect the underlying steel sacrificially if they contain 92 to 95% metallic zinc in the dry film and if the film is in electrical contact with the steel surface at a sufficient number of points. They are effective where steel is subjected to high humidity and water immersion. Under normal conditions, zinc-rich coatings are long lasting and most effective where a regular maintenance program may be difficult. In applications in which steel is immersed in brackish or salt water, zinc-rich coatings, along with a suitable top coat, should be used. Most zinc-rich paints are of the air-drying type although oven-cured primers containing a high content of zinc dust are available.

The type of zinc dust used is a heavy powder, light blue-gray in color, with spherically shaped particles having an average diameter of approximately 4 mm. Such powder normally contains 95 to 97% free metallic zinc with a total zinc content exceeding 99%.

**Surface Preparation.** Zinc-rich primers must be applied over clean steel surfaces to provide the metal-to-metal contact essential to successful performance of the coating. Abrasive blasting is the most effective method of cleaning steel. Although white metal blast-cleaning (NACE No. 1) is preferred, near-white SSPC-SP-10 or Commercial Blast Cleaning SSPC-SP-6 is acceptable (Ref 52).

Where the zinc is supplied as a separate component, it should be added slowly to the vehicle with constant agitation. After a homogeneous mix is obtained, the primer may be applied with air spray. Airless spray may also be used, but the nozzles may wear quickly. Because zinc settles rapidly, continuous agitation of the paint is essential during application, and fluid lines should be kept as short as possible.

To obtain a wet coat, the gun should be kept within 30 cm (1 ft) of the surface. Uneven film thickness due to brushing or rolling may result in mudcracking in the thick portions. Zinc-rich primers should be applied at a dry film thickness of 0.06 to 0.08 mm (2.5 to 3.5 mils).

**The Nature of the Zinc-Rich Coating.** Depending on the binder, zinc-rich coatings fall into two classes: organic and inorganic. The inorganic solvent-base types are derived from organic alkyl silicates, which become totally inorganic upon curing. Each offers particular protection characteristics, and each requires different preparation of the steel surface. The following comparisons should be helpful in selecting the most useful binder system.

**The organic zinc-rich coatings** are formed by using zinc dust as a pigment in an organic binder. This binder may be any of the well-known coating vehicles, such as chlorinated rubber and epoxy. The zinc dust must be in sufficient concentration so that the zinc particles are in particle-to-particle contact throughout the film. Thus, zinc provides cathodic protection. In the case of the organic binder, there is no reaction with the underlying surface other than for the organic vehicle to wet the steel surface thoroughly and to obtain mechanical adhesion.

Organic zinc-rich coatings do not require a white blast preparation of the steel surface, although a commercial blast should be included if the application is heavy service. For mild-service applications, the organic coating can be applied to a well-hand-cleaned surface, even if traces of rust are present.

Some proponents feel that maintaining proper humidity during surface preparation, application, and curing is not necessary. Because this type of coating is more flexible than inorganic coatings, exacting surface preparation for bonding to a substrate is not required. Finally, although organic coatings are more compatible with top coats, they are somewhat less abrasion resistant than the inorganic types.

As to the advantages of these coatings, organic zinc-rich coatings require less critical surface preparation, allow greater variation in application techniques, are less sensitive to varying climatic conditions during application and curing, and are more flexible and more resistant to chemical environments. Their disadvantages include flammability, blistering, harmful solvent effects, sensitivity to atmospheric influences, and relatively low heat resistance.

For better resistance against continuous exposure to salt water and to acid or alkali chemical fumes, zinc-rich coatings should be top coated with organic topcoats to provide a totally organic system, with optimum intercoat compatibility. A top coating may also be applied to provide color or to prevent gradual erosion of the zinc coating. Although zinc-rich coatings vary in application characteristics, they can be applied by brush or spray, and depending on the specific formulation, one coat can vary in thickness from 0.05 to 0.2 mm (2 to 7 mils).

**Inorganic Zinc-Rich Coatings.** Many inorganic zinc-rich coatings use water solutions of alkali silicates as vehicles. Others use phosphates, silicones, and modifications of these groups.

Self-cured coatings are two-component materials consisting of zinc dust and a vehicle; they are mixed immediately before application. Postcured coatings are three-component materials that consist of zinc dust, the vehicle to be mixed with it before application, and a curing agent that is applied on top of the coating.

The inorganic zinc coating forms its film and its adhesion to the steel surface by methods quite different from those of the organics. The coating system is a chemically reactive system, and the chemical activity is similar for either the water- or the solvent-base inorganic. Zinc is the principal reactive element in the inorganic coating systems and is primarily responsible for the development of initial insolubility. Depending on the formulation, other metal ions may be present in the system that also react and aid in the insolubilization of the coating. The silicate vehicle can also react with the underlying iron surface to form a chemical bond with the iron or steel substrate.

Inorganic zinc-rich coatings commonly require a white metal blast as preparation for the steel surface. Because inorganic coatings generally have limited flexibility and tend to break or crack upon bending or impact, careful preparation of the steel surface is required to ensure a good bond between the coating and the steel. However, despite the difficulties of preparation, these inorganic coatings are unaffected by solvents, oils, petroleum products, aliphatics, aromatics, ketones, and alcohols. They do not chalk, peel, or lose thickness over long periods of time. Also, they are easier to weld through and have excellent abrasion resistance and surface hardness.

Inorganic zinc-rich coatings offer good conductivity; good adhesion to clean steel; excellent resistance to weather, sunlight, and variations in temperature; resistance to radiation, heat, and abrasion; and reduced undercutting. Conversely, these coatings require unusually good surface preparation, display a lack of distensibility and adhesion to some metals other than steel and zinc, require moderate temperatures and atmospheric humidity for cure, and exhibit unsatisfactory durability under conditions of continuous immersion in electrolytes, and a lack of resistance to strong acids and alkalies.

### *Zinc Dust/Zinc Oxide Paint Versus Zinc-Rich Coating*

Whether to use a zinc dust/zinc oxide paint or a zinc-rich coating depends on a number of factors, including cost of surface preparation, paint application, and anticipated length of surface. Zinc dust/zinc oxide coatings are ideal for rural or semi-industrial atmospheres. They are particularly effective on galvanized surfaces.

The widely used zinc dust/zinc oxide primers based on ordinary drying oil media do not give general electrolytic protection against corrosion and therefore do not fall in the category of zinc-rich paints.

Zinc-rich coatings are preferred for the protection of steel or galvanized steel structures exposed to marine environments or immersed in seawater. Applications include interiors of floating roof tanks, cooling tower piping, pipe racks and exterior piping in refineries, stacks, chemical plant maintenance, offshore drilling platforms, aboveground pipelines, structural steel before erection, exterior of pressure vessels, ammonia tanks, ship holds, and air conditioning equipment.

A top coat finish may be necessary in aggressive atmospheres. The top coat must adapt to the environment and must guarantee compatibility with, and adhesion to, the zinc-rich primer.

**Advantages and Limitations of Zinc-Rich Paints.** Zinc-rich primers offer a more versatile form for applying zinc to steel than galvanization; large, continuous complex shapes and fabricated new or existing structures can be easily coated at manufacturing shops or in the field. Their performance has earned them a prominent place in the field of corrosion protection coatings. However, the limitations of zinc-rich paints include cost, difficulty in applying, and the requirement of clean steel surfaces. They must be top coated in severe environments (pH under 6.0 and over 10.5).

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## Porcelain Enameling

Porcelain enamels are glass coatings applied primarily to products made of steel sheet, cast iron, or aluminum to improve appearance and protect the metal surface from corrosion. Porcelain enamels are distinguished from other ceramic coatings by their predominantly vitreous nature and the types of applications for which they are used, and from paint by their inorganic composition and the fusion of the coating matrix to the substrate metal. Porcelain enamels of all compositions are matured at 425 °C (800 °F) or above.

Several basic methods are used to apply porcelain enamels to the base metal. These include dipping, flow coating, electrodeposition, manual spray, electrostatic spray, and dry-powder spray. The best method of application for a particular part is determined by quantity and quality requirements, the type of material being applied, units produced per hour, capital investment, labor cost, and, ultimately, part cost. Details on application techniques for porcelain enameling are provided in the article "Porcelain Enameling" in this Volume.

**Coating Materials** The frits for porcelain enamel are designed and manufactured to meet specific end-use applications and processing requirements. Porcelain enamel frits for sheet steel are classified as either ground coat or cover coat types. Ground coat enamels contain metallic oxides that promote adherence to the steel substrate and may be used as a single functional coat or as a base coat for additional cover coats. Table 30 gives the composition of a typical ground coat enamel. Cover coat enamels (Table 31) are normally applied over ground coats for appearance and/or to improve the chemical and physical properties of the coating. Cover coats may also be applied directly to properly prepared decarburized steel substrates.

**Table 30 Melted-oxide compositions of frits for ground coat enamels for sheet steel**

| Constituent | Composition, % | | | |
|---|---|---|---|---|
| | Regular blue-black enamel | Alkali-resistant enamel | Acid-resistant enamel | Water-resistant enamel |
| $SiO_2$ | 33.74 | 36.34 | 56.44 | 48.00 |
| $B_2O_3$ | 20.16 | 19.41 | 14.90 | 12.82 |
| $Na_2O$ | 16.74 | 14.99 | 16.59 | 18.48 |

|  |  |  |  |  |
|---|---|---|---|---|
| $K_2O$ | 0.90 | 1.47 | 0.51 | . . . |
| $Li_2O$ | . . . | 0.89 | 0.72 | 1.14 |
| CaO | 8.48 | 4.08 | 3.06 | 2.90 |
| BaO | 9.24 | 8.59 | . . . | . . . |
| ZnO | . . . | 2.29 | . . . | . . . |
| $Al_2O_3$ | 4.11 | 3.69 | 0.27 | . . . |
| $ZrO_2$ | . . . | 2.29 | . . . | 8.52 |
| $TiO_2$ | . . . | . . . | 3.10 | 3.46 |
| CuO | . . . | . . . | 0.39 | . . . |
| $MnO_2$ | 1.43 | 1.49 | 1.12 | 0.52 |
| NiO | 1.25 | 1.14 | 0.03 | 1.21 |
| $Co_3O_4$ | 0.59 | 1.00 | 1.24 | 0.81 |
| $P_2O_5$ | 1.04 | . . . | . . . | 0.20 |
| $F_2$ | 2.32 | 2.33 | 1.63 | 1.94 |

**Table 31 Melted oxide compositions of frits used for cover coat enamels for sheet steel**

| **Constituent** | **Composition, wt%** |  |  |
|---|---|---|---|
|  | **Titania white enamel** | **Semi-opaque enamel** | **Clear enamel** |
| $SiO_2$ | 44.67 | 44.92 | 54.26 |
| $B_2O_3$ | 14.28 | 16.40 | 12.38 |
| $Na_2O$ | 8.27 | 8.67 | 6.55 |

| | | | |
|---|---|---|---|
| $K_2O$ | 6.99 | 8.12 | 11.32 |
| $Li_2O$ | 0.98 | 0.45 | 1.14 |
| ZnO | . . . | 0.74 | . . . |
| $ZrO_2$ | 1.98 | 3.34 | 1.40 |
| $Al_2O_3$ | 0.31 | 0.16 | . . . |
| $TiO_2$ | 18.49 | 13.05 | 10.04 |
| $P_2O_5$ | 1.32 | 0.88 | . . . |
| MgO | 0.5 | . . . | . . . |
| $F_2$ | 2.21 | 3.27 | 2.91 |

Because all porcelain enamels are variations of borosilicate glass, they are characterized by end use and not by chemical composition. Some common designations for those with particular characteristics are acid-resistant, alkali-resistant, heat-resistant, glossy, low-gloss, and matte.

**Steel Substrates.** Typical compositions of the various grades of low-carbon sheet iron or steel that are commercially available for porcelain enameling are listed in Table 32. Cold-rolled sheet steels used for porcelain enameling can be divided into three groups:

- Extra-low carbon steels (a maximum of 0.008% C), including HSLA steels in which the carbon is stabilized by the addition of titanium or niobium
- Low-carbon steels containing about 0.02% C (these steels are suitable for ground or two-coat enameling)
- Conventional cold-rolled sheets with higher carbon contents of about 0.06% (such sheets have a tendency toward primary boiling and sagging and are used in less critical ground coat and two-coat enameling applications)

**Table 32 Compositions of low-carbon steels used for porcelain enameling**

| Type of steel | Composition, %[a] | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | C | Mn | P | S | Al | Ti | Nb | B |
| Replacement steel for enameling iron | 0.02-0.05 | 0.15-0.3 | 0.015[b] | 0.015[b] | 0.03-0.07 | . . . | . . . | 0.006 |
| Decarburized | 0.005 | 0.2-0.3 | 0.01 | 0.02 | [c] | . . . | . . . | . . . |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Titanium-stabilized | 0.05 | 0.30 | 0.01 | 0.02 | 0.05 | 0.30 | . . . | . . . |
| Interstitial-free | 0.005 | 0.20 | 0.01 | 0.02 | . . . | 0.04 | 0.09 | . . . |
| Cold-rolled | 0.06 | 0.35 | 0.01 | 0.02 | (c) | . . . | . . . | . . . |

(a) All compositions contain balance of iron.

(b) Maximum.

(c) Some steels may be supplied as aluminum-killed products. Data from Porcelain Enamel Institute

Hot-rolled steels are generally used for porcelain enameled water heater tanks and for other applications where thickness and strength requirements dictate their use. When hot-rolled steels are used, components should be coated on one side only to minimize processing defects such as fishscales.

**Coating Properties.** Porcelain enamel is used extensively because of its resistance to household chemicals and foods. Mild alkaline or acid environments are generally involved in household applications. Special enamels or glass compositions are available to resist most acids--except for hydrofluoric or concentrated phosphoric--to temperatures of 230 °C (450 °F). Compositions may be formulated to resist alkali concentrations up to a pH of 12 at temperatures as high as 95 °C (200 °F).

The hardness of porcelain enamels ranges from 3.4 to 6.0 on the Moh's scale. Porcelain enamels show a high degree of abrasion resistance. Abrasion resistance can be increased by adding crystalline particles to the enamel composition by a devitrification heat treatment.

## Thermal Spray Coatings

Thermal spray coatings are surface coatings engineered to provide original equipment with resistance to wear, erosion, abrasion, corrosion, and oxidation. Thermal spraying is also used to repair and upgrade in-service equipment. In general, thermal spray coatings can be applied to a range of substrate materials, including metals, ceramics, plastics, and polymer composites. Such coatings often are used instead of paint because of their predictable service life, increased effectiveness, and lower life-cycle costs.

Thermal spray processes deposit finely divided metallic or nonmetallic feedstock surfacing material in a molten or semimolten condition onto a properly prepared, grit-blasted substrate to form a coating. The thermal spray feedstock material (wire, cored wire, ceramic rod, or powder) is heated to its plastic or molten state by combustion (flame, high-velocity oxygen fuel, or detonation) or by electric (arc or plasma) processes. The material is then accelerated toward the substrate. The particles or droplets strike the surface, flatten, and form thin platelets (splats) that conform, adhere, and interlock with roughened surface irregularities and with each other. As the sprayed particles impinge on the substrate, they cool and build up, particle by particle, into a lamellar-structured coating. Figure 7 in the preceding article "Surface Engineering of Cast Irons" in this Volume shows the lamellar structure of particle splats, oxide inclusions, and unmelted particles in a cross section of a typical thermal spray coating. In general, the substrate temperature can be kept at 200 °C (390 °F) or below to prevent metallurgical changes in the substrate material. Details of the thermal spray process can be found in Ref 53 and the article "Thermal Spray Coatings" in this Volume.

The properties of a thermal spray coating depend on such factors as its porosity, the cohesion between particles, adhesion to the substrate (including interface integrity), and the chemistry of the coating material. The particles bond to the substrate mechanically (the primary mechanism), metallurgically, or chemically. Particle impact velocity, particle size, substrate roughness, particle temperature, and substrate temperature influence bond strength.

Aluminum and zinc thermal spray coatings have a long history of corrosion protection in structural steel work, including:

- Buildings
- Bridges
- Towers
- Radio and TV antenna masts
- Steel gantry structures
- High-power search radar aerials
- Overhead walkways
- Railroad overhead line support columns
- Electrification masts
- Tower cranes
- Traffic island posts
- Street and bridge railings

**Corrosion Protection by Thermal Spraying.** Thermal spray coatings are used extensively for the corrosion protection of steel and iron in a wide range of environments. Their long-term effectiveness (20 years or more) in rural, industrial, and marine environments is well documented (Ref 54, 55, 56, 57).

The selection of a thermal spray coating depends on the service environment, desired service life, operating duty cycle, and available maintenance and repair support. Tables 33 and 34 give current service-life information for thermal spray coatings in various service environments, and Fig. 22 and 23 plot the corresponding required thickness specifications. The service-life estimates for 85Zn-15Al alloy and 90Al-10MMC (metal-matrix composite) coatings--introduced in the late 1970s and 1980s, respectively--are based on accelerated laboratory tests and service applications through 1992. In a marine environment, powder spray coatings with higher aluminum contents exhibit improved corrosion resistance (Ref 55). Where resistance to wear and/or abrasion is required in addition to corrosion protection, 90Al-10MMC coatings should be considered. The 90Al-10MMC wire is composed of 90 vol% Al and 10 vol% $Al_2O_3$.

**Table 33 Service life estimates for 85Zn-15Al thermal spray coatings in selected corrosive environments**

| Type of exposure | Coating thickness required for indicated service life | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 5-10 years | | 10-20 years | | 20-40 years | | >40 years | |
| | µm | in. | µm | in. | µm | in. | µm | in. |
| Rural atmosphere | . . . | . . . | 75-125 | 0.003-0.005 | 125-175 | 0.005-0.007 | 250-300 | 0.010-0.012 |
| Industrial atmosphere | . . . | . . . | 150-200 | 0.006-0.008 | 300-375 | 0.012-0.015 | 350-400 | 0.014-0.016 |
| Marine atmosphere | . . . | . . . | 250-300 | 0.010-0.012 | 300-375 | 0.012-0.015 | 350-400 | 0.014-0.016 |
| Freshwater immersion | 150-200 | 0.006-0.008 | 250-350 | 0.010-0.014 | 300-375 | 0.012-0.015 | . . . | . . . |
| Saltwater immersion | 250-300 | 0.010-0.012 | 350-400 | 0.014-0.016 | . . . | . . . | . . . | . . . |

**Table 34 Service-life estimates for aluminum and 90Al-10MMC (vol%) thermal spray coatings**

| Type of exposure | Coating thickness required for indicated service life[(a)] |
|---|---|

|  | **5-10 years** |  | **10-20 years** |  | **20-40 years** |  | **>40 years** |  |
|---|---|---|---|---|---|---|---|---|
|  | **µm** | **in.** | **µm** | **in.** | **µm** | **in.** | **µm** | **in..** |
| Rural atmosphere | . . . | . . . | . . . | . . . | 150-200 | 0.006-0.008 | . . . | . . . |
| Industrial atmosphere | . . . | . . . | 150-200 | 0.006-0.008 | 250-300 | 0.010-0.012 | 250-375 | 0.010-0.015 |
| Marine atmosphere | 150-200 | 0.006-0.008 | 200-250 | 0.008-0.010 | 250-300 | 0.010-0.012 | 250-375 | 0.010-0.015 |
| Freshwater immersion | 150-200 | 0.006-0.008 | 200-250 | 0.008-0.010 | 250-300 | 0.010-0.012 | . . . | . . . |
| Saltwater immersion | 200-250 | 0.008-0.010 | 250-300 | 0.010-0.012 | 300-350 | 0.012-0.014 | . . . | . . . |
| High-temperature (100-540 °C, or 210-1000 °F) | 150-200 | 0.006-0.008 | 200-250 | 0.008-0.010 | 250-300 | 0.010-0.012 | . . . | . . . |
| Wear, abrasion, erosion, and impact (90/10 MMC preferred) | 150-200 | 0.006-0.008 | 250-300 | 0.010-0.012 | . . . | . . . | . . . | . . . |

(a) With exception of wear abrasion, erosion, and impact properties, data for aluminum and 90Al-10MMC thermal spray coatings are identical.

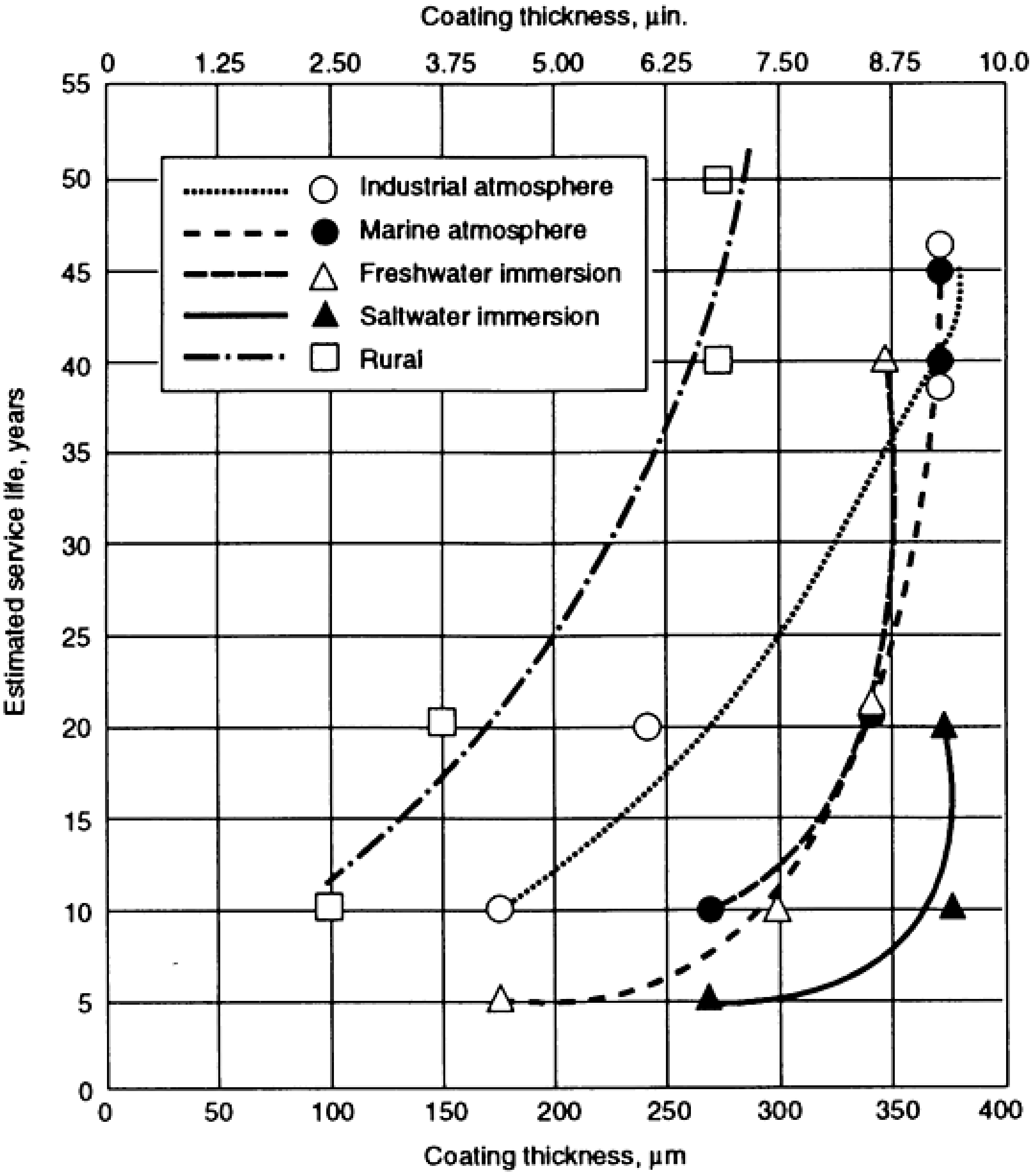

Fig. 22 Plot of service life versus coating thickness as a function of environment for an 85Zn-15Al thermal spray coating

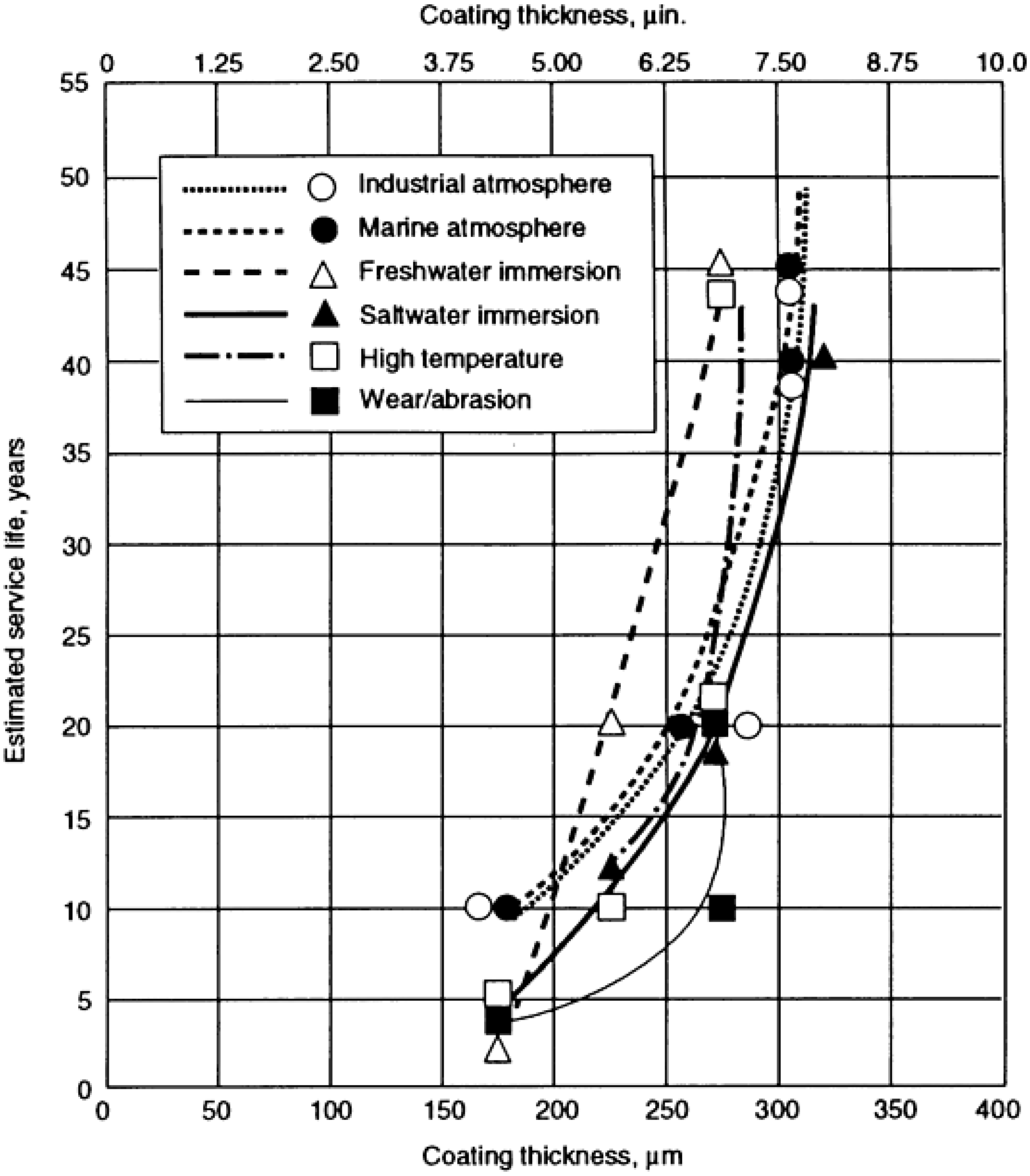

**Fig. 23 Plot of service life versus coating thickness as a function of environment for a 90Al-10MMC (vol%) thermal spray coating**

Coatings of aluminum, zinc, and their alloys and composites provide broad atmospheric protection. Aluminum and zinc are anodic to steel and protect the ferrous substrate in electrolytic solutions. When applied sufficiently thick to prevent through-porosity, they provide both barrier and cathodic protection. When applied too thinly or when cut through to expose the underlying steel, these coatings provide galvanic protection. Aluminum corrodes less rapidly than zinc in highly acidic conditions, while zinc performs better in alkaline conditions. Aluminum thermal spray coatings immediately oxidize to form a loosely adherent $Al_2O_3$ protective film that prevents further oxidation. Thus, there is no advantage to applying aluminum coatings in a thickness greater than that which prevents through-porosity (150 to 200 µm, or 0.006 to 0.008 in.) unless wear or abrasion resistance is required in addition to corrosion resistance. Aluminum thermal spray coatings have greater wear, abrasion, and erosion resistance than zinc coatings.

Zinc alloyed with aluminum forms an effective corrosion-resistant coating, combining the attributes of both elements. The greater electrochemical activity of zinc provides greater galvanic protection than aluminum. Aluminum, with its lower electrochemical activity and a loosely adherent aluminum oxide film, provides long-term protection even when the coating is porous and gives better wear, abrasion, and erosion resistance than zinc.

Aluminum and aluminum composite thermal spray coatings can be used where the temperature is greater than 200 °C (390 °F). Aluminum composite coatings are used when resistance to wear, abrasion, and erosion is required beyond that provided by aluminum and zinc.

**Wear coatings applied by thermal spraying** are used to resist abrasion, erosion, cavitation, and fretting, and to reduce friction. These coatings consist of a wide range of metals and their alloys, ceramics, cermets, carbides, and even low-friction plastics. Typical coating hardness ranges from 20 to 70 HRC. Table 35 lists friction and wear (hardfacing) applications for various thermal spray materials.

**Table 35 Thermal spray coatings used for hardfacing applications**

| Type of wear | Coating material | Coating process[(a)] | Applications |
|---|---|---|---|
| Adhesive wear | Aluminum bronze | OFW, EAW, OFP, PA, HVOF | Babbitt bearings, hydraulic press sleeves, thrust bearing shoes, piston guides, compressor crosshead slippers |
| | Soft bearing coatings: | | |
| | Tobin bronze | OFW, EAW | |
| | Babbitt | OFW, EAW, OFP | |
| | Tin | OFW,EAW, OFP, | |
| | Hard bearing coatings: | | |
| | Mo/Ni-Cr-B-Si blend | PA | Bumper crankshafts for punch press, sugar cane grinding roll journals, antigalling sleeves, rudder bearings, impeller shafts, pinion gear journals, piston ring (internal combustion); fuel pump rotors |
| | Molybdenum | OFW,EAW, PA | |
| | High-carbon steel | OFW, EAW | |
| | Alumina/titania | OFP, PA | |
| | Tungsten carbide | OFP, PA, HVOF | |
| | Co-Mo-Cr-Si | PA, HVOF | |
| | Fe-Mo-C | PA | |

| | | | |
|---|---|---|---|
| Abrasive wear | Aluminum oxide | PA | Slush-pump piston rods, polish rod liners, and sucker rod couplings (oil industry); concrete mixer screw conveyors; grinding hammers (tobacco industry); core mandrels (dry-cell batteries); buffing and polishing fixtures; fuel-rod mandrels |
| | Chromium oxide | PA | |
| | Tungsten carbide | PA, HVOF | |
| | Chromium carbide | PA, HVOF | |
| | Ni-Cr-B-SiC/WC (fused) | OFP, HVOF | |
| | Ni-Cr-B-SiC (fused) | OFP, HVOF | |
| | Ni-Cr-B-SiC (unfused) | HVOF | |
| Surface fatigue wear | | | |
| Fretting: Intended motion applications | Molybdenum | OFW, PA | Servomotor shafts, lathe and grinder dead centers, cam followers, rocker arms, piston rings (internal combustion), cylinder liners |
| | Mo/Ni-Cr-B-SiC | PA | |
| | Co-Mo-Cr-Si | PA, HVOF | |
| Fretting: Small amplitude oscillatory displacement applications: | | | |
| Low temperature (<540 °C, or 1000 °F) | Aluminum bronze | OFW, EAW, PA, HVOF | Aircraft flap tracks (air-frame component); expansion joints and mid-span supports (jet engine components) |
| | Cu-Ni-In | PA, HVOF | |
| | Cu-Ni | PA, HVOF | |
| High temperature (>540 °C or 1000 °F) | Co-Cr-Ni-W | PA, HVOF | Compressor air seals, compressor stators, fan duct segments and stiffeners (all jet engine components) |
| | Chromium carbide | PA, HVOF | |
| Erosion | Chromium carbide | PA,HVOF | Exhaust fans, hydroelectric valves, cyclone dust collectors, dump valve plugs and seats, exhaust valve seats |

| | | | |
|---|---|---|---|
| | Tungsten carbide | PA, HVOF | |
| | WC/Ni-Cr-B-Si-C(fused) | OFP, HVOF | |
| | WC/Ni-Cr-B-SiC (unfused) | OFP, HVOF | |
| | Chromium oxide | PA | |
| Cavitation | Ni-Cr-B-SiC-Al-Mo | PA | Wear rings (hydraulic turbines), water turbine buckets, water turbine nozzles, diesel engine cylinder liners, pumps |
| | Ni-Al/Ni-Cr-B-SiC | PA | |
| | Type 316 stainless steel | PA | |
| | Ni-Cr-B-SiC (fused) | OFP, HVOF | |
| | Ni-Cr-B-SiC (unfused) | HVOF | |
| | Aluminum bronze | PA, HVOF | |
| | Cu-Ni | PA, HVOF | |

(a) OFW, oxyfuel wire spray; EAW, electric arc wire spray;OFP, oxyfuel powder spray; PA, plasma arc spray; HVOF, high-velocity oxyfuel powder spray

**Oxidation Protection.** Thermal spray coatings are extensively used by industry to protect steel components and structures from heat oxidation at surface temperatures to 1095 °C (2000 °F). By ensuring long-term protection, thermal spray coatings show real economic advantages during the service lives of such items. Coatings such as pure aluminum, aluminum-iron, nickel-chromium, and MCrAlY are particularly effective in protecting low-alloy and carbon steels.

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## Hardfacing

Hardfacing may be broadly defined as the application of a wear-resistant material, in depth, to the vulnerable (or worn) surfaces of a component by a weld overlay or thermal spray process. This discussion deals with the weld overlay materials used to resist wear; the thermal spray materials are covered in the previous section in this article. More detailed information on hardfacing process and alloy selection can be found in Ref 47 and 53.

**Welding processes** used to apply hardfacing materials range from the traditional (for example, oxyacetylene torch) to the new and sophisticated (for example, plasma-transferred arc, PTA, and laser methods). To accommodate these different overlay processes, the hardfacing materials are available in a variety of forms. The most popular processes, and the forms most commonly associated with each process, are listed in Table 36.

**Table 36 Characteristics of welding processes used in hardfacing**

| Welding process | Mode of application | Form of hardfacing alloy | Weld-metal dilution, % | Deposition | | Minimum thickness[(a)] | | Deposit efficiency, % |
|---|---|---|---|---|---|---|---|---|
| | | | | kg/h | lb/h | mm | in. | |
| OAW | Manual | Bare cast rod, tubular rod | 1-10 | 0.5-2 | 1-4 | 0.8 | $\frac{1}{32}$ | 100 |
| | Manual | Powder | 1-10 | 0.5-2 | 1-4 | 0.8 | $\frac{1}{32}$ | 85-95 |
| | Automatic | Extra-long bare cast rod, tubular wire | 1-10 | 0.5-7 | 1-15 | 0.8 | $\frac{1}{32}$ | 100 |
| SMAW | Manual | Flux-covered cast rod, flux-covered tubular rod | 10-20 | 0.5-5 | 1-12 | 3.2 | $\frac{1}{8}$ | 65 |
| Open arc | Semiautomatic | Alloy-cored tubular wire | 15-40 | 2-11 | 5-25 | 3.2 | $\frac{1}{8}$ | 80-85 |
| | Automatic | Alloy-cored tubular wire | 15-40 | 2-11 | 5-25 | 3.2 | $\frac{1}{8}$ | 80-85 |
| GTAW | Manual | Bare cast, tubular rod | 10-20 | 0.5-3 | 1-6 | 2.4 | $\frac{1}{32}$ | 98-100 |
| | Automatic | Various forms(b) | 10-20 | 0.5-5 | 1-10 | 2.4 | $\frac{1}{32}$ | 98-100 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| SAW | Automatic, single wire | Bare tubular wire | 30-60 | 5-11 | 10-25 | 3.2 | $\frac{1}{8}$ | 95 |
| | Automatic, multiwire | Bare tubular wire | 15-25 | 11-27 | 25-60 | 4.8 | $\frac{3}{16}$ | 95 |
| | Automatic, series arc | Bare tubular wire | 10-25 | 11-16 | 25-35 | 4.8 | $\frac{3}{16}$ | 95 |
| PAW | Automatic | Powder(c) | 5-15 | 0.5-7 | 1-15 | 0.8 | $\frac{1}{32}$ | 85-95 |
| | Manual | Bare cast rod, tubular rod | 5-15 | 0.5-4 | 1-8 | 2.4 | $\frac{3}{32}$ | 98-100 |
| | Automatic | Various forms(b) | 5-15 | 0.5-4 | 1-8 | 2.4 | $\frac{3}{32}$ | 98-100 |
| GMAW | Semiautomatic | Alloy-cored tubular wire | 10-40 | 0.9-5 | 2-12 | 1.6 | $\frac{1}{16}$ | 90-95 |
| | Automatic | Alloy-cored tubular wire | 10-40 | 0.9-5 | 2-12 | 1.6 | $\frac{1}{16}$ | 90-95 |
| Laser | Automatic | Powder | 1-10 | (d) | (d) | 0.13 | 0.005 | 85-95 |

(a) Recommended minimum thickness of deposit.

(b) Bare tubular wire; extra-long (2.4 m, or 8 ft) bare cast rod; tungsten carbide powder with cast rod or bare tubular wire.

(c) With or without tungsten carbide granules.

(d) Varies widely depending on powder feed rate and laser input power

**Hardfacing materials** fall into six categories:

- Build-up alloys
- Metal-to-metal wear alloys
- Metal-to-earth abrasion alloys
- Tungsten carbides (for extreme earth sliding and cutting wear)
- Nonferrous alloys

- Stainless steels

The build-up alloys are not designed to resist wear but to return a worn part back to, or near, its original dimensions and to provide adequate support for subsequent layers of true hardfacing materials. However, these alloys are sometimes used as wear-resistant materials under mild wear conditions.

The build-up alloys fall into two categories: alloy steels and austenitic manganese steels. The alloy steel build-up materials are used with carbon steel and alloy steel substrates; the austenitic manganese steels are used for the joining, repair, and/or protection of manganese steel components. Specific build-up alloy compositions and properties are given in Table 37. Typical examples of applications where build-up alloys are used include tractor rails, railroad rail ends, steel mill table rolls, and large slow-speed gear teeth.

**Table 37 Composition, hardness, and abrasion data for build-up alloys and metal-to-metal wear alloys**

| **Alloy** | **Composition, wt%** | | | | | | | **Hardness, HRC** | **Abrasion, volume loss** | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | **Low-stress(c)** | | **High-stress(d)** | |
| | **Fe** | **Cr** | **C** | **Si** | **Mn** | **Mo** | **Ni** | | **mm$^3$** | **in.$^3$ × 10$^{-3}$** | **mm$^3$** | **in.$^3$ × 10$^{-3}$** |
| **Build-up weld overlay** | | | | | | | | | | | | |
| EFe1(a) | bal | 2 | 0.1 | 1.0 | 1 | 1.5 | . . . | 37 | 88 | 5.4 | 49 | 3.0 |
| EFeMn-C(a) | bal | 4 | 0.8 | 1.3 | 14 | . . . | 4 | 18 | 65 | 4.0 | 57 | 3.5 |
| EFeMn-Cr(a) | bal | 15 | 0.5 | 1.3 | 15 | 2.0 | 1 | 24 | 93 | 5.7 | 46 | 2.8 |
| **Metal-to-metal weld overlay** | | | | | | | | | | | | |
| EFe2(a) | bal | 3 | 0.2 | 1.0 | 1 | 1.0 | 1 | 48 | 54 | 3.3 | 66 | 4.0 |
| EFe3(b) | bal | 6 | 0.7 | 1.0 | 1 | 1.0 | . . . | 59 | 60 | 3.7 | 68 | 4.1 |

(a) Two-layer SMA deposit process.

(b) Two-layer SAW deposit process.

(c) Dry sand/rubber wheel test (ASTM G 65, Procedure B): Load 13.6 kg (30 lb); 200 rev.

(d) Slurry/steel wheel test (ASTM B 611, modified): load 22.7 kg (50 lb); 250 rev

Alloys in the metal-to-metal category (commonly referred to as machinery hardfacing alloys) are martensitic, air-hardening steels that can be applied several layers thick and can be finish machined (although with some difficulty) if adequate equipment is used. They are recommended for wearing, industrial, heavy-duty, nonlubricated parts. These materials are also sometimes referred to as "super build-up" alloys. If a machined finish is required, three layers are generally applied, with the assumption that the top layer will be removed during machining. A single layer is usually adequate because of the effects of substrate/overlay intermixing (dilution).

Typical compositions and properties of metal-to-metal wear alloys are listed in Table 37. In hostile environments, a higher chromium content is beneficial. ER420 (American Welding Society, AWS, classification), and modified versions containing nickel, molybdenum, and niobium (or vanadium), are therefore the natural choice when high temperatures and mildly corrosive environments are encountered. For applications using steel mill hot-work rolls (which demand considerable hot hardness, resistance to oxidation, and resistance to thermal fatigue) both ER420 and EFe3 have been found suitable. Other applications for the metal-to-metal wear alloys in Table 37 include tractor rollers and crane wheels (EFe2), pincer guide shoes (EFe3), and blast furnace bells (ER420).

Most of the materials in the metal-to-earth, carbide, and nonferrous alloy categories consist of hard particles within a metallic matrix, and, for many, it is the hard constituent that provides resistance to wear. The primary function of the metal-to-earth abrasion alloys and tungsten carbides is abrasion resistance. The metal-to-earth alloys are high-chromium white irons in which chromium carbides are formed during alloy solidification. The tungsten carbides are actually composite materials, and their use involves the transfer of discrete tungsten carbide particles (which in the welding consumable forms are encased in a steel tube) across the welding arc and into the molten weld pool, where they are subsequently "frozen" into the overlay structure by the matrix formed from the melting of the steel tube. Typical applications for these material types include shovel teeth, rock crusher parts, plowshares, and auger flights.

The nonferrous hardfacing alloys are used in environments that are too aggressive for the ferrous hardfacing alloys or where high resistance to a specific type of wear (other than abrasion) is required. They are classified as follows:

- Cobalt-base/carbide type
- Cobalt- and nickel-base/Laves type
- Nickel-base/boride type
- Bronze type

Whereas the ferrous hardfacing alloys and tungsten carbide composites find extensive use in agriculture, mining, construction, and the steel industry, the nonferrous alloys are typically used in the chemical processing, power, automotive, and oil industries, all of which require resistance to a hostile environment in addition to resistance to wear. The cobalt-base alloys are especially resistant to deformation and chemical attack at high temperatures (500 °C $< T \leq$ 900 °C, or 930 °F $< T \leq$ 1650 °F) and are used to protect dies and guide rolls in the steel industry. Other common applications of the nonferrous hardfacing alloys include valve seating surfaces (both control valves and diesel exhaust valves), pump parts, extrusion screw flights, rock bit bearings, marine bearings, and glass molding hardware.

The stainless steel weld overlays include both cobalt-free and cobalt-containing austenitic stainless steels. The cobalt-free grades, which contain nominally 0.8% C, 25% Cr, 4.5% Mn, 3.0% Si, 7.0% Ni, 2.0% Mo, and 0.1% N, have been developed to replace cobalt-base hardfacing alloys in nuclear power plant applications (valve overlays). The cobalt-containing grades, which contain nominally 0.2% C, 17% Cr, 9.5% Mn, 2.5% Si, 9% Co, and 0.2% N, have been developed for the repair of the cavitation erosion damage of turbines used in hydroelectric power plants.

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## Vapor-Deposited Coatings

Vapor-deposited coatings are sometimes used for the protection of steel, although the cost of such coatings can be prohibitive. In vapor deposition, whether it be physical vapor deposition (PVD) or chemical vapor deposition (CVD), the coating material is transported to the substrate in the form of individual atoms or molecules. A wide range of coating materials can be applied by vapor deposition. If applied to a sufficient thickness, the coating is essentially pore free and dense, thus providing excellent barrier protection. Processing details for various PVD/CVD coating methods can be found in the articles contained in the Section entitled "Vacuum and Controlled-Atmosphere Coating and Surface Modification Processes" in this Volume.

Ion plating of aluminum coatings on steel is used by the aircraft industry to protect high-strength steel components, such as landing gear, and as a fastener coating to reduce the galvanic effects of steel fasteners inserted in an aluminum structure. Ion plating has several advantages over other aluminum coating processes. The aluminum deposit is very adherent and passes the bend-to-break test. The deposit does not affect the mechanical properties of the substrate and can be applied with precise thickness control on a wide range of shapes. Both the coating and the coating process are nontoxic and do not contribute to pollution. Because of these advantages, ion plating of aluminum can be used in a wide range of applications and is particularly effective as a replacement for cadmium coatings, which can cause hydrogen embrittlement of high-strength steels. Vapor deposition of aluminum does not produce hydrogen; therefore, it does not cause embrittlement. Vapor-deposited aluminum protects against stress-corrosion cracking (SCC) and has a temperature limit of 495 °C (925 °F). It is less expensive than most other barrier coatings. Vapor deposition is also replacing hot dipping of aluminum on steel in some applications. During immersion in hot dipping, a brittle intermetallic compound layer of iron-aluminum is formed; this limits the formability of the steel. In addition, the coating contains iron impurities, which may be a severe shortcoming in highly corrosive environments (Ref 58).

Another important application area for vapor-deposited coatings on ferrous alloys is the use of PVD coatings to enhance the service life of high-speed tool steels. Examples of increased tool life obtained when using TiN and/or TiC PVD coated tools are described in the article "Surface Engineering of Specialty Steels" in this Volume.

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## Surface Modification

Surface modification processes, which involve altering the surface composition or structure of a material by the use of high-energy or particle beams, include ion implantation and laser surface processing. Although used far less on steels than the coating processes described previously in this article, surface modification techniques can significantly improve the wear and corrosion resistance of steel substrates.

### *Ion Implantation*

Ion implantation is the process of modifying the physical or chemical properties of the near surface of a solid by embedding appropriate atoms into it from a beam of ionized particles. The use of accelerated electron beams can produce penetration into a substrate surface on the order of 0.1 to 0.2 μm (1000 to 2000 Å) at 100 kV, and with higher accelerating voltages the potential for depth of penetration is increased. Surfaces may be treated by ion implantation to produce an effective alloyed surface layer where the composition varies as a function of depth.

Although virtually any element in the periodic table can be injected into near-surface regions of a solid using ion implantation, the ions that improve the properties of steels include:

- Adhesive and abrasive wear: Ni, Ti + C, Y, and Ta + C
- Fatigue wear: B, N, and Ti
- Corrosion and oxidation wear: Cr, Ta, and Y
- Friction: Ti, Ti + C, Ag, Sn, and Au

The most common use of ion implantation for improving the properties of ferrous alloys involves tool steels used in metalworking and machining applications (see the article "Surface Engineering of Specialty Steels" in this Volume). Other end-use applications of ion implantation include improved wear, corrosion, and rolling contact fatigue in bearing alloys such as type 440C stainless steel and 52100 bearing steel (Ref 59, 60).

### Laser Surface Processing

Lasers with continuous outputs of 0.5 to 10 kW can be used to modify the metallurgical structure of a surface and to tailor the surface properties without adversely affecting the bulk properties. Surface modification of steels via lasers can take the following four forms:

- Laser transformation hardening
- Laser surface melting
- Laser surface alloying
- Laser cladding (hardfacing)

Figure 24 shows typical ranges of conditions for various processes. The laser power, power density, and interaction time are the primary variables. Other variables, such as the composition of the atmosphere during treatment or the rate of material addition, are determined by the details of the processing--for example, the necessity of shielding against oxidation and the desired thickness, composition, and structure of the surface layer.

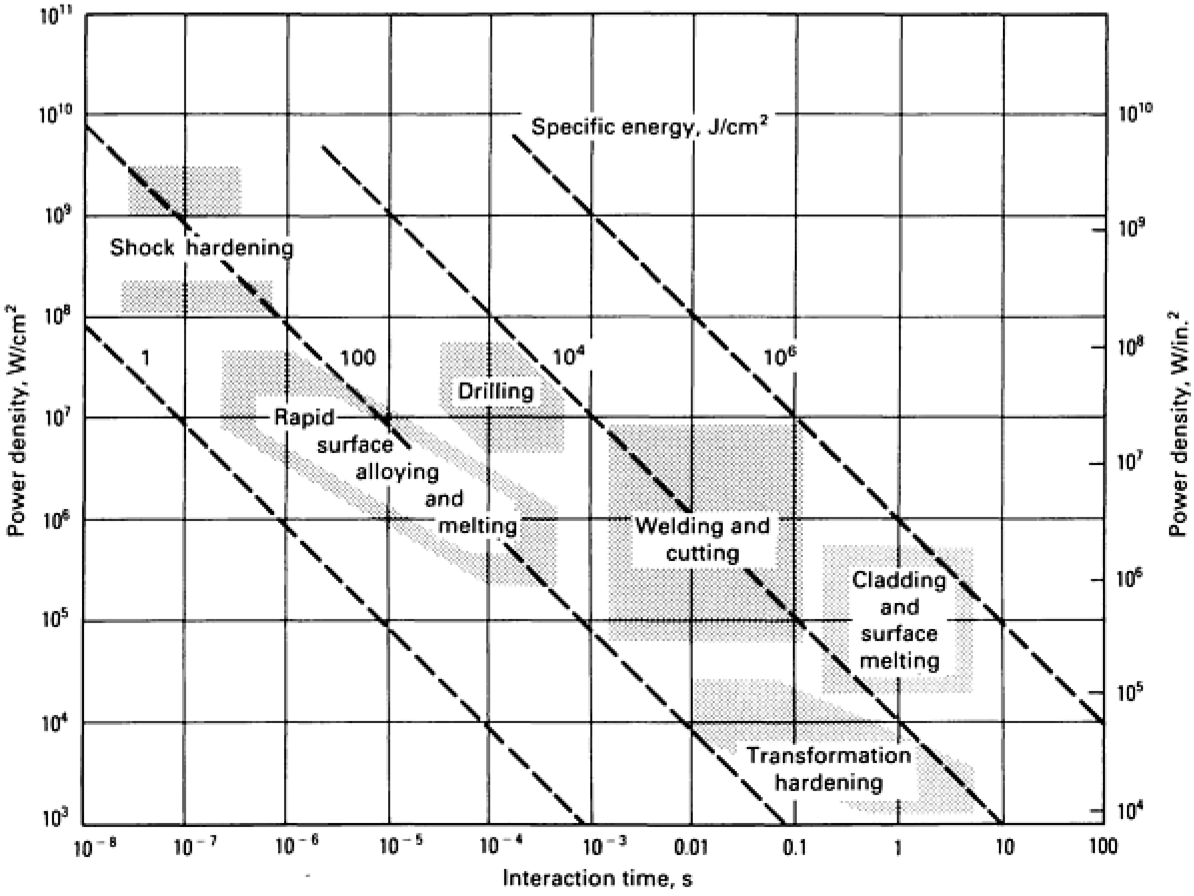

**Fig. 24 Interaction times and power densities necessary for various laser surface modification processes**

The laser beam modified layer can range in thickness from 0.01 to 5 mm (0.4 to 200 mils), depending on the processing variables, although thicknesses of 0.05 to 1 mm (2 to 40 mils) are more common. The longer the interaction time of the laser beam with the material, the deeper the processed layer will be. Of the processes shown in Fig. 24, the area labeled

"Cladding and surface melting" delineates process parameters that typically affect the material to depths from 0.5 to 5 mm (20 to 200 mils) and result in metallurgical structures similar to welded structures. The parameters designated "Rapid surface alloying and melting" affect a surface layer only 0.02 to 0.6 mm (0.8 to 24 mils) thick, but result in quench rates to $10^7$ K/s and therefore allow for the production of novel metallurgical structures and alloys. Because laser transformation hardening is the most commercially viable (with regard to steels) of the laser processing methods listed above, it will be described further below. Additional information on laser surface processing can be found in Ref 61. Laser cladding, or laser hardfacing, is also described in Ref 53.

**Laser surface heat treatment** is widely used to harden localized areas of steel machine components such as gears and bearings. The heat generated by the absorption of the laser light is controlled to prevent melting, and therefore is used to selectively austenitize local surface regions which transform to martensite as a result of rapid cooling by the conduction of heat into the bulk of the workpiece. This process is referred to as laser transformation hardening to differentiate it from laser surface melting and alloying phenomena (Fig. 24). There is no chemistry change produced by laser surface heat treating of steels.

Laser heat treatment produces thin surface zones which are heated and cooled very rapidly, resulting in very fine martensitic microstructures, even in steels with relatively low hardenability. High hardness and good wear resistance with less distortion result from this process.

Steels which have been successfully laser surface hardened include plain carbon steels (1040, 1045, 1050, 1070) and alloy steels (4140, 4340, 52100) (Ref 62, 63). Typical case depths for steels range from 0.75 to 1.3 mm (0.030 to 0.050 in.) depending on the laser power range (Fig. 25). Hardness values as high as 60 HRC are routinely achieved using laser surface hardening.

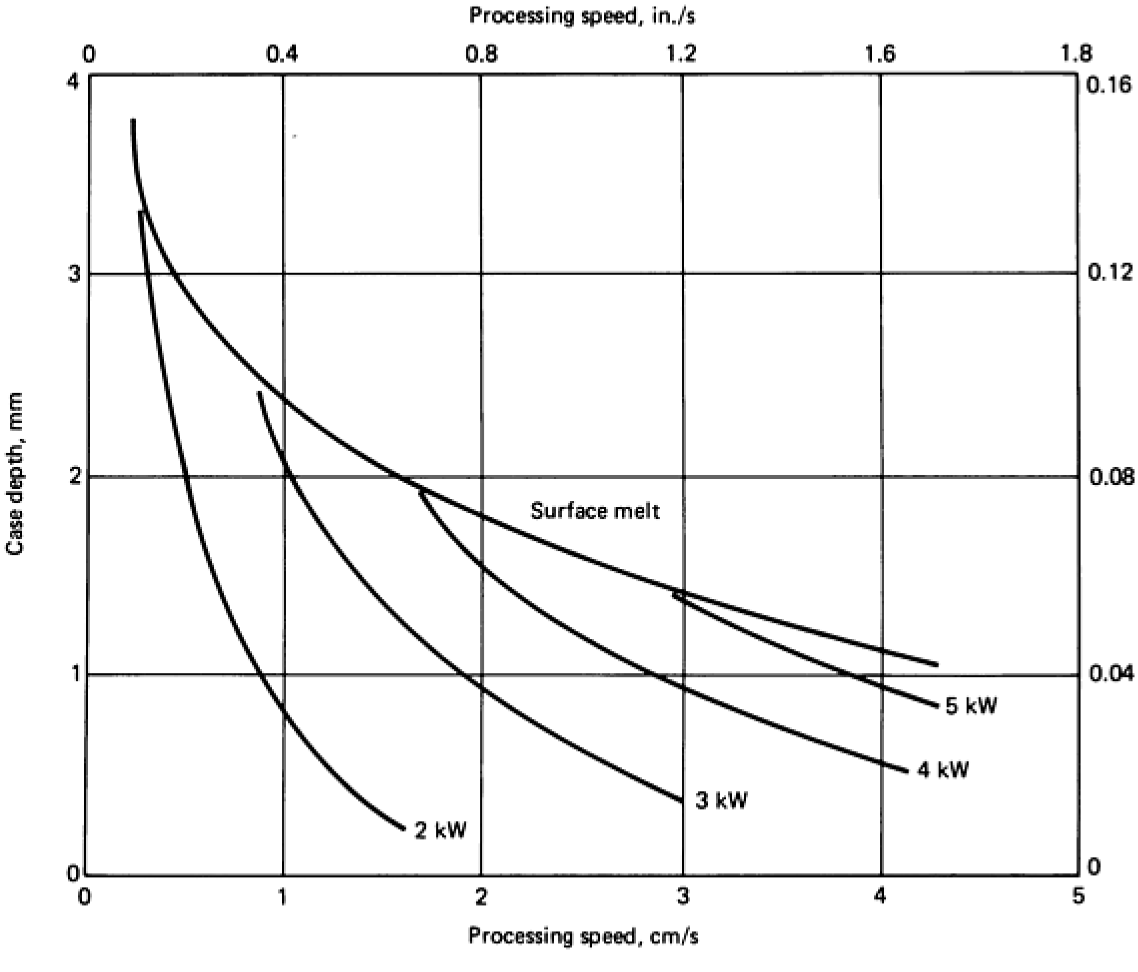

**Fig. 25 Effect of laser processing speed and power output on case depth thickness of laser hardened 1078 carbon steel**

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## Surface Hardening (Ref 64)

Surface hardening is used to extend the versatility of certain steels by producing combinations of properties not readily attainable in other ways. For many applications, wear and the most severe stresses act only on the surface of a part. Therefore, the part may be fabricated from a formable low- or medium-carbon steel, and is surface hardened by a final heat treatment after all other processing has been accomplished. Surface hardening also reduces distortion and eliminates cracking that might accompany through hardening, especially in large sections. While an extensive review is beyond the scope of this article, two major approaches to surface hardening will be described below. One approach does not change composition and consists of hardening the surface by flame, induction, laser, or electron beam heating. The other approach changes surface composition and includes the applications of such diffusion techniques as carburizing, nitriding, and carbonitriding. Table 38 compares the relative benefits of the five most common surface hardening processes. More detailed information on surface hardening of steels can be found in *Heat Treating,* Volume 4 of the *ASM Handbook.*

**Table 38 Relative benefits of five common surface-hardening processes**

| **Process** | **Benefits** |
|---|---|
| Carburizing | Hard, highly wear-resistant surface (medium case depth); excellent capacity for contact load; good bending fatigue strength; good resistance to seizure; excellent freedom from quench cracking; low-to-medium-cost steels required; high capital investment required |
| Carbonitriding | Hard, highly wear-resistant surface (shallow case depths); fair capacity for contact load; good bending fatigue strength; good resistance to seizure; good dimensional control possible; excellent freedom from quench cracking; low-cost steels usually satisfactory; medium capital investment required |
| Nitriding | Hard, highly wear-resistant surface (shallow case depths); fair capacity for contact load; good bending fatigue strength; excellent resistance to seizure; excellent dimensional control possible; good freedom from quench cracking (during pretreatment); medium-to-high-cost steels required; medium capital investment required |
| Induction hardening | Hard, highly wear-resistant surface (deep case depths); good capacity for contact load; good bending fatigue strength; fair resistance to seizure; fair dimensional control possible; fair freedom from quench cracking; low-cost steels usually satisfactory; medium capital investment required |
| Flame hardening | Hard, highly wear-resistant surface (deep case depths); good capacity for contact load; good bending fatigue strength; fair resistance to seizure; fair dimensional control possible; fair freedom from quench cracking; low-cost steels usually satisfactory; low capital investment required |

### *Flame, Induction, and High-Energy Beam Methods*

**Flame hardening** consists of austenitizing the surface of a steel by heating with an oxyacetylene or oxyhydrogen torch and immediately quenching with water. The result is a hard surface layer of martensite over a softer interior core with a ferrite-pearlite structure. There is no change in composition, and therefore the flame-hardened steel must have adequate carbon content for the desired surface hardness. The rate of heating and the conduction of heat into the interior appear to be more important in establishing case depth than the use of a steel of high hardenability.

Flame-heating equipment may be a single torch with a specially designed head or an elaborate apparatus that automatically indexes, heats, and quenches parts. Large parts such as gears and machine tool ways, with sizes or shapes that would make furnace heat treatment impractical, are easily flame hardened. With improvements in gas-mixing equipment, infrared temperature measurement and control, and burner design, flame hardening has been accepted as a reliable heat-treating process that is adaptable to general or localized surface hardening for small or medium-to-high production requirements.

**Induction heating** is an extremely versatile heating method that can perform uniform surface hardening, localized surface hardening, through hardening, and tempering of hardened pieces. Heating is accomplished by placing a steel part in the magnetic field generated by high-frequency alternating current passing through an inductor, usually a water-cooled copper coil. The depth of heating produced by induction is related to the frequency of the alternating current: The higher the frequency, the thinner or more shallow the heating. Therefore, deeper case depths and even through hardening are produced by using lower frequencies. The electrical considerations involve the phenomena of hysteresis and eddy currents. Because secondary and radiant heat are eliminated, the process is suited for production line areas.

**High-energy beam methods** for surface hardening include laser surface transformation hardening described earlier and electron beam (EB) hardening. Electron beam hardening, like laser treatment, is used to harden the surfaces of steels. The EB heat-treating process uses a concentrated beam of high-velocity electrons as an energy source to heat selected surface areas of ferrous parts. Electrons are accelerated and are formed into a directed beam by an electron beam gun. After exiting the gun, the beam passes through a focus coil, which precisely controls beam density levels (spot size) at the workpiece surface and then passes through a deflection coil. To produce an electron beam, a high vacuum of $10^{-5}$ torr ($1.3 \times 10^{-3}$ Pa) is needed in the region where the electrons are emitted and accelerated. This vacuum environment protects the emitter from oxidizing and avoids scattering of the electrons while they are still traveling at a relatively low velocity.

Like laser beam hardening, the EB process eliminates the need for quenchants but requires a sufficient workpiece mass to permit self-quenching. A mass of up to eight times that of the volume to be EB hardened is required around and beneath the heated surfaces.

### *Diffusion Methods*

As previously mentioned, surface hardening by diffusion involves the chemical modification of a surface. The basic process used is thermochemical because some heat is needed to enhance the diffusion of hardening species into the surface and subsurface regions of a part.

Methods of hardening by diffusion include several variations of hardening species (such as carbon or nitrogen) and of the process method used to handle and transport the hardening species to the surface of the part. Process methods for exposure involve the handling of hardening species in forms such as gas, liquid, or ions. These process variations naturally produce differences in typical case depth and hardness. Table 39 compares the characteristics of various diffusion treatments.

**Table 39 Typical characteristics of diffusion treatments**

| **Process** | **Nature of case** | **Process temperature, °C ( °F)** | **Case hardness, Typical case depth** | **HRC** | **Typical base metals** | **Process characteristics** |
|---|---|---|---|---|---|---|
| **Carburizing** | | | | | | |
| Pack | Diffused carbon | 815-1090 | 125 μm-1.5 mm (5-60 | 50- | Low-carbon steels, low- | Low equipment costs, difficult to |

| | | | | | | |
|---|---|---|---|---|---|---|
| | | (1500-2000) | mils) | 63(a) | carbon alloy steels | control case depth accurately |
| Gas | Diffused carbon | 815-980 (1500-1800) | 75 µm-1.5 mm (3-60 mils) | 50-63(a) | Low-carbon steels, low-carbon alloy steels | Good control of case depth, suitable for continuous operation, good gas controls required, can be dangerous |
| Liquid | Diffused carbon and possibly nitrogen | 815-980 (1500-1800) | 50 µm-1.5 mm (2-60 mils) | 50-65(a) | Low-carbon steels, low-carbon alloy steels | Faster than pack and gas processes, can pose salt disposal problem, salt baths require frequent maintenance |
| Vacuum | Diffused carbon | 815-1090 (1500-2000) | 75 µm-1.5 mm (3-60 mils) | 50-63(a) | Low-carbon steels, low-carbon alloy steels | Excellent process control, bright parts, faster than gas carburizing, high equipment costs |
| **Nitriding** | | | | | | |
| Gas | Diffused nitrogen, nitrogen compounds | 480-590 (900-1100) | 125 µm-0.75 mm (5-30 mils) | 50-70 | Alloy steels, nitriding steels, stainless steels | Hardest cases from nitriding steels, quenching not required, low distortion, process is slow, is usually a batch process |
| Salt | Diffused nitrogen, nitrogen compounds | 510-565 (950-1050) | 2.5 µm-0.75 mm (0.1-30 mils) | 50-70 | Most ferrous metals including cast irons | Usually used for thin hard cases <25 µm (1 mil), no white layer, most are proprietary processes |
| Ion | Diffused nitrogen, nitrogen compounds | 340-565 (650-1050) | 75 µm-0.75 mm (3-30 mils) | 50-70 | Alloy steels, nitriding steels, stainless steels | Faster than gas nitriding, no white layer, high equipment costs, close case control |
| **Carbonitriding** | | | | | | |
| Gas | Diffused carbon and nitrogen | 760-870 (1400-1600) | 75 µm-0.75 mm (3-30 mils) | 50-65(a) | Low-carbon steels, low-carbon alloy steels, stainless steel | Lower temperature than carburizing (less distortion), slightly harder case than carburizing, gas control critical |
| Liquid (cyaniding) | Diffused carbon and nitrogen | 760-870 (1400-1600) | 2.5-125 µm (0.1-5 mils) | 50-65(a) | Low-carbon steels | Good for thin cases on noncritical parts, batch process, salt disposal problems |
| Ferritic nitrocarburizing | Diffused carbon and nitrogen | 480-590 (900-1090) | 2.5-25 µm (0.1-1 mil) | 40-60(a) | Low-carbon steels | Low-distortion process for thin case on low-carbon steel, most processes are proprietary |

Source: Ref 64

(a) Requires quench from austenitizing temperature.

**Carburizing** is the addition of carbon to the surface of low-carbon steels at temperatures (generally between 850 and 950 °C, or 1560 and 1740 °F) at which austenite, with its high solubility for carbon, is the stable crystal structure. Hardening is accomplished when the high-carbon surface layer is quenched to form martensite so that a high-carbon martensite case with good wear and fatigue resistance is superimposed on a tough, low-carbon steel core. Carburizing steels for case hardening usually have base-carbon contents of about 0.2%, with the carbon content of the carburized layer generally being controlled at between 0.8 and 1% C.

Carburizing methods include:

- Gas carburizing
- Vacuum carburizing
- Plasma carburizing
- Salt bath carburizing
- Pack carburizing

These methods introduce carbon by the use of gas (atmospheric-gas, plasma, and vacuum carburizing), liquids (salt bath carburizing), or solid compounds (pack carburizing). All of these methods have advantages and limitations, but gas carburizing is used most often for large-scale production because it can be accurately controlled and involves a minimum of special handling.

**Nitriding** is a surface-hardening heat treatment that introduces nitrogen into the surface of steel at a temperature range of 500 to 550 °C (930 to 1020 °F) while it is in the ferritic condition. Thus, nitriding is similar to carburizing in that surface composition is altered but different in that nitrogen is added into ferrite instead of austenite. Because nitriding does not involve heating into the austenite phase field and a subsequent quench to form martensite, nitriding can be accomplished with a minimum of distortion and with excellent dimensional control. Process methods for nitriding include gas, liquid (salt bath), and plasma (ion) nitriding.

Nitrided steels are generally medium-carbon (quenched and tempered) steels that contain strong nitride-forming elements such as aluminum, chromium, vanadium, and molybdenum. The most significant hardening is achieved with a class of alloy steels (nitralloy type) that contain about 1% Al. When these steels are nitrided, the aluminum forms AlN particles, which strain the ferrite lattice and create strengthening dislocations. Titanium and chromium are also used to enhance case hardness, although case depth decreases as alloy content increases. The microstructure also influences nitridability because ferrite favors the diffusion of nitrogen and because a low carbide content favors both diffusion and case hardness. Usually alloy steels in the heat-treated (quenched and tempered) state are used for nitriding.

**Carbonitriding** is a surface-hardening heat treatment that introduces carbon and nitrogen in the austenite of steel. This treatment is similar to carburizing in that the austenite composition is changed and high surface hardness is produced by quenching to form martensite. However, because nitrogen enhances hardenability, carbonitriding makes possible the use of low-carbon steel to achieve surface hardness equivalent to that of high-alloy carburized steel without the need for drastic quenching, resulting in less distortion and reducing the danger of cracking the work. To some extent, hardening is also dependent on nitride formation.

Although the process of carbonitriding can be performed with gas atmospheres or salt baths, the term carbonitriding often refers solely to treatment in a gas atmosphere. Basically, carbonitriding in a salt bath is the same as cyanide bath hardening. In both processes, nitrogen enhances hardenability and case hardness but inhibits the diffusion of carbon.

**Ferritic nitrocarburizing** involves the diffusion of carbon and nitrogen into the ferrite phase and the formation of a thin white layer of carbonitrides. The diffusion of nitrogen into the substrate is necessary for fatigue resistance. The case depths are thin (Table 39), but have a reduced tendency to spall, compared to the white layer formed during conventional nitriding. Ferritic nitrocarburizing, which is used to improve the anti-skuffing properties of steels, can be carried out by gas or plasma (ion) methods.

## Reference cited in this section

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# Surface Engineering of Stainless Steels

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## Introduction

STAINLESS STEELS are iron-base alloys that contain a minimum of approximately 11% Cr, the amount needed to prevent the formation of rust in unpolluted atmospheres (hence the designation "stainless"). Few stainless steels contain more than 30% Cr or less than 50% Fe. They achieve their stainless characteristics through the formation of an invisible and adherent chromium-rich oxide surface film. This oxide forms and heals itself in the presence of oxygen. Other elements added to improve particular characteristics include nickel, molybdenum, copper, titanium, aluminum, silicon, niobium, nitrogen, sulfur, and selenium. Carbon is normally present in amounts ranging from less than 0.03% to over 1.0% in certain martensitic grades.

Although stainless steel is naturally passivated by exposure to air and other oxidizers, additional surface treatments often are needed to prevent corrosion. Passivation, pickling, electropolishing, and, in some cases, mechanical cleaning are important surface treatments for the successful performance of stainless steel used for piping, pressure vessels, tanks, and machined parts in a wide variety of applications, including pulp mills, nuclear power plants, hospital sterilization systems, food processing equipment, biotechnology processing plants, breweries, electronic-chip washing facilities, swimming pool hardware, water treatment plants, and chemical process plants.

Following a brief overview of the various types of stainless steels, this article will describe the various cleaning, finishing, and coating processes associated with engineered stainless steel surfaces. Determining which treatment should be used for specific applications is sometimes confusing. A good place to start is with ASTM A 380 (Ref 1), which is an excellent resource document for the cleaning and descaling of stainless steel parts, equipment, and systems, although it does not cover electropolishing.

## Reference

1. "Standard Practice for Cleaning and Descaling Stainless Steel Parts, Equipment, and Systems," A 380, *Annual Book of ASTM Standards,* ASTM, 1988

## Designations for Stainless Steels

In the United States, wrought grades of stainless steels are generally designated by the American Iron and Steel Institute (AISI) numbering system, the Unified Numbering System (UNS), or by the proprietary name of the alloy. In addition, designation systems have been established by most of the major industrial nations. Of the two institutional numbering systems used in the U.S., AISI is the oldest and most widely used. Most of the grades have a three-digit designation; the 200 and 300 series are generally austenitic stainless steels, whereas the 400 series are either ferritic or martensitic. Some of the grades have a one- or two-letter suffix that indicates a particular modification of the composition.

The UNS system is a broader-based system that comprises a list of all metallic materials, including stainless steel. This system includes a considerably greater number of stainless steels than AISI, because it incorporates all of the more recently developed stainless steels. The UNS designation for a stainless steel consists of the letter S, followed by a five-digit number. For those alloys that have an AISI designation, the first three digits of the UNS designation usually correspond to an AISI number. When the last two digits are 00, the number designates a basic AISI grade. Modifications of the basic grades use two digits other than zeroes.

Table 1 provides the compositional limits for select stainless steels, listed by UNS and AISI type designations and separated into the basic families described below. Where AISI type designations are not available, common trade names are listed. These names, the third commonly used identification of stainless steels, have often become the popular means of identifying a particular alloy.

**Table 1 Composition of selected standard and special stainless steels**

| UNS designation | AISI type | Composition, wt% max | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | C | Mn | Si | P | S | Cr | Ni | Mo | N | Others |
| **Ferritic alloys** | | | | | | | | | | | |
| S40500 | 405 | 0.08 | 1.00 | 1.00 | 0.040 | 0.030 | 11.50-14.50 | . . . | . . . | . . . | 0.10-0.30 Al |
| S40900 | 409 | 0.08 | 1.00 | 1.00 | 0.045 | 0.045 | 10.50-11.75 | 0.50 | . . . | . . . | 6 × C-0.75 Ti |
| S43000 | 430 | 0.12 | 1.00 | 1.00 | 0.040 | 0.030 | 16.00-18.00 | . . . | . . . | . . . | . . . |
| S43020 | 430F | 0.12 | 1.25 | 1.00 | 0.060 | 0.15(a) | 16.00-18.00 | . . . | 0.60 | . . . | . . . |
| S43023 | 430FSe | 0.12 | 1.25 | 1.00 | 0.060 | 0.060 | 16.00-18.00 | . . . | . . . | . . . | 0.15 min Se |
| S43400 | 434 | 0.12 | 1.00 | 1.00 | 0.040 | 0.030 | 16.00-18.00 | . . . | 0.75-1.25 | . . . | . . . |
| S44200 | 442 | 0.20 | 1.00 | 1.00 | 0.040 | 0.030 | 18.00-23.00 | . . . | . . . | . . . | . . . |
| S44300 | 443(b) | 0.20 | 1.00 | 1.00 | 0.040 | 0.030 | 18.00-23.00 | 0.50 | . . . | . . . | 0.90-1.25 Cu |
| S44400 | 444(b) | 0.025 | 1.00 | 1.00 | 0.040 | 0.030 | 17.50-19.50 | 1.00 | 1.75-2.50 | 0.025 | [0.20 + 4 (C + N)]-0.80 Ti + Nb |
| S44600 | 446(b) | 0.20 | 1.50 | 1.00 | 0.040 | 0.030 | 23.00-27.00 | . . . | . . . | 0.25 | . . . |
| S18200 | 18-2FM(c) | 0.08 | 1.25-2.50 | 1.00 | 0.040 | 0.15(a) | 17.50-19.50 | . . . | 1.50-2.50 | . . . | . . . |
| **Martensitic alloys** | | | | | | | | | | | |
| S40300 | 403 | 0.15 | 1.00 | 0.50 | 0.040 | 0.030 | 11.50- | . . . | . . . | . . . | . . . |

| UNS designation | AISI type | Composition, wt% max | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | C | Mn | Si | P | S | Cr | Ni | Mo | N | Others |
| | | | | | | | 13.00 | | | | |
| S41000 | 410 | 0.15 | 1.00 | 1.00 | 0.040 | 0.030 | 11.50-13.00 | . . . | . . . | . . . | . . . |
| S41400 | 414 | 0.15 | 1.00 | 1.00 | 0.040 | 0.030 | 11.50-13.50 | 1.25-2.50 | . . . | . . . | . . . |
| S41600 | 416 | 0.15 | 1.25 | 1.00 | 0.060 | 0.15[(a)] | 12.00-14.00 | . . . | 0.60 | . . . | . . . |
| S41610 | 416 Plus X[(d)] | 0.15 | 1.50-2.50 | 1.00 | 0.060 | 0.15[(a)] | 12.00-14.00 | . . . | 0.60 | . . . | . . . |
| S41623 | 416Se | 0.15 | 1.25 | 1.00 | 0.060 | 0.060 | 12.00-14.00 | . . . | . . . | . . . | 0.15 min Se |
| S42000 | 420 | 0.15[(a)] | 1.00 | 1.00 | 0.040 | 0.030 | 12.00-14.00 | . . . | . . . | . . . | . . . |
| S42010 | TrimRite[(e)] | 0.15-0.30 | 1.00 | 1.00 | 0.040 | 0.030 | 13.50-15.00 | 0.25-1.00 | 0.40-1.00 | . . . | . . . |
| S42020 | 420F | 0.15[(a)] | 1.25 | 1.00 | 0.060 | 0.15[(a)] | 12.00-14.00 | . . . | 0.60 | . . . | . . . |
| S42023 | 420FSe[(b)] | 0.30-0.40 | 1.25 | 1.00 | 0.060 | 0.060 | 12.00-14.00 | . . . | 0.60 | . . . | 0.15 min Se; 0.60 Zr or Cu |
| S43100 | 431 | 0.20 | 1.00 | 1.00 | 0.040 | 0.030 | 15.00-17.00 | 1.25-2.50 | . . . | . . . | . . . |
| S44002 | 440A | 0.60-0.75 | 1.00 | 1.00 | 0.040 | 0.030 | 16.00-18.00 | . . . | 0.75 | . . . | . . . |
| S44003 | 440B | 0.75-0.95 | 1.00 | 1.00 | 0.040 | 0.030 | 16.00-18.00 | . . . | 0.75 | . . . | . . . |
| S44004 | 440C | 0.95-1.20 | 1.00 | 1.00 | 0.040 | 0.030 | 16.00-18.00 | . . . | 0.75 | . . . | . . . |
| S44020 | 440F[(b)] | 0.95-1.20 | 1.25 | 1.00 | 0.040 | 0.10-0.35 | 16.00-18.00 | 0.75 | 0.40-0.60 | 0.08 | . . . |

| UNS designation | AISI type | Composition, wt% max | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | C | Mn | Si | P | S | Cr | Ni | Mo | N | Others |
| S44023 | 440FSe[(b)] | 0.95-1.20 | 1.25 | 1.00 | 0.040 | 0.030 | 16.00-18.00 | 0.75 | 0.60 | 0.08 | 0.15 min Se |
| **Austenitic alloys** | | | | | | | | | | | |
| S20100 | 201 | 0.15 | 5.50-7.50 | 1.00 | 0.060 | 0.030 | 16.00-18.00 | 3.50-5.50 | . . . | 0.25 | . . . |
| S20161 | Gall-Tough[(e)] | 0.15 | 4.00-6.00 | 3.00-4.00 | 0.040 | 0.040 | 15.00-18.00 | 4.00-6.00 | . . . | 0.08-0.20 | . . . |
| S20300 | 203EZ[(f)] | 0.08 | 5.00-6.50 | 1.00 | 0.040 | 0.18-0.35 | 16.00-18.00 | 5.00-6.50 | 0.50 | . . . | 1.75-2.25 Cu |
| S20910 | 22-13-5[(c)] | 0.06 | 4.00-6.00 | 1.00 | 0.040 | 0.030 | 20.50-23.50 | 11.50-13.50 | 1.50-3.00 | 0.20-0.40 | 0.10-0.30 Nb; 0.10-0.30 V |
| S21000 | SCF19[(e)] | 0.10 | 4.00-7.00 | 0.60 | 0.030 | 0.030 | 18.00-23.00 | 16.00-20.00 | 4.00-6.00 | 0.15 | 2.00 Cu |
| S21300 | 15-15LC[(e)] | 0.25 | 15.00-18.00 | 1.00 | 0.050 | 0.050 | 16.00-21.00 | 3.00 | 0.50-3.00 | 0.20-0.80 | 0.50-2.00 Cu |
| S21800 | Nitronic 60[(g)] | 0.10 | 7.00-9.00 | 3.50-4.50 | 0.040 | 0.030 | 16.00-18.00 | 7.00-9.00 | . . . | 0.08-0.20 | . . . |
| S21904 | 21-6-9LC[(e)] | 0.04 | 8.00-10.00 | 1.00 | 0.060 | 0.030 | 19.00-21.50 | 5.50-7.50 | . . . | 0.15-0.40 | . . . |
| S24100 | 18-2Mn[(c)] | 0.15 | 11.00-14.00 | 1.00 | 0.060 | 0.030 | 16.50-19.50 | 0.50-2.50 | . . . | 0.20-0.45 | . . . |
| S28200 | 18-18 Plus[(e)] | 0.15 | 17.00-19.00 | 1.00 | 0.045 | 0.030 | 17.00-19.00 | . . . | 0.50-1.50 | 0.40-0.60 | 0.50-1.50 Cu |
| . . . | Nitronic 30[(g)] | 0.10 | 7.00-9.00 | 1.00 | . . . | . . . | 15.00-17.00 | 1.50-3.00 | . . . | 0.15-0.30 | 1.00 Cu |
| S30100 | 301 | 0.15 | 2.00 | 1.00 | 0.045 | 0.030 | 16.00-18.00 | 6.00-8.00 | . . . | . . . | . . . |
| S30200 | 302 | 0.15 | 2.00 | 1.00 | 0.045 | 0.030 | 17.00- | 8.00- | . . . | . . . | . . . |

| UNS designation | AISI type | Composition, wt% max | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | C | Mn | Si | P | S | Cr | Ni | Mo | N | Others |
| | | | | | | | 19.00 | 10.00 | | | |
| S30300 | 303 | 0.15 | 2.00 | 1.00 | 0.20 | 0.15(a) | 17.00-19.00 | 8.00-10.00 | 0.60 | . . . | . . . |
| S30310 | 303 Plus X(d) | 0.15 | 2.50-4.50 | 1.00 | 0.20 | 0.25(a) | 17.00-19.00 | 7.00-10.00 | 0.75 | . . . | . . . |
| S30323 | 303Se | 0.15 | 2.00 | 1.00 | 0.20 | 0.060 | 17.00-19.00 | 8.00-10.00 | . . . | . . . | 0.15 min Se |
| S30330 | 303 Cu(b) | 0.15 | 2.00 | 1.00 | 0.15 | 0.10(a) | 17.00-19.00 | 6.00-10.00 | . . . | . . . | 2.50-4.00 Cu; 0.10 Se |
| S30400 | 304 | 0.08 | 2.00 | 1.00 | 0.045 | 0.030 | 18.00-20.00 | 8.00-10.50 | . . . | . . . | . . . |
| S3043 | 304L | 0.03 | 2.00 | 1.00 | 0.045 | 0.030 | 18.00-20.00 | 8.00-12.00 | . . . | . . . | . . . |
| S30430 | 302 HQ(b) | 0.10 | 2.00 | 1.00 | 0.045 | 0.030 | 17.00-19.00 | 8.00-10.00 | . . . | . . . | 3.00-4.00 Cu |
| S30431 | 302 HQ-FM(e) | 0.06 | 2.00 | 1.00 | 0.040 | 0.14 | 16.00-19.00 | 9.00-11.00 | . . . | . . . | 1.30-2.40 Cu |
| S30452 | 304 HN(b) | 0.08 | 2.00 | 1.00 | 0.045 | 0.030 | 18.00-20.00 | 8.00-10.50 | . . . | 0.16-0.30 | . . . |
| S30500 | 305 | 0.12 | 2.00 | 1.00 | 0.045 | 0.030 | 17.00-19.00 | 10.00-13.00 | . . . | . . . | . . . |
| S30900 | 309 | 0.20 | 2.00 | 1.00 | 0.045 | 0.030 | 22.00-24.00 | 12.00-15.00 | . . . | . . . | . . . |
| S30908 | 309S | 0.08 | 2.00 | 1.00 | 0.045 | 0.030 | 22.00-24.00 | 12.00-15.00 | . . . | . . . | . . . |
| S31000 | 310 | 0.25 | 2.00 | 1.50 | 0.045 | 0.030 | 24.00-26.00 | 19.00-22.00 | . . . | . . . | . . . |
| S31008 | 310S | 0.08 | 2.00 | 1.50 | 0.045 | 0.030 | 24.00-26.00 | 19.00-22.00 | . . . | . . . | . . . |

| UNS designation | AISI type | Composition, wt% max | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | C | Mn | Si | P | S | Cr | Ni | Mo | N | Others |
| S31600 | 316 | 0.08 | 2.00 | 1.00 | 0.045 | 0.030 | 16.00-18.00 | 10.00-14.00 | 2.00-3.00 | . . . | . . . |
| S31603 | 316L | 0.030 | 2.00 | 1.00 | 0.045 | 0.030 | 16.00-18.00 | 10.00-14.00 | 2.00-3.00 | . . . | . . . |
| S31620 | 316F | 0.08 | 2.00 | 1.00 | 0.20 | 0.10(a) | 17.00-19.00 | 12.00-14.00 | 1.75-2.50 | . . . | . . . |
| S31700 | 317 | 0.08 | 2.00 | 1.00 | 0.045 | 0.30 | 18.00-20.00 | 11.00-15.00 | 3.00-4.00 | . . . | . . . |
| S31703 | 317L | 0.030 | 2.00 | 1.00 | 0.045 | 0.030 | 18.00-20.00 | 11.00-15.00 | 3.00-4.00 | . . . | . . . |
| S32100 | 321 | 0.08 | 2.00 | 1.00 | 0.045 | 0.030 | 17.00-19.00 | 9.00-12.00 | . . . | . . . | 5 × C min Ti |
| S34700 | 347 | 0.08 | 2.00 | 1.00 | 0.045 | 0.030 | 17.00-19.00 | 9.00-13.00 | . . . | . . . | 10 × C min Nb |
| S34720 | 347F(b) | 0.08 | 2.00 | 1.00 | 0.045 | 0.18-0.35 | 17.00-19.00 | 9.00-12.00 | . . . | . . . | 10 × C-1.10 Nb |
| S34723 | 347FSe(b) | 0.08 | 2.00 | 1.00 | 0.11-0.17 | 0.030 | 17.00-19.00 | 9.00-12.00 | . . . | . . . | 10 × C-1.10 Nb; 0.15-0.35 Se |
| S38400 | 384 | 0.08 | 2.00 | 1.00 | 0.045 | 0.030 | 15.00-17.00 | 17.00-19.00 | . . . | . . . | . . . |
| N08020 | 20Cb-3(e) | 0.07 | 2.00 | 1.00 | 0.045 | 0.035 | 19.00-21.00 | 32.00-38.00 | 2.00-3.00 | . . . | 8 × C-1.00 Nb; 3.00-4.00 Cu |
| **Duplex alloys** | | | | | | | | | | | |
| S31803 | 2205(c) | 0.030 | 2.00 | 1.00 | 0.030 | 0.020 | 21.0-23.0 | 4.50-6.50 | 2.50-3.50 | 0.08-0.20 | . . . |
| S32550 | Alloy 255(c) | 0.04 | 1.50 | 1.00 | 0.04 | 0.03 | 24.0-27.0 | 4.50-6.50 | 2.00-4.00 | 0.10-0.25 | 1.50-2.50 Cu |
| S32900 | 329 | 0.20 | 1.00 | 0.75 | 0.040 | 0.030 | 23.00- | 2.50- | 1.00- | . . . | . . . |

| **UNS designation** | **AISI type** | **Composition, wt% max** | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | **C** | **Mn** | **Si** | **P** | **S** | **Cr** | **Ni** | **Mo** | **N** | **Others** |
| | | | | | | | 28.00 | 5.00 | 2.00 | | |
| S32950 | 7-Mo Plus(e) | 0.03 | 2.00 | 0.60 | 0.035 | 0.010 | 26.0-29.0 | 3.50-5.20 | 1.00-2.50 | 0.15-0.35 | . . . |
| **Precipitation-hardenable alloys** | | | | | | | | | | | |
| S13800 | PH13-8 Mo(g) | 0.05 | 0.20 | 0.10 | 0.010 | 0.008 | 12.25-13.25 | 7.50-8.50 | 2.00-2.50 | 0.01 | 0.90-1.35 Al |
| S15500 | 15-5PH(g) | 0.07 | 1.00 | 1.00 | 0.040 | 0.030 | 14.00-15.50 | 3.50-5.50 | . . . | . . . | 0.15-0.45 Nb; 2.50-4.50 Cu |
| S15700 | 15-7PH(g) | 0.09 | 1.00 | 1.00 | 0.040 | 0.030 | 14.00-16.00 | 6.50-7.25 | 2.00-3.00 | . . . | 0.75-1.50 Al |
| S17400 | 17-4PH(g) | 0.07 | 1.00 | 1.00 | 0.040 | 0.030 | 15.50-17.50 | 3.00-5.00 | . . . | . . . | 0.15-0.45 Nb; 3.00-5.00 Cu |
| S17700 | PH 17-7(g) | 0.09 | 1.00 | 1.00 | 0.040 | 0.040 | 16.00-18.00 | 6.50-7.75 | . . . | . . . | 0.75-1.50 Al |
| S35000 | 633(b) | 0.07-0.11 | 0.50-1.25 | 0.50 | 0.040 | 0.030 | 16.00-17.00 | 4.00-5.00 | 2.50-3.25 | 0.07-0.13 | . . . |
| S35500 | 634(b) | 0.10-0.15 | 0.50-1.25 | 0.50 | 0.040 | 0.030 | 15.00-16.00 | 4.00-5.00 | 2.50-3.25 | 0.07-0.13 | . . . |
| S45000 | Custom 450(e) | 0.05 | 1.00 | 1.00 | 0.030 | 0.030 | 14.00-16.00 | 5.00-7.00 | 0.50-1.00 | . . . | 8 × C min; 1.25-1.75 Cu |
| S45500 | Custom 455(e) | 0.05 | 0.50 | 0.50 | 0.040 | 0.030 | 11.00-12.50 | 7.50-9.50 | 0.50 | . . . | 0.10-0.50 Nb; 1.50-2.50 Cu 0.80-1.40 Ti |
| S66286 | A286(c) | 0.08 | 2.00 | 1.00 | 0.040 | 0.030 | 13.50-16.00 | 24.0-27.0 | 1.00-1.50 | . . . | 0.35 Al; 0.0010-0.010 B 1.90-2.35 Ti; 0.10-0.50 V |

Note: All compositions include Fe as balance.

(a) Minimum, rather than maximum wt%.

(b) Designation resembles AISI type, but is not used in that system.

(c) Common trade name, rather than AISI type.

(d) Trade name of Crucible Inc.

(e) Trade name of Carpenter Technology Corporation.

(f) Trade name of Al-Tech Corp.

(g) Trade name of Armco Inc.

## Classification of Stainless Steels

Stainless steels can be divided into five families. Four are based on the characteristic crystallographic structure/microstructure of the alloys in the family: ferritic, martensitic, austenitic, or duplex (austenitic plus ferritic). The fifth family, the precipitation-hardenable alloys, is based on the type of heat treatment used, rather than microstructure.

**Ferritic stainless steels** are so named because their body-centered-cubic (bcc) crystal structure is the same as iron at room temperature. These alloys are magnetic and cannot be hardened by heat treatment. In general, ferritic stainless steels do not have particularly high strength. Their annealed yield strengths range from 275 to 350 MPa (40 to 50 ksi), and their poor toughness and susceptibility to sensitization limit their fabricability and the usable section size. Their chief advantages are their resistance to chloride stress-corrosion cracking, atmospheric corrosion, and oxidation, at a relatively low cost.

Ferritic stainless steels contain between 11 and 30% Cr, with only small amounts of austenite-forming elements, such as carbon, nitrogen, and nickel. Their general use depends on their chromium content.

The low-chromium (11%) alloys (S40500 and S40900, the latter being the most widely used ferritic stainless steel), have fair corrosion and oxidation resistance and good fabricability at low cost. They have gained wide acceptance for use in automotive exhaust systems.

The intermediate-chromium (16 to 18%) alloys (S43000 and S43400) are used for automotive trim and cooking utensils. These alloys are not as readily fabricated as the lower chromium alloys, because of their poor toughness and weldability.

The high-chromium (19 to 30%) alloys (S44200 and S44600), which are often referred to as superferritics, are used for applications that require a high level of corrosion and oxidation resistance. These alloys often contain either aluminum or molybdenum and have a very low carbon content. Their fabrication is possible because of special melting techniques that can achieve very low carbon, as well as very low nitrogen contents. Stabilizing elements, like titanium and niobium, can be added to prevent sensitization and to improve as-welded properties.

**Austenitic stainless steels** constitute the largest stainless family, in terms of number of alloys and usage. Like the ferritic alloys, they cannot be hardened by heat treatment. However, their similarity ends there. The austenitic alloys are nonmagnetic, and their structure is face-centered-cubic (fcc), like high-temperature (900 to 1400 °C, or 1650 to 2550 °F) iron. They possess excellent ductility, formability, and toughness, even at cryogenic temperatures. In addition, they can be substantially hardened by cold work.

Although nickel is the chief element used to stabilize austenite, carbon and nitrogen are also used, because they are readily soluble in the fcc structure. A wide range of corrosion resistance can be achieved by balancing the ferrite-forming elements, such as chromium and molybdenum, with austenite-forming elements.

Austenitic stainless steels can be subdivided into two categories: chromium-nickel alloys, such as S30400 and S31600, and chromium-manganese-nitrogen alloys, such as S20100 and S24100. The latter group generally contains less nickel and maintains the austenitic structure with high levels of nitrogen. Manganese (5 to 20%) is necessary in these low-nickel alloys to increase nitrogen solubility in austenite and to prevent martensite transformation. The addition of nitrogen also increases the strength in austenitic alloys. Typical chromium-nickel alloys have tensile yield strengths from 200 to 275 MPa (30 to 40 ksi) in the annealed condition, whereas the high-nitrogen alloys have yield strengths up to 500 MPa (70 ksi).

As previously mentioned, austenitic alloys can be substantially hardened by cold working. The degree of work hardening depends on the alloy content, with increasing alloy content decreasing the work-hardening rate. Austenitic stainless steels that have a low alloy content, such as S20100, S20161, S30100, and S30400, often become magnetic because of the transformation to martensite when sufficiently cold worked or heavily deformed in machining or forming operations. The rapid work hardening of S20161 is a major advantage in sliding wear. In S30430, copper is intentionally added to lower the work-hardening rate for enhanced headability in the production of fasteners.

Another property that depends on alloy content is corrosion resistance. Molybdenum is added to S31700 and S31600 to enhance corrosion resistance in chloride environments. High-chromium grades (S30900 and S31000) are used in oxidizing environments and high-temperature applications, whereas a high-nickel grade (N08020) is used in severe reducing acid environments. To prevent intergranular corrosion after elevated-temperature exposure, titanium or niobium is added to stabilized carbon in S32100 or S34700. Also, lower-carbon grades (AISI L or S designations), such as S30403 (type 304L), have been established to prevent intergranular corrosion. Highly alloyed materials (the superaustenitics) containing 20 to 26% Cr, 18 to 26% Ni, 6% Mo, and 0.1 to 0.2% N have been developed for enhanced resistance to chloride stress-corrosion cracking. Some of the more corrosion-resistant alloys, such as N08020 (20Cb-3), have nickel levels high enough (32 to 38% Ni) to rate classification as nickel-base alloys.

**Martensitic stainless steels** are similar to iron-carbon alloys that are austenitized, hardened by quenching, and then tempered for increased ductility and toughness. These alloys are magnetic, and their heat-treated structure is body-centered tetragonal (bct). In the annealed condition, they have a tensile yield strength of about 275 MPa (40 ksi) and are generally machined, cold formed, and cold worked in this condition.

The strength obtained by heat treatment depends on the carbon content of the alloy. Increasing carbon content increases strength, but decreases ductility and toughness. The most commonly used alloy in this family is S41000, which contains about 12% Cr and 0.1% C. This alloy is tempered to a variety of hardness levels, from 20 to 40 HRC. Both chromium and carbon contents are increased in alloys S42000, S44002, S44003, and S44004. The first of these contains 14% Cr and 0.3% C and has a hardness capability of 50 HRC. The other three alloys contain 16% Cr and from 0.6 to 1.1% C. These alloys are capable of 60 HRC, and a tensile yield strength of 1900 MPa (280 ksi). The amount of primary carbides increases with increased carbon content in these three alloys.

Wear resistance for martensitic stainless steels is very dependent on carbon content. S44004 (1.1% C) has excellent adhesive and abrasive wear, similar to tool steels, whereas S41000 (0.1% C) has relatively poor wear resistance. The key to adhesive wear resistance is a high hardness. Abrasive wear resistance requires both high hardness and primary carbides. Molybdenum and nickel can be added to martensitic stainless steel to improve corrosion and toughness properties. Nickel also serves to maintain the desired microstructure, preventing excessive free ferrite when higher chromium levels are used to improve corrosion resistance. However, the addition of these elements is somewhat restricted, because higher amounts result in a microstructure that is not fully martensitic.

**Precipitation-hardenable (PH) stainless steels** are chromium-nickel grades that can be hardened by an aging treatment. These grades are classified as austenitic (such as S66286), semi-austenitic (such as S17700), or martensitic (such as S17400). The classification is determined by their solution-annealed microstructure. The semi-austenitic alloys are subsequently heat treated, so that the austenite transforms to martensite. Cold work is sometimes used to facilitate the aging reaction. Various alloying elements, such as aluminum, titanium, niobium, or copper, are used to achieve aging. They generally form intermetallic compounds, but in S17400, fine copper precipitates are formed.

Like the martensitic stainless steels, PH alloys can attain high tensile yield strengths, up to 1700 MPa (250 ksi). Cold working prior to aging can result in even higher strengths. The PH grades generally have good ductility and toughness with moderate-to-good corrosion resistance. A better combination of strength and corrosion resistance is achieved than with the martensitic alloys. These improved properties are related to their higher chromium, nickel, and molybdenum contents, as well as their restricted carbon (0.040 max) levels. The low carbon content of the martensitic PH stainless steels is especially critical for toughness and good ductility. However, this low carbon content reduces the wear resistance of these alloys.

The most well-known precipitation-hardenable stainless steel is S17400. It contains chromium and nickel, as do all precipitation-hardenable stainless steels, with copper for age hardening and niobium for stabilizing the carbon. The age-hardening agents used in other alloys include titanium (S45500), aluminum (S13800), and niobium (S45000). Molybdenum can be added to improve mechanical properties or corrosion resistance. Both molybdenum and copper are added for corrosion resistance in S45000. Carbon is normally restricted, except in semiaustenitic alloys such as S35500, which require it to provide the desired phase transformations.

**Duplex stainless steels** are chromium-nickel-molybdenum alloys that are balanced to contain a mixture of austenite and ferrite, and are magnetic, as well. Their duplex structure results in improved stress-corrosion cracking resistance, compared with the austenitic stainless steels, and improved toughness and ductility, compared with the ferritic stainless steels. They are capable of tensile yield strengths ranging from 550 to 690 MPa (80 to 100 ksi) in the annealed condition, which is approximately twice the strength level of either phase alone.

The original alloy in this family was the predominantly ferritic S32900. The addition of nitrogen to duplex alloys, such as S32950 and S31803, increases the amount of austenite to nearly 50%. In addition, nitrogen improves as-welded corrosion properties, chloride corrosion resistance, and toughness. The improvement in toughness is probably related to the higher amount of austenite present, which makes it possible to produce heavier product forms, such as plates and bars.

## Stainless Steel Mill Finishes (Ref 2)

The standard industry designations for stainless steel finishes are classified by mill form, as there are separate finishes (or conditions) for sheet, strip, plate, bar, rod, wire, and tubing. Table 2 classifies the various stainless steel product forms. More detailed information on stainless steel product forms can be found in Ref 3.

**Table 2 Classification of stainless steel product forms**

| Item | Description | Thickness | | Width | | Diameter or size | |
|---|---|---|---|---|---|---|---|
| | | mm | in. | mm | in. | mm | in. |
| Sheet | Coils and cut lengths: | | | | | | |
| | Mill finishes No. 1, 2D, and 2B | <5 | $<\frac{3}{16}$ | ≥610 | ≥24 | . . . | . . . |
| | Polished finishes No. 3, 4, 6, 7, and 8 | <5 | $<\frac{3}{16}$ | All widths | | . . . | . . . |
| Strip | Cold finished, coils, or cut lengths | <5 | $<\frac{3}{16}$ | <610 | <24 | . . . | . . . |
| Plate | Flat rolled or forged | ≥5 | $\geq\frac{3}{16}$ | >25 | >10 | . . . | . . . |
| Bar | Hot-finished rounds, squares, octagons, and hexagons | . . . | . . . | . . . | . . . | ≥6 | $\geq\frac{1}{4}$ |

|  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|
|  | Hot-finished flats | $\geq 3$ | $\geq \frac{1}{8}$ | 6-25 | $\frac{1}{4}$-10 | . . . | . . . |
|  | Cold-finished rounds, squares, octagons, and hexagons | . . . | . . . | . . . | . . . | >13 | $> \frac{1}{2}$ |
|  | Cold-finished flats | . . . | . . . | $\geq 9.5$ | $\geq \frac{3}{8}$ | . . . | . . . |
| Wire | Cold finished only: round, square, octagon, hexagon, flat wire | 0.25 to <5 | 0.010 to $< \frac{3}{16}$ | 1.6 to <9.5 | $\frac{1}{16}$ to $< \frac{3}{8}$ | $\leq 13$ | $\leq \frac{1}{2}$ |
| Pipe and tubing | Several different classifications, with differing specifications, are available. For information on standard sizes, consult Committee of Stainless Steel Producers, AISI. |  |  |  |  |  |  |
| Extrusions | Not considered "standard" shapes, but of potentially wide interest. Currently limited in size to approximately 165 mm ($6\frac{1}{2}$ in.) diam circle, or structurals to 125 mm (5 in.) diam. |  |  |  |  |  |  |

Source: Ref 2

### *Sheet Finishes*

Stainless steel sheets are produced on continuous mills or hand mills. The steel is usually cast in ingot form and rolled on a slabbing or a blooming mill to slabs or sheet bars. Alternatively, the steel may be cast directly in slab form ready for finish hot rolling.

Sheets produced on continuous mills from slabs are rolled into coils and are further processed by annealing, descaling, and cold reducing to specified thickness, then further annealing and descaling. Coils or lengths cut from coils may then be subjected to light cold rolling for finish on dull or bright rolls.

Sheet finishes (Table 3) are designated by a system of numbers: No. 1, 2D, and 2B for rolled (unpolished) finishes; and No. 3, 4, 6, 7, and 8 for polished finishes.

**Table 3 Standard mechanical sheet finishes**

| **Finish** | **Description** |
|---|---|
| **Unpolished or rolled finishes** |  |
| No. 1 | A rough, dull surface that results from hot rolling to the specified thickness followed by annealing and descaling |
| No. 2D | A dull finish that results from cold rolling followed by annealing and descaling, and may perhaps get a final light roll pass through unpolished rolls. A 2D finish is used where appearance is of no concern. |
| No. | A bright, cold-rolled finish resulting in the same manner as No. 2D finish, except that the annealed and descaled sheet receives a |

| | |
|---|---|
| 2B | final light roll pass through polished rolls. This is the general-purpose cold-rolled finish that can be used as is, or as a preliminary step to polishing. |
| **Polished finishes** | |
| No. 3 | An intermediate polished surface obtained by finishing with a 100-grit abrasive. Generally used where a semifinished polished surface is required. A No. 3 finish usually receives additional polishing during fabrication. |
| No. 4 | A polished surface obtained by finishing with a 120 to 150-mesh abrasive, following initial grinding with coarser abrasives. This is a general-purpose bright finish with a visible "grain" that prevents mirror reflection. |
| No. 6 | A dull satin finish having lower reflectivity than No. 4 finish. It is produced by tampico brushing the No. 4 finish in a medium of abrasive and oil. It is used for architectural applications and ornamentation where a high luster is undesirable, and to contrast with brighter finishes. |
| No. 7 | A highly reflective finish that is obtained by buffing finely ground surfaces but not to the extent of completely removing the grit lines. It is used chiefly for architectural and ornamental purposes. |
| No. 8 | The most reflective surface, which is obtained by polishing with successively finer abrasives and buffing extensively until all grit lines from preliminary grinding operations are removed. It is used for applications such as mirrors and reflectors. |

Source: Ref 2

**No. 1** is a very dull finish produced by first hot rolling the steel on hand sheet mills to the specified thickness and then annealing and descaling. It is used in industrial applications for resistance to heat or corrosion, where a smooth finish is not of particular importance.

**No. 2D** is a dull finish produced on either hand sheet mills or continuous mills by cold rolling to the specified thickness, annealing, and descaling. The dull finish may result from the descaling operation or may be developed by a final light cold roll pass on dull rolls. This finish is favorable to the surface retention of lubricants in deep drawing operations. It generally is used in forming deep-drawn articles that may be polished after fabrication.

**No. 2B** is a bright, cold-rolled finish commonly produced in the same way as No. 2D, except that the annealed and descaled sheet receives a final light cold-roll pass on polished rolls. It is a general-purpose finish used for all but exceptionally difficult deep drawing applications. This finish is more readily polished than No. 1 or 2D.

**No. 3** is an intermediate polished finish for use where a semifinished polished surface is required and a further finishing operation follows fabrication. For sheets or articles that will not be subject to additional finishing or polishing, No. 4 finish is recommended.

**No. 4** is a general-purpose polished finish widely used for architectural panels and trim, and for dairy, restaurant, and kitchen equipment. Following initial grinding with coarser abrasives, sheets are finally finished with lubricated 120- to 150-mesh abrasive belts.

**No. 6** is a dull satin finish having lower reflectivity than No. 4. It is produced by tampico brushing No. 4 finished sheets in a medium of abrasive and oil and is used for architectural applications and ornamentation where a high luster is undesirable. It also is used to contrast with brighter finishes.

**No. 7** is a finish with a high degree of reflectivity, produced by buffing a finely ground surface without removing the grit lines. It is used chiefly for architectural and ornamental purposes.

**No. 8** is the most reflective finish and is obtained by polishing with successively finer abrasives and buffing extensively with very fine buffing rouges. The surface is essentially free of grit lines from preliminary grinding operations. This finish is most widely used for press plates, as well as for small mirrors and reflectors. Sheets can be produced with one or both sides polished. When polished on one side only, the other side may be rough ground in order to obtain the necessary flatness. The relationship between abrasive grit numbers and surface roughness in terms of microinches is sometimes a basis for specification. The values are approximately as follows:

| Abrasive grit no. | Surface roughness | |
|---|---|---|
| | μm | μin. |
| 500 | 0.10 to 0.25 | 4 to 10 |
| 320 | 0.15 to 0.38 | 6 to 15 |
| 240 | 0.20 to 0.51 | 8 to 20 |
| 180 | 0.64 max | 25 max |
| 120 | 1.14 max | 45 max |

### *Strip Finishes*

Hot-rolled stainless steel strip is a semifinished product obtained from the hot rolling of slabs or billets and is produced for conversion by cold rolling. Cold-rolled stainless steel strip is manufactured from hot-rolled, annealed, and pickled strip by cold rolling on polished rolls. Depending on the thickness desired, the cold rolling requires various numbers of passes through the mill to effect the necessary reduction and to secure the desired surface characteristics and mechanical properties. Only three rolled (unpolished) finishes (No. 1, No. 2, and bright annealed) and one polished finish (mill buffed) are commonly supplied on stainless steel strip.

**No. 1 finish** is produced by cold rolling, annealing, and pickling. Appearance varies from dull gray matte to fairly reflective, depending largely on stainless steel type. This finish is used for severely drawn or formed parts, as well as for applications where the brighter No. 2 finish is not required, such as parts to be used at high temperatures. No. 1 finish for strip approximates No. 2D finish for sheet in corresponding chromium-nickel or chromium-nickel-manganese types.

**No. 2 finish** is produced by the same treatment used for No. 1 finish, followed by a final light cold-rolling pass, which generally is done using highly polished rolls. This final pass produces a smoother and more reflective surface, the appearance of which varies with stainless steel type. No. 2 finish for strip is a general-purpose finish widely used for household appliances, automotive trim, tableware, and utensils. No. 2 finish for strip approximates No. 2B finish for sheet in corresponding chromium-nickel or chromium-nickel-manganese stainless steels.

**Bright annealed finish** is a bright, cold-rolled, highly reflective finish retained by final annealing in a controlled-atmosphere furnace. The purpose of atmosphere control is to prevent scaling or oxidation during annealing. The atmosphere usually consists of either dry hydrogen or dissociated ammonia. Bright annealed strip is used most extensively for automotive trim.

**Mill-buffed finish** is a highly reflective finish obtained by subjecting either No. 2 or bright annealed coiled strip to a continuous buffing pass. The purpose of mill buffing is to provide a finish uniform in color and reflectivity. It also can provide a surface receptive to chromium plating. This type of finish is used chiefly for automotive trim, household trim, tableware, utensils, fire extinguishers, and plumbing fixtures.

**Grade Limitations.** Not all of the standard compositions of stainless steel strip are available in each of the standard mill finishes. Surface finishes of these products depend on end use rather than any restriction imposed by the supplier. Table 4 lists the finishes most often applied to sheet and strip of a number of standard grades of austenitic, martensitic, and ferritic steels.

### Table 4 Mill finishes available on stainless steel sheet and strip

See text for explanation of numerical designations of finishes

| Type | Sheet | | Strip |
|---|---|---|---|
| | Unpolished | Polished | |
| **Austenitic steels**[(a)] | | | |
| 201 | 2D, 2B | [(b)] | 1, 2 |
| 202 | 2D, 2B | 3, 4 | 1, 2 |
| 301 | 2D, 2B | [(b)] | 1, 2 |
| 302 | 2D, 2B | 3, 4, 6, 7 | 1, 2 |
| 302B | 2D | [(b)] | . . . |
| 304 | 2D, 2B | 3, 4, 6, 7 | 1, 2 |
| 304L | 2D, 2B | 4 | 1, 2 |
| 305 | 2D, 2B | [(b)] | 1, 2 |
| 309, 309S | 2D | [(b)] | 1, 2 |
| 310 | 2D | [(b)] | 1, 2 |
| 316 | 2D, 2B | 4 | 1, 2 |
| 316L | 2D, 2B | [(b)] | 1, 2 |
| 321 | 2D, 2B | [(b)] | 1, 2 |
| 347 | 2D, 2B | [(b)] | 1, 2 |

| | | | |
|---|---|---|---|
| 348 | 2D, 2B | (b) | 1, 2 |
| **Martensitic steels** | | | |
| 403 | 2D, 2B | (b) | 1, 2 |
| 410 | 2D, 2B | (b) | 1, 2 |
| 420 | (c) | (c) | 1, 2 |
| 440A, B, and C | (c) | (c) | (d) |
| **Ferritic steels**(a) | | | |
| 430 | 2D, 2B | 3, 4 | 1, 2 |
| 446 | 2D, 2B | (b) | 1, 2 |

(a) All grades listed, in both sheet and strip form, are regularly available in the smooth rolled and bright annealed condition.

(b) Usually not polished.

(c) Not available in sheet form.

(d) Material available in strip form on special order only; finish negotiated with supplier

### *Plate Finishes*

Stainless steel plates usually are produced by hot rolling from slabs, which have been directly cast or rolled from ingots; some plates may be produced by direct rolling from the ingot. Plates are generally produced in the annealed condition and are either blast cleaned or pickled. When blast cleaned, the plates are subjected to further cleaning in appropriate acids to remove possible iron contamination. Stainless steel plate can be produced in the conditions and surface finishes shown in Table 5.

**Table 5 Conditions and surface finishes for stainless steel plate**

| **Condition and finish** | **Description and remarks** |
|---|---|
| Hot rolled | Scale not removed; not heat treated; plate not recommended for final use in this condition(a) |
| Hot or cold rolled, annealed or heat treated | Scale not removed; use of plate in this condition generally confined to heat- |

| | |
|---|---|
| | resisting applications; scale impairs corrosion resistance.(a) |
| Hot or cold rolled, annealed or heat treated, blast cleaned or pickled | Condition and finish commonly preferred for corrosion-resisting and most heat-resisting applications |
| Hot or cold rolled, annealed, descaled, and temper passed | Smoother finish for specialized applications |
| Hot rolled, annealed, descaled, cold rolled, annealed, descaled, optionally temper passed | Smooth finish with greater freedom from surface imperfections than any of the above |
| Hot or cold rolled, annealed or heat treated, surface cleaned and polished | Polished finishes similar to the polished finishes on sheet |

Source: Ref 2

(a) Surface inspection is not practicable for plate that has not been pickled or otherwise descaled.

Table 5 indicates that polished finishes similar to those for sheet are available for plate. Technically speaking, there is no No. 4 finish for plate, nor is there a No. 8 finish. However, arrangements can be made either with a mill or an independent polisher to grind and polish plate in the same manner as sheet. This work should be specified on the basis of submitted samples.

Plate commonly is conditioned by localized grinding to remove surface imperfections on either or both surfaces; ground areas are well flared and the thickness is not reduced below the allowable tolerance in any of these areas.

### *Bar Finishes*

Hot-finished bars are commonly produced by hot rolling, forging, or pressing ingots to intermediate-size blooms or billets, which are subsequently hot rolled, forged, or extruded to final dimensions. (In some mills, the process starts with continuous cast sections.) The selection of rolling, forging, or extruding as the finishing method depends on several factors, including the composition of the steel and the final size. It is common practice to process bars in straight lengths, although smaller bars produced by rolling may be coiled.

Following hot rolling or forging, hot-finished bars may be subjected to various operations, including annealing or other heat treating; cleaning by pickling, blast cleaning, or other methods of descaling; rough turning; and machine straightening. When only improved surface is required, as for bars intended for forging, bars can be turned or ground.

Cold-finished bars are produced from hot-finished bars by additional operations to give close tolerance, improved surface finish, or specific mechanical properties.

Stainless steel bar is produced in the conditions and surface finishes given in Table 6. It is important that both condition and finish be specified, because each finish is applicable only to certain conditions.

**Table 6 Conditions and surface finishes for stainless steel bar**

| **Condition** | **Surface finish** |
|---|---|
| Hot worked only | Scale not removed (except for spot conditioning) |

| | |
|---|---|
| | Rough turned(a)(b) |
| | Blast cleaned |
| Annealed or otherwise heat treated | Scale not removed (except for spot conditioning) |
| | Rough turned(a) |
| | Pickled or blast cleaned and pickled |
| | Cold drawn or cold rolled |
| | Centerless ground(a) |
| | Polished(a) |
| Annealed and cold worked to high tensile strength(c) | Cold drawn or cold rolled |
| | Centerless ground(a) |
| | Polished(a) |

Source: Ref 2

(a) Applicable to round bar only.

(b) Bar of 400-series stainless steels that are highly hardenable, such as types 414, 420, 420F, 431, 440A, 440B, and 440C, are annealed before rough turning. Other hardenable types, such as types 403, 410, 416, and 416Se, also may require annealing, depending on composition and size.

(c) Produced only in mill orders; made predominantly in types 301, 302, 303Se, 304, 304N, 316, and 316N.

The finish on stainless steel bar is generally the result of processes used to size the bar or to improve the surface and usually not for purposes of achieving a certain surface appearance. Turning, for instance, improves the surface by removing undesirable defects. It is difficult, if not impossible, to obtain a hot-rolled surface that the customer can use without removal of a portion of the "skin." Turning is accomplished by passing the bar through a turning machine or lathe, using one or more passes depending on the amount of material to be removed.

Sometimes the final surface or dimension of round bar can be achieved only by centerless grinding. Centerless grinding differs from turning in that a grinding wheel is used for metal removal instead of a cutting tool, and more accurate dimensions and better surface finish are obtained. The centerless grinding machine is constructed so that the bar is supported under the greater portion of its length as well as under the grinding wheel, other than at the ends.

In some cases, a highly polished bar is desired rather than the standard centerless ground finish. In this case, centerless ground bars are passed through a polishing or lapping machine that imparts a higher degree of polish. Flat or shaped bars cannot be centerless ground, so any finish requirements are achieved by methods similar to those used for strip.

### *Wire Finishes*

Stainless steel wire is a product derived by cold finishing a coiled hot-rolled and annealed rod for the purpose of obtaining desired size with dimensional accuracy, improved surface, and specific mechanical properties. Wire is produced in a number of tempers and finishes. The finishes on wire are usually applied to meet the requirements of further processing, such as drawing, forming into parts, or coiling into springs.

**Oil- or grease-drawn finish** is a special bright finish for wire intended for uses such as racks and handles, where the finish supplied is to be the final finish of the end product. In producing this finish, lower drawing speeds are necessary and additional care in processing is needed to provide a surface with few scratches and with only a very light residue of lubricant.

**Diamond-drawn finish** is a very bright finish generally limited to wet-drawn stainless steel wire in fine sizes. Drawing speeds are necessarily reduced to obtain the desired brightness.

**Copper-coated wire** is supplied when a special finish is required for lubrication in an operation such as spring coiling or cold heading. Generally, copper-coated wire is drawn after the coating, the amount depending on the desired cold-worked temper of the wire.

**Tinned wire** is coated by passing single strands through a bath of molten tin. Tinned wire is used in soldering applications. The temper of the finished wire is controlled by processing prior to tinning.

**Lead-coated wire** is coated by passing single strands through, or immersing bundles of wire in, a bath of molten lead. The wire is then drawn to final size, with the lead forming a thin coating over the entire surface. This coating is useful on wire for coil springs, where it serves as a lubricant during coiling operations.

### *Tubing and Pipe Finishes*

Hot-finished tubular products produced by the seamless processes have a surface finish comparable to hot-rolled bars. Welded tubular products produced from hot-rolled sheets, strip, or plate retain the general surface finish of those flat rolled products. Thin-wall tubular products, due to greater reduction during the rolling operation and the lower finishing temperatures, may have a smoother surface than those with heavy walls.

Stainless steel tubular products are cold worked to improve dimensional limits or--in the case of welded tubing--to control the weld bead on the inside, or to condition the weld for grain refinement during the annealing operation. Cold finishing may include cold drawing, tube reducing, or swaging. Tubes may also be rough turned (machined) or honed, such as for hydraulic cylinders.

Tubular products may be polished, but instead of "typical" finish designations, the polished finishes for tubing are usually indicated by the grit size, such as 80, 120, 180, or 320 grit. Note that for the exterior surface of round tubing, grit lines are longitudinal. Tubing may be specified polished on the outside, the inside, or both surfaces. Welded and cold-finished seamless tubing is suitable for grinding or polishing and is produced in sizes up to 168 mm (6 $\frac{5}{8}$ in.) OD with polished outside surfaces. It is not practical to polish interior surfaces or tubes with an inner diameter of less than 19 mm ($\frac{3}{4}$ in.).

### *Preservation of Mill Finishes*

In making a finished part, the original mill finish may be retained with little or no modification, depending on fabrication requirements. If this finish is satisfactory, no additional finishing operations are necessary. Therefore, every effort should be made to preserve the mill finish while the steel is in storage or being processed. The following preventive measures will serve to minimize additional cleaning and polishing:

- Steel should be kept in original containers or wrappers until fabrication actually begins.
- Steel should be stored indoors, on clean racks, shelves, or platforms, and should be covered wherever possible.
- Storage areas should be kept free of shop dirt, pickling or plating fumes, particles of scale from steel fabrication, and other contaminants.
- Storage areas should not be located beneath line shafting from which lubricating oils and grease may fall.
- Fabricating equipment should be cleaned of all residues before being used for a new operation on stainless steel.
- Steel should be handled with clean gloves or cloths, to avoid fingerprints.
- Only marking materials that leave no permanent blemishes on work should be used.
- Whenever feasible, paper or other protective covering should be placed on all surfaces between processes.
- Chips should not be removed by compressed air, which may contain oil or other contaminants.

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## Abrasive Blast Cleaning

Aspects of abrasive blast cleaning that apply particularly or exclusively to stainless steel include sandblasting, shot blasting, and wet blasting. For more complete information, see the article "Mechanical Cleaning Systems" in this Volume.

**Sandblasting** is effective for rapidly removing heavy or tightly adhering scale before acid pickling. Applied to stainless steel, it is not a complete cleaning procedure. Types of work for which it is frequently used include heavily scaled plate sections, forgings and castings, and parts made of straight chromium steel that have developed a tightly adhering scale during annealing. It is fast and economical when used in conjunction with a final pickling treatment.

Only clean silica sand should be used. If the sand is iron-bearing or becomes contaminated with scale, minute particles of these contaminants can become embedded in the metal. The only sure way to remove such contaminants and to produce a thoroughly clean, rust-free surface is to follow the blasting with an acid pickling treatment.

Sandblasting should not be used on materials that are too light to stand the blast pressure, because distortion results from the local stretching caused by impingement of the sand. The blast should be kept moving to avoid excessive cutting at localized points.

**Shot Blasting.** The use of carbon steel shot, steel wire, or iron grit as blasting media is not recommended as they may cause particles of iron to become embedded and seriously detract from the corrosion resistance of stainless steel surfaces. Unless these contaminants are completely removed by acid pickling, they can rust and begin pitting.

The use of stainless steel shot or grit reduces the danger of rusting, but it cannot eliminate the possibility of residual oxide scale. Final pickling is mandatory for maximum corrosion resistance of surfaces so treated.

Stainless steels, and particularly those of the 300 series, work harden when they are subjected to cold working. Therefore, if work hardening of the surface is undesirable for a particular application, shot blasting should not be used.

**Wet blasting** is adaptable for use with stainless steel. Various abrasives conveyed in liquid carriers are discharged at the work by compressed air. A variety of finishes can be obtained through selection of abrasives and adjustment of pressures. Finishes that are much smoother than those resulting from blasting with dry sand and that are similar in appearance to a No. 6 (tampico-brushed) finish may be obtained by wet blasting. As in sandblasting, a final pickling treatment and water washing are required.

## Acid Descaling (Pickling)

Acid descaling, or pickling, is the removal of heavy, tightly adherent oxide films resulting from hot-forming operations, thermal treatments (such as annealing or hardening), or welding (Ref 4). Because most stainless steel products received from the producing mill have been pickled, descaling is required only as a result of subsequent manufacturing operations.

In evaluating the different methods for removing scale, it should be kept in mind that scale on stainless steel is far more complex than scale formed on plain carbon steel. The scale on stainless steel consists of oxides of chromium, nickel, and/or other alloying elements--in addition to iron--and the ease by which it can be removed depends on base metal composition and the thermal treatment to which it is exposed. The problem may be further complicated by the presence of lubricants. Lubricants and other contamination should be removed before thermal treatment.

When the metal is exposed to hot gases containing oxygen, a heavy scale is formed. A heavy scale, because it is readily exposed to the oxygen only near the surface, may be oxygen rich at the surface and metal rich near the base metal. Most oxygen-rich scale is readily soluble in common pickling acids, but the metal-rich scale may require acids aggressive to the base metal itself. For this reason, pickling is sometimes preceded by a preconditioning step, such as an alkaline salt bath, or scale removal by mechanical means, such as shot blasting.

The final step, however, involves elimination of scale and other surface defects through removal of the normal, protective oxide layer and 25 to 40 μm (0.001 to 0.0015 in.) of the substrate metal by pickling the surface in a nitric-hydrofluoric acid ($HNO_3$-HF) bath. The protective film then reforms in air over the freshly cleaned surface. This oxide film is uniform and leaves the stainless surface in its normal passive condition.

Although pickling is not strictly a passivating treatment, it provides many of the same benefits. Pickling is most useful for localized cleaning of welded areas, but also can be used to improve the corrosion resistance of mechanically cleaned surfaces.

Disposal of pickle liquor is a growing problem that tends to limit pickling by immersion to those fabricator and chemical cleaning contractors who have pickle tanks and approved arrangements for disposal.

Pickling at the steel mill removes the oxide scale that forms during annealing. Mill pickling also removes manganese sulfides or other inclusions in the surface and removes surface layers that may have been depleted of chromium during annealing.

ASTM A 380 (Ref 1) lists three pickling solutions for stainless steel (Table 7). Fabricated austenitic stainless steels can be pickled by immersion in a standard 10% $HNO_3$, 2% HF bath at 50 °C (120 °F). For localized pickling or if the fabricated component is too large to be immersed, commercial $HNO_3$-HF pickle pastes can be just as effective. Pickle paste can be applied with a paint roller or nylon brush.

**Table 7 Acid descaling (pickling) of stainless steel**

| Alloy(a) | Condition(b) | Code | Treatment | | | Time(e), min |
|---|---|---|---|---|---|---|
| | | | Solution, vol%(c) | Temperature | | |
| | | | | °C | °F | |
| 200, 300, and 400 series, precipitation hardening, and maraging alloys (except free-machining alloys) | Fully annealed only | A | $H_2SO_4$ (8-11)(d)<br>Follow by treatment D or F, Annex A2 (ASTM A 380), as appropriate | 66-82 | 150-180 | 5-45 max |
| 200 and 300 series; 400 series containing 16% Cr or more; precipitation-hardening alloys (except | Fully annealed only | B | $HNO_3$ (15-25%) plus HF (1-8%)(f)(g) | 21-60 max | 70-140 max | 5-30 |

| | | | | | | |
|---|---|---|---|---|---|---|
| free-machining alloys) | | | | | | |
| All free-machining alloys and 400 series containing less than 16% Cr | Fully annealed only | C | $HNO_3$ (10-15%) plus HF ($\frac{1}{2}$-1 $\frac{1}{2}$%)(f)(g) | 20 (up to 60 with caution) | 70 (up to 140 with caution) | 5-30 |

Source: Ref 1

(a) This table is also applicable to the cast grades equivalent to the families of wrought materials listed.

(b) Other heat treatments may be acceptable if proven by experience: see sections 5.2.1, A2.4, and A2.5 of ASTM A 380 for further information.

(c) Solution prepared from reagents of following weight percent: $H_2SO_4$, 98; $HNO_3$, 67; HF, 70.

(d) Tight scale may be removed by a dip in this solution for a few minutes followed by water rinse and $HNO_3$-HF treatment as noted.

(e) Minimum contact times necessary to obtain the desired surface should be used in order to prevent overpickling. Tests should be made to establish correct procedures for specific applications.

(f) For reasons of convenience and handling safety, commercial formulations containing fluoride salts may be found useful in place of HF for preparing $HNO_3$-HF solutions.

(g) After pickling and water rinsing, an aqueous caustic permanganate solution containing 10% NaOH and 4 wt% $KMnO_4$, 71 to 82 °C (160 to 180 °F), 5 to 60 min, may be used as a final dip for removal of smut, followed by thorough water rinsing and drying.

Paste must be washed off within 15 to 30 min of application, or corrosion will initiate. Personnel need protective clothing and training in safe handling procedures.

Although postfabrication pickling improves the performance of stainless steels in a variety of applications, until recently there has been very little research data to support field experience. Quantitative data on the increase in critical pitting temperature in ferric chloride ($FeCl_3$) (ASTM G 48) shows that pickling provides a 2.5 to 10 °C (4.5 to 18 °F) improvement in performance (Fig. 1). While not large, the improvements in lightly ground surfaces and glass-bead-blasted surfaces are uniformly positive, indicating that pickling provides benefits beyond those obtained with the best controlled mechanical treatments. Additional information on acid pickling of stainless steels can be found in the article "Pickling and Descaling" in this Volume.

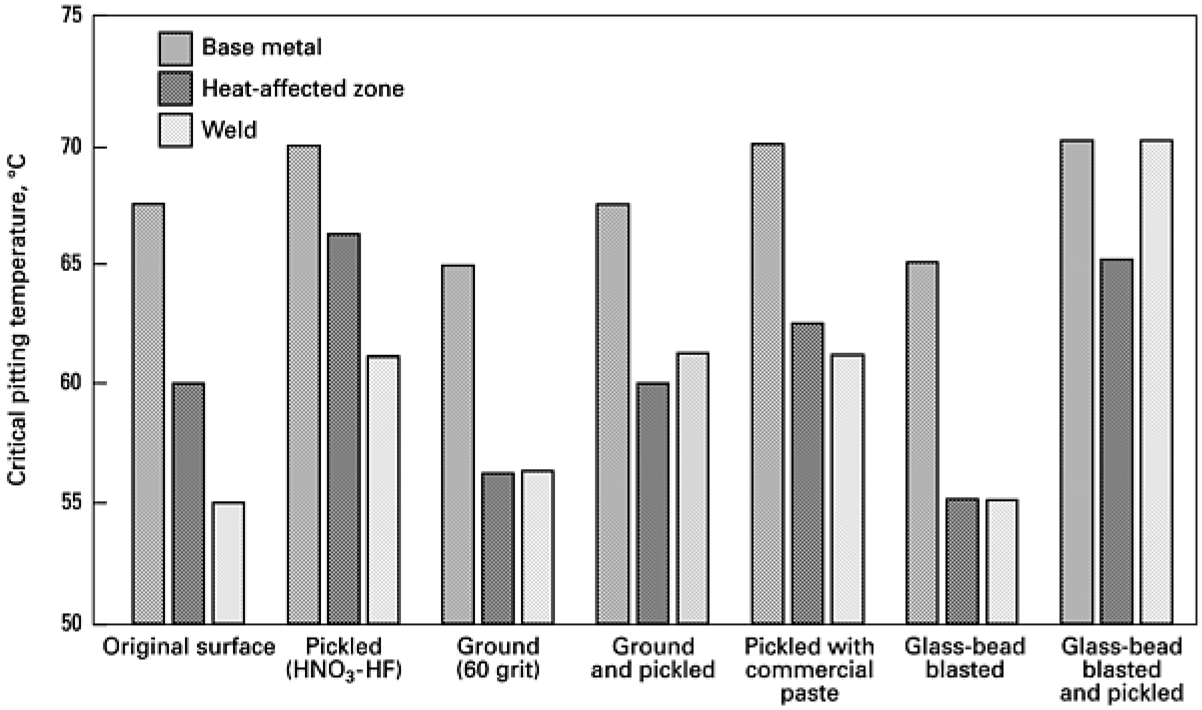

**Fig. 1 Pickling of stainless steel increases the critical pitting temperature in $FeCl_3$ in the base metal, heat-affected zone, and weld areas. Mechanical cleaning treatments that are performed without a subsequent pickling treatment decrease the critical pitting temperature. Source: Ref 5**

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4. *Cleaning and Descaling Stainless Steels,* No. 9001, American Iron and Steel Institute, 1982 (reprinted by Nickel Development Institute, 1988)
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## Salt Bath Descaling

The removal of oxide scale can be accelerated by using baths of molten sodium hydroxide (NaOH) to which certain reagents are added. These baths can be used with virtually all grades of stainless steel. Salt bath descaling has several advantages:

- It acts only on the scale and does not result in metal loss or etching.
- It does not preferentially attack areas in which intergranular carbides are present.
- It is particularly useful in descaling the straight chromium grades without the preliminary sandblasting that is frequently required prior to acid descaling.

Use of molten salts is not recommended for those stainless steels that precipitation harden at the operating temperature of the bath. Procedures and equipment for descaling in molten salt are described in the article "Molten Salt Bath Cleaning" in this Volume.

## Sequence of Descaling Methods

Usually, more than one method of cleaning is used to remove scale from stainless steel. For instance, in mill processing sheet, salt bath descaling and acid pickling often are used for a cold-rolled product and abrasive blast cleaning and acid pickling for a hot-rolled product.

In a continuous annealing and pickling line, multistep cleaning usually occurs twice in producing stainless steel sheet. The sequence of operations is: hot roll, anneal, descale, pickle, cold reduce 30 to 50%, anneal, descale, and pickle. As shown in Fig. 2, salt descaling is used for cold-rolled sheet, whereas the salt is bypassed and abrasive blast cleaning is used when a hot-rolled product is being cleaned. Salt also can be eliminated on low-chromium cold-rolled sheet.

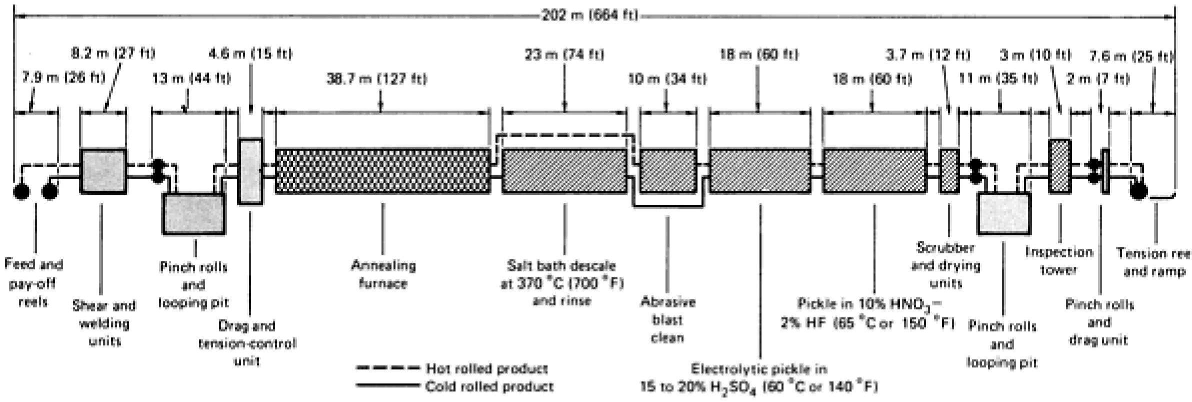

**Fig. 2 Sequence of annealing and scale-removing operations in mill processing of stainless steel sheet**

Cold-rolled sheet is left in the salt bath 10 to 15 min. Oxides are not removed from the surface. The rack of hot sheet is transferred to a water bath, and the violent reaction that results on immersion blasts much of the scale from the steel. The surface is essentially free of scale, but quite dull and dirty. To remove the last remnants of oxide, the rack is transferred to a 10 to 15% sulfuric acid ($H_2SO_4$) solution at 70 °C (160 °F) for 3 to 5 min. After removal from the $H_2SO_4$ tank, the rack of sheet steel is rinsed and then immersed for 1 to 2 min in $HNO_3$-HF (8 to 10% $HNO_3$, 1 to 2% HF) at 60 °C (140 °F). This removes all smut and residue and produces a white finish. The sheet is finally rinsed, removed from the rack, scrubbed, and dried with an air blast.

## Cleaning Stainless Steels

Cleaning includes all operations necessary for the removal of surface contaminants from metals to ensure maximum corrosion resistance of the metal, prevention of product contamination, and achievement of desired appearance (Ref 1). Selection of cleaning processes is influenced mainly by the type of contaminant to be removed, the required degree of cleanliness, and cost.

Dirt deposits on stainless steel, which include accumulated dust and dirt, finger marks, and identification markings, are easily removed (Ref 4). Frequently, warm water with or without detergent is sufficient. Next in order are mild nonscratching abrasive powders such as typical household cleaners. These can be used with warm water, bristle brushes, stainless steel brushes, sponges, or clean cloths. Ordinary carbon steel brushes or steel wool should be avoided as they may leave particles embedded on surfaces which can lead to rusting. For slightly more aggressive cleaning, a small amount of vinegar can be added to the scouring powder. Cleaning should always be followed by rinsing in clean hot water. When water is known to contain mineral solids, which leave water spots, it is good practice to wipe the surfaces completely with dry towels. Some companies use oil impregnated cloths to remove water spots and enhance appearance. Commercial metal cleaners may also be considered, but it is important to make certain that they can be used on stainless steels.

Finger marks are probably the most troublesome of unwanted marks on stainless steel (Ref 4). They not only detract from overall appearance of smoothly polished or bright finishes, but they also can "burn in" quite deeply during annealing or other thermal treatments, leaving permanent marks which can be removed only by grinding. Fortunately, they can be easily prevented through the use of clean gloves, or they can be removed by gentle rubbing with a paste of soda ash (sodium carbonate) and water applied with a soft rag. Again, this should be followed by a thorough warm water rinse.

Most inspection stamps and identification marks applied at the mill are ink, which can be removed by applying a solvent on a rag and rubbing (Ref 4). Selection of solvent is determined by the type of ink used. Solvents should be rinsed from the stainless steel with warm water, repeating the treatment if necessary.

Commonly used methods for the removal of greases, drawing compounds, and machining oils include:

- Alkaline cleaning
- Emulsion cleaning
- Solvent cleaning
- Vapor degreasing
- Ultrasonic cleaning
- Acid cleaning

Each of these are described briefly below and in greater detail in the articles contained in the Section "Surface Cleaning" in this Volume. Additional information can also be found in ASTM Standard A 380 (Ref 1).

**Alkaline cleaning** is used to remove soils from the surface of metals. Soils removed through alkaline cleaning include oil, grease, waxy solids, metallic particles, dust, carbon particles, and silica. Alkaline cleaners are applied by immersion or spray, and the metal is cleaned by emulsification, dispersion, saponification, or combinations of these mechanisms. The cleaning step is usually followed by a water rinse and a drying stage. Alkaline cleaner compositions are discussed in the article "Alkaline Cleaning" in this Volume.

**Emulsion cleaning** is a process for removing oily deposits and other common contaminants from metals by solution with the aid of a soap or other emulsifying agent (an emulsifying agent is one which increases the stability of a dispersion of one liquid in another). It is effective for removing a wide variety of contaminants including pigmented and unpigmented drawing compounds and lubricants, cutting fluids, and residues resulting from liquid penetrant inspection. Emulsion cleaning is used when rapid, superficial cleaning is required and when a light residual film of oil is not objectionable. Depending on the solvent used, cleaning is done at temperatures from 10 to 80 °C (50 to 180 °F). Compositions and operating temperatures for emulsion cleaners are described in the article "Emulsion Cleaning" in this Volume.

**Solvent cleaning** is a process for removing contaminants from metal surfaces by immersion or by spraying or swabbing with common organic solvents such as the aliphatic petroleums, chlorinated hydrocarbons, or blends of these two classes of solvents. Cleaning is usually performed at, or slightly above, room temperature. Parts are cleaned by being immersed and soaked in the solvent, with or without agitation. Parts that are too large to be immersed are sprayed or wiped with the solvent. Properties of cleaning solvents are described in the article "Solvent Cold Cleaning and Vapor Degreasing" in this Volume.

**Vapor degreasing** is a generic term applied to a cleaning process that uses the hot vapors of a chlorinated or fluorinated solvent to remove soils, particularly oils, greases, and waxes. The cleanliness and chemical stability of the degreasing solvent are critical factors in the efficiency of the vapor and possible chemical attack of the metal. Water in the degreasing tank or on the item being cleaned may react with the solvent to form hydrochloric acid, which may be harmful to the metal. No water should be present in the degreasing tank or on the item being cleaned. Acids, oxidizing agents, and cyanides must also be prevented from contaminating the solvent. Vapor degreasing systems and procedures are described in the article "Solvent Cold Cleaning and Vapor Degreasing" in this Volume.

**Ultrasonic Cleaning.** Ultrasonic transducers, which convert electrical energy into ultrasonic vibrations, can be used in conjunction with some solvent cleaning systems to loosen and remove contaminants from deep recesses and other difficult to reach areas, particularly in small workpieces. Cavitation in the liquid produced by the high-frequency sound causes microagitation of the solvent in even tiny recesses of the workpiece, making the method especially desirable for cleaning parts or assemblies having an intricate configuration. More detailed information can be found in the article "Ultrasonic Cleaning" in this Volume.

**Acid cleaning** is a process in which a solution of a mineral acid, organic acid, or acid salt, in combination with a wetting agent and detergent, is used to remove oxide, shop soil, and similar contaminants from metal surfaces, with or without application of heat. Acid cleaning is not generally effective for removal of oils, greases, and waxes. Surfaces should be precleaned to remove oils and greases before acid cleaning. Common techniques for acid cleaning are immersion, swabbing, and spraying. Maximum surface quality is best achieved by using a minimum cleaning time at a given acid concentration and temperature. After acid cleaning the surfaces must be thoroughly rinsed with clean water to remove all traces of the acid and thoroughly dried after the final water rinse. To minimize staining, surfaces must not be permitted to dry between successive steps of the acid cleaning and rinsing procedure. A neutralizing treatment may be required under some conditions; if used, neutralization must be followed by repeated water rinsing to remove all trace of the neutralizing agent followed by thorough drying after the final water rinse. Suggested solutions, contact times, and solution temperatures for acid cleaning of stainless steels are given in ASTM A 380. Additional information can also be found in the section "Passivation Treatments" in this article and in the article "Acid Cleaning" in this Volume.

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## Mass Finishing

Mass finishing provides methods that can be advantageously used for surface treating stainless steels include barrel finishing, vibratory finishing, and centrifugal barrel finishing. Mass finishing methods are adaptable to removal of burrs, scale, and residual flux, and they also can be used for light surface treatment, such as cleaning, burnishing, or coloring. For more information, see the article "Mass Finishing Methods" in this Volume.

**Post-Treatments.** Once a mass finishing treatment is completed, stainless steel parts are rinsed thoroughly in water and dipped in a 20 vol% solution of $HNO_3$ at 50 °C (120 °F) for 10 to 15 min. This is followed by another water rinse. If any oxide scale remains on the work after mass finishing, it must be removed by acid pickling.

## Finishing Methods

This section deals with the finishing of stainless steels as practiced by the fabricator or manufacturer--specifically, grinding (used here to mean metal removal for the purpose of altering surface finish, not to achieve close dimensional tolerances), polishing, and buffing. Table 8 summarizes the sequence of operations for the grinding, polishing, and buffing of stainless steels.

**Table 8 Sequence of grinding, polishing, and buffing operations for stainless steels**

| Operation | Stage | Wheels | Grit size | Abrasive | Method | Purpose |
|---|---|---|---|---|---|---|
| Grinding | Rough | Solid wheels; rubber or bakelite bonded, soft body | 20-30 | Manufactured types, such as $Al_2O_3$ or SiC | Dry | For rough work on castings, forgings, and weld beads that may require it. Castings usually sandblasted initially |
| Grinding | Finish | Same as above; or setup disk wheels or abrasive belts | 36-80 | Manufactured types, such as $Al_2O_3$ or SiC | Dry | For subsequent operations on the above and also preliminary to polishing operations on hot-rolled plate. May also be employed for touch-up work (removing deep scratches and tool marks prior to polishing) |
| Polishing | Rough | Setup disk canvas | 80-100 | Manufactured types, | Grease stick | To produce a rough polished finish and to remove imperfections left |

|  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|
|  |  | compress wheels or abrasive belts |  | such as $Al_2O_3$ or SiC |  | by hand wheel grinding. Also use as a preparatory operation for a final polish corresponding to standard No. 4 mill finish. This is the usual starting on cold-rolled sheet. |
| Polishing | No. 4 finish | Setup disk canvas compress wheels or abrasive belts | 120-150 | Manufactured types, such as $Al_2O_3$ or SiC | Grease stick | To provide a finish similar to standard No. 4 mill finish. Variations in fineness of finish should be expected with variations in condition of grit as between a new or worn belt. |
| Polishing | No. 6 finish (tampico) | Tampico brush type | Start with No. 4 finish | . . . | Pumice pastes made up on the job, or commercially available manufactured compositions | To provide a finish corresponding to standard No. 6 mill finish |
| Polishing | Pre-No. 7 finish | Made-up cloth wheels or abrasive belts | 180 | Manufactured types | Grease stick | To provide a finish preparatory to buffing for standard No. 7 finish. May be used as final finish on drawn parts and architectural trim |
| Polishing | Pre-No. 8 finish | Made-up cloth wheels or abrasive belts | 240 to flour | Manufactured types or Turkish emery | Grease stick | To provide a final polished finish preliminary to a mirror finish |
| Polishing | Satin finishing | Full disk buffs, loose or concentric sewed |  | Greaseless compounds applied to the wheel as required. These are available in many grit sizes. | . . . | A method of producing satin finishes. Fineness of finish varies with composition employed. |
| Buffing | Cutting | Bias-type, sewed piece, or fill disk buffs |  | Use stainless steel cutting compound on buff. | . . . | Apply as needed to remove any residual polishing lines or other imperfections prior to color buffing for high-luster finishes such as No. 7. May be applied directly to bright cold-rolled strip |
| Buffing | Coloring | Full disk or bias-type buff |  | Use stainless steel coloring compound. | . . . | For final coloring to bright lusters such as No. 7 and mirror. High speeds for brightness (approximately 50 m/s, or 10,000 sfm). Lower speeds for satinlike finish (approximately 20 to 30 m/s, or 3500 to 6000 sfm) |

Source: Ref 2

Before discussing each of these processes, it is useful to review the inherent characteristics of stainless steels that set these materials apart from other metals, and to emphasize the ever-present need to avoid any practices that may result in a loss in corrosion resistance or a reduction in mechanical property values. For example, stainless steels, as a group, are characterized by:

- *High tensile strength.* This fact determines the power necessary for efficient metal removal in grinding and polishing.
- *High surface hardness.* This governs the selection of abrasive materials and their cutting behavior.
- *Low heat conductivity.* This requires attention to precautionary measures that will prevent rapid or excessive rise in temperature, which can cause heat tint discoloration and, possibly, a reduction in corrosion resistance.
- *Rapid work hardening.* This necessitates proper grinding techniques, especially of austenitic grades in which residual stresses at the metal surface may affect in-service corrosion resistance.
- *Need for cleanliness.* This means attention must be given to grinding and polishing media to keep it clean and free of iron particles, which can be picked up if used with carbon or alloy steel products.

### Grinding

Grinding is used for preliminary surface conditioning before polishing, and as a means of removing excess metal from weld beads and flash from forgings and castings. It also is used for dressing gas-cut welding edges. These operations usually require coarse or rough grinding. However, as the refinement of the surface increases with the use of finer abrasives, grinding begins to approach polishing; the dividing line between fine grinding and polishing is seldom clear cut.

**Solid wheels** are used for coarse grinding and include the vitreous and rubber-bonded or plastic-bonded types. They should be free-cutting to avoid loading and glazing. Abrasives frequently used are aluminum oxide ($Al_2O_3$) and silicon carbide (SiC), in grit sizes ranging from 20 to 36 (for initial or coarse cutting) to 60 (for subsequent finishing work). Surface speeds for solid wheels usually range between 25.5 and 30 m/s (5000 and 6000 sfm). For safety, wheels should never be operated above their maximum permissible speed. To realize the maximum cutting efficiency of which they are capable, they should not be run at less than recommended speeds.

**Wheel Operation.** Grinding wheels should never be forced; forcing causes excessive wheel breakdown and localized high temperature in the workpiece. In addition, the wheel should not be allowed to ride on the workpiece with insufficient pressure, because this causes rapid glazing of the wheel.

The elimination of heat buildup in localized zones is of major importance with stainless steel. The low thermal conductivity of stainless steel contributes to increased thermal distortion. This applies particularly to the chromium-nickel grades, of which the coefficients of thermal expansion are relatively high. Holding the metal at low temperature avoids heat tinting, which becomes evident at 230 to 260 °C (445 to 500 °F) and above. Marked increases in metal temperature can reduce the hardness of heat-treated grades and precipitate carbides in the unstabilized chromium-nickel grades, which are susceptible to intergranular corrosion.

**Rough surfaces** on weldments, castings, and forgings are cut down to the general finish contour with a solid wheel of either $Al_2O_3$ or SiC of grit size from 20 to 40, and with a bond loose enough to allow the wheel to remain open and free-cutting without excessive wheel wear. Again, it is important to prevent local overheating, which can cause either mechanical or metallurgical damage, and to avoid excessive metal removal, allowing sufficient material for further finishing. Surface contamination is not important at this stage of finishing.

The next roughing operation, which in many applications may replace the solid-wheel operation, requires the use of a portable disk grinder, powered by air or electricity, using abrasive disks coated with $Al_2O_3$ ranging in grit size from 80 to 120. Localized overheating may be prevented by applying a small stream of water or water-soaked rags to the side not being ground.

**Weld Beads.** Excess metal in weld beads ordinarily is removed by grinding, although an initial cut may be made with a cold chisel when the size of the bead warrants. Grinding procedures and precautions conform to those previously described, except that the width of weld beads precludes right-angle cutting with successive grit sizes. Usually, a raised bead will take a fairly coarse grit at the outset. Canting of wheels must be avoided; otherwise, grooves may be cut parallel to the bead and undesirable thinness will result. Limiting stops attached to portable grinders may be installed to prevent canting and excessive metal removal.

When grinding is to be followed by polishing, as for weld joints on polished sheet, the grinding operation must terminate sufficiently above the level of the base metal to allow enough metal for final polishing to finish flush, without a ridge or groove. Limiting stops on grinding machines are helpful.

For economic reasons, grinding of weld joints in cold-rolled or polished sheet should be held to a minimum by using welding procedures that avoid high beads of excess metal. The grinding step can often be eliminated, allowing the workpiece to go directly into the polishing operations where finer abrasives are used.

Metal adjacent to beads that are being ground should be protected from flying bits of metal cuttings by shields of material such as paper. Wet rags may be laid on the workpiece to absorb heat and reduce thermal distortion, particularly on thin-gage material.

**Progressive Grinding.** To remedy an existing surface condition, such as removing scale patterns or indentations from hoisting clamps on an annealed plate, a series of wheels of decreasing grit size is often needed. The initial grit size is selected on the basis of which coarseness is needed to remove the major portion of the unwanted condition. After the workpiece has been partly dressed down, the operation is completed by using a graduated series of successively finer wheels until the desired final finish is attained. The use of a relatively soft plastic wheel impregnated with fine, sharp grit makes it possible to reduce the number of finishing operations, because of the combination of free cutting and wheel resilience for ease in blending.

The direction of wheel traverse across the work is changed by 90° with each change in grit size to remove residual grinding lines. As each change is made, workpiece surfaces should be brushed thoroughly to remove any particles of the preceding abrasive or of metal cuttings that mar the performance of the finer grit to follow. The progression from coarse to fine grit size may be made in steps of 20 to 40 mesh.

When using a flat disk grinder, with which cutting is performed against the face (instead of the rim) of the wheel, a rotary or circular traversing motion is most frequently used. This eliminates the need for reversing the direction of grinding with each change of grit size.

**Belt Grinding.** Belts carrying abrasives of various grit sizes are widely used for grinding and polishing stainless steel surfaces. Although many complex shapes can be belt ground, a simple projection may make belt grinding impossible; for example, the studs welded to a cookware pot or pan to which the handle is affixed. In this application, the finishing operations, from grinding to color buffing, must be completed before the studs are welded in place. Grit sizes and belt speeds for abrasive grit roughing and polishing are given in Table 9.

**Table 9 Grit sizes and belt speeds for abrasive belt roughing and polishing of stainless steels[a]**

| Product | Roughing | | | | Rough polishing | | | Polishing | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Obstruction or roughness removed | Grit size, mesh | Belt speed | | Grit size, mesh | Belt speed | | Grit size for for successive stages, mesh | Belt speed | | Polishing aid[b] |
| | | | m/s | sfm | | m/s | sfm | | m/s | sfm | |
| Billets, alloy or stainless steel | . . . | . . . | . . . | . . . | 50 | 17.9 | 3500 | . . . | . . . | . . . | G |
| Cutlery, stainless steel | | | | | | | | | | | |
| Blades--tapering | . . . | 50 | 28 | 5500 | 80 | 28 | 5500 | 180 | 28 | 5500 | G |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Forks or knives | . . . | . . . | . . . | . . . | 80 | 26.5 | 5200 | 1500 | 26.5 | 5200 | G |
| Spoons | . . . | . . . | . . . | . . . | . . . | . . . | . . . | 150, 220 | 26.5 | 5200 | G |
| Hypodermic needles, stainless steel | . . . | . . . | . . . | . . . | . . . | . . . | . . . | 320(c), 400(c) | 23.5 | 4600 | WSO |
| Jet blades, stainless steel | | | | | | | | | | | |
| Airfoil | . . . | . . . | . . . | . . . | 50 | 28 | 5500 | 120 | 28 | 5500 | O |
| Longitudinal | . . . | . . . | . . . | . . . | . . . | . . . | . . . | 80, 100, 120, 150, 180 | (d) | (d) | O |
| Stainless steel | | | | | | | | | | | |
| Coil (series 300) | Pits | 60 | 17.3 | 3400 | 80 | 17.3 | 3400 | 120, 150 | 17.3 | 3400 | O |
| Pots and pans | Wrinkles | 80 | 25.5 | 5000 | . . . | . . . | . . . | 220, 320(c) | 25.5 | 5000 | G |
| Press plates | Scratches | 80 | 20.4 | 4000 | 100 | 20.4 | 4000 | 120, 150, 180, 240, 320 | 20.4 | 4000 | G |
| Sheets, No. 3 finish | . . . | . . . | . . . | . . . | 80 | 20.4 | 4000 | 100 | 20.4 | 4000 | G |
| Sheets, No. 4 finish | Inclusions | 100 | 20.4 | 4000 | 120 | 20.4 | 4000 | 150(c) | 20.4 | 4000 | G |
| Sheets, No. 7 finish | Inclusions | 100 | 20.4 | 4000 | 150 | 20.4 | 4000 | 180(c), 240(c), 280(c) | 20.4 | 4000 | G |
| Tubes | . . . | . . . | . . . | . . . | 150 | 17.9 | 3500 | 220, 280, 320 | 23 | 4500 | O |
| Turbine nozzles and buckets | . . . | . . . | . . . | . . . | 80 | 25.5 | 5000 | 120 | 23 | 4500 | G |

Source: Ref 2

(a) Abrasive belts coated with $Al_2O_3$, unless grit size is footnoted to indicate otherwise.

(b) G, grease; O, oil; WSO, water-soluble oil.

(c) Silicon carbide.

(d) Fixture abrasive, reciprocating.

**Mechanized Belt Grinding.** In mechanized belt grinding, longer belts provide a longer belt life and dissipate heat more effectively. Thus, longer belts frequently are operated without a coolant, eliminating a post-grinding cleaning operation.

In belt grinding of rectangular stainless steel sinks, for example, it was necessary to use short belts to reach all internal surfaces. Each sink was ground in a machine with four grinding heads indexing about the main column of the machine while the sink was held in a cradle that rotated in a horizontal plane. A narrow belt ground the radii between the bottom and the side walls of the sink. Wider belts were used to grind the side walls; these belts were comparatively short and required the use of a coolant. Belt abrasives varied in grit size from 80 to 220 mesh, depending on the desired finish.

On a typical grinding machine using a 2200 mm (86 in.) wide abrasive belt and powered by a 250-hp ac motor, a positive hydraulic reciprocating drive permits instantaneous variations in table speed; belt speed is fixed at 25.5 m/s (5000 sfm). The 2200 mm (86 in.) belt travels over a conventional vertical-head assembly consisting of a dynamically balanced upper idler roll of steel and a rubber-covered serrated lower contact roll. A pneumatic belt-centering device ensures positive tracking of the abrasive belt and is adjustable to compensate for belts of different widths. Incorporated into the entire worktable is a 2200 mm (86 in.) wide vacuum chuck 4.9 m (16 ft) long. To produce single or compound tapers, a worktable can be tilted to any angle, for either right-hand or left-hand tapered sheets.

**Belt life** is influenced primarily by belt speed, type of material being ground and its hardness, pressure of the belt against the work, type of contact roll, type of lubricant (if a lubricant is required), and uniformity of the finish desired. In belt grinding of stainless steel, the recommended belt speed is approximately 20 m/s (4000 sfm).

With the exception of the precipitation-hardening stainless steels, the hardness of the steel has a greater effect on the life of a grinding belt than its composition. Hardness also affects surface finish, and a high-quality finish is easier to obtain on a harder stainless than on one that is softer. With precipitation-hardening alloys, best grinding results are obtained with a waterproof cloth abrasive belt and a water-soluble oil lubricant.

Pressure of the workpiece against the abrasive belt is probably the most important factor affecting belt life. Excessive pressure on a new belt causes glazing of the abrasive and greatly reduces cutting action. Therefore, new belts should be subjected to very light pressures during the break-in period and until the belt is capable of maintaining a uniform cutting action. A light belt pressure is preferred, and increased stock removal should be obtained by changing to a coarser belt.

The contact roll that backs up the abrasive belt is another important factor; a properly serrated contact roll may increase belt life by as much as 60%. The angle of the serration affects both belt life and finish. To obtain fine finishes, contact rolls serrated at an angle of 75° to the axis of the spindle should be used. Rough finishing requires a 30° angle. For general work, contact rolls may be made with a 45° serration, using a 9.5 mm ($\frac{3}{8}$ in.) groove and 9.5 mm ($\frac{3}{8}$ in.) land. Hardness of the contact roll should range between 50 to 65 on the Shore scleroscope A-scale.

When lubricants are used, they should maintain free-cutting (nonloading) edges, add color to the finished product, maintain a cool cutting surface, and be easy to apply. Lubricants may be in the form of grease sticks, waxes, or cutting oils. Cutting oils generally are more effective when they are diluted as much as 4 to 1 with kerosene.

**Safety.** Metal fines collected in a container near machines during the belt grinding of stainless steel should be removed regularly, because the fines, together with polishing compounds or oils that are collected with them, constitute a potential fire hazard. Fires in the duct system can be extremely serious because of the high air flow in the ducts. Fire-extinguishing equipment should be close to any machines using abrasive belts.

When wide abrasive belts are used, equipment with automatic tracking to center the belt in relation to the work is advantageous. All abrasive belt machinery should be equipped with motors that are totally enclosed.

Safety training for operators should begin with thorough instruction in the proper use of equipment, because most severe injuries result from improper use. Most common injuries are burns, cuts, and eye injuries. Serious accidents may arise from the snagging of parts because of improper loading, improper use of lubricating devices, and careless placement of hands and arms while the machine is in operation.

## *Polishing*

Polishing operations use abrasives that are mounted on prepared shaped wheels or on belts that provide a resilient backing. The stainless steel to be polished may be in either a smooth rolled or a previously ground condition. For the smooth rolled condition, the starting grit size should be selected in a range of 150 to 220. For the ground condition, the initial grit should be coarse enough to remove or smooth out any residual cutting lines or other surface imperfections left from grinding. In either instance, the treatment with the initial grit should be continued until a clean, uniform, blemish-free surface texture is obtained. The initial grit size to use on a preground surface may be set at about 20 numbers finer than the last grit used in grinding and may be changed, if necessary, after inspection. A tallow lubricant may be used to reduce the sharpness of cutting. With broad-belt grinding of stainless steel sheet, the use of a lubricant or coolant is mandatory.

After completion of the initial stage of polishing, wheels or belts are changed to provide finer grits. The step-up in fineness is usually by 30 to 40 numbers. Each succeeding treatment is continued until all residual marks of the preceding cut are removed. Grease in stick form is applied to wheels carrying abrasives of 150 mesh and finer. Aluminum oxide buffing compounds and powdered pumice are preferred for use with abrasives of 200 mesh and finer grit size.

**Polishing speeds** are generally somewhat higher than those used in grinding. A typical speed for a coated-wheel operation is 38 m/s (7500 sfm).

The same precautions that must be observed in the grinding of stainless steel are equally applicable to polishing:

- Avoidance of iron or other contamination
- Care of wheels and belts when not in use
- Restriction of the use of wheels and belts to stainless steel only
- Avoidance of excessive pressure while polishing
- Operation at proper speeds
- Avoidance of localized heat buildup because of dwelling at one spot
- Removal of loose cuttings and bits of abrasive from work surfaces before changing from one grit size to another

## *Buffing*

Buffed finishes are produced on stainless steel surfaces by using equipment, materials, and techniques that are similar to those used on other materials (see the article "Finishing Methods Using Multipoint or Random Cutting Edges" in this Volume). However, the skill needed for producing the high lusters obtainable on stainless steel is gained only through actual experience. Buffed finishes are not recommended for the stabilized grades of stainless steel, such as types 321 and 347, because these materials contain fine, hard particles of titanium or niobium compound that show up as pits on bright finishes.

The first step in applying a buffed finish of desired luster and color is that of providing a smooth surface, free of scratches and any other defects. For this reason, buffing is generally performed in two stages: the first is known as hard buffing (or cutting down); the second, as color buffing.

**Hard buffing** follows polishing, which generally ends with the use of abrasives of 200- to 250-mesh grit size. The fine scratches left by polishing are cut down with a buff that carries no previously glued on abrasive. Instead, such abrasive as is needed is applied intermittently to the buffing wheel as it rotates, either by rubbing a cutting compound in bar or stick form against it or by spraying it with a liquid compound. These cutting compounds contain (1) very fine artificial abrasives, such as $Al_2O_3$, of about 300-mesh grit size; and (2) a stiff grease or other material that acts as a binder. They adhere to the wheel by impregnating the cloth disks. Hard buffing may be conducted at from 33 m/s (6500 sfm) up to a maximum of 51 m/s (10,000 sfm).

**Color buffing** is performed in the same manner as hard buffing, except that a coloring compound is substituted for the cutting compound and speeds are held below 36 m/s (7000 sfm). Various compounds (rouges and other extremely fine abrasives) for use on stainless steel are available commercially, both in bar form for hand application and in liquid form for automatic application. The use of any material that may result in loss of corrosion resistance by stainless steel surfaces should be avoided.

**Direct color buffing,** without previous polishing or hard buffing, may be satisfactory for certain applications, such as:

- A color-buffing wheel may be applied directly on type 430 that has been given a finishing pass on a polished mill roll after final pickling.
- Small articles blanked from bright finished straight chromium steel strip and then tumbled for burr removal may have a satisfactory appearance if run under a color buff for brightening.
- Smooth, defect-free surfaces that have been electrolytically polished provide a good base for color buffing. By masking before buffing, contrasting surface effects can be obtained, as a result of the difference in reflectivity obtainable by electrolytic polishing and by color buffing.

Color buffing, however, does not remove scratches or other surface defects because cloth wheels without coarse abrasives, which are used for color buffing, do not remove surface imperfections. Therefore, the continued presence of such imperfections on finished products must be expected.

**Effect of Polishing and Buffing on Corrosion Resistance.** In addition to altering the appearance of stainless steels, polishing and buffing may have a considerable effect on the corrosion resistance of these materials. For example, a steel with a No. 2B finish as received from the mill has excellent corrosion resistance. This can be adversely affected by polishing with coarse abrasive, but it can be fully restored by polishing to a No. 4 finish or higher. Polishing to a No. 7 or 8 finish, by removing very fine pits and other surface defects, improves corrosion resistance over that afforded by the original No. 2B finish.

Tanks for storing raw milk provide a commercial example of the importance of a polished finish to sanitary and corrosion-resistance properties. According to the sanitary codes, these tanks must be made of 300-series stainless steel, and all surfaces that come in contact with the milk must be polished to a pit-free No. 4 finish or better. The high finish not only promotes sanitary properties, but also provides improved resistance to corrosion by the chlorine-bearing chemical used in scouring the tanks after each use.

Several polishing and buffing compounds contain iron and iron compounds, which can be highly deleterious to the corrosion resistance of stainless steel. The amount of iron in these compounds that can be tolerated is extremely small (for maximum protection, less than 0.01% Fe). If more than one polishing operation is involved, slightly more iron can be tolerated in the early stages of polishing, but the final stage should be virtually iron-free. Magnetic oxides of iron are as damaging as iron powder; the oxides generally occur in Turkish emery as well as in several synthetic abrasives. Their presence is most accurately determined by chemical analysis.

**Cleaning and Passivation After Buffing.** Cleaning is always required after a final buffing operation in which a surface finish of No. 4 or finer is achieved. The workpiece is vapor degreased or is cleaned with whiting (precipitated calcium carbonate), powdered chalk, or dehydrated lime, which is applied with a soft flannel cloth. This picks up the grease or lubricant from a color-buffing operation. The workpiece must then be protected from damage in handling.

Passivation is not required after buffing or fine polishing if the surface obtained is chemically clean and free of oil, grease, or adhesives used in the polishing media. A clean surface passivates itself naturally when it is exposed to air. However, if foreign metal, such as iron, has been picked up in the buffing operation, it must be removed by pickling or passivation.

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## Matching Mill Finishes

In the fabrication of No. 4 polished sheet, it frequently is necessary to refinish weld zones to blend them with the original finish. Although it is virtually impossible to match a machine-polished surface except by duplicating the original polishing, a close blending may be obtained by skillful use of manual methods.

If the original machine-polished lines are parallel with the line of the weld, the bead can be dressed down by grinding with a hard or soft wheel and then finished by polishing with, progressively, No. 80 and No. 120 (and possibly No. 150) grit on a setup wheel driven by a portable machine. The traversing of this wheel should be kept in line with the run of the bead so that its cut lines are kept parallel with those of the original machine-polished surface.

To avoid residual ridges or grooves, the metal of the joint should be brought flush with that of the base metal. For a given starting grit size, the depth of the scratches produced depends on the amount of use it has received; thus, samples should be run before starting on finish work.

If the machine-polished lines are not parallel with the line of the weld, final manual polishing should be done in the direction of the machine polishing. If the original polish lines on the two sides of a joint are not parallel with each other (for example, if they are parallel with the bead on one side and perpendicular to the bead on the other) the best procedure is to run the polishing cut lines along (not across) the bead. The girth weld between a tank shell and head exemplifies this problem. The cut lines of the shell extend around the unit and lie parallel with the girth joint, whereas the cut lines on the head are perpendicular, parallel, and at an angle around the periphery. Swinging such an assembly on the faceplate of a large lathe would permit repolishing the head and dressing the weld joint on the same setup, thus rendering parallel all of the cut lines on the head, joint, and shell. For this application, abrasive paper (or pieces cut from a belt) may be backed up with a block of wood or some softer material and guided by hand along the line of the weld joint.

## Electrocleaning and Electropolishing

**Electrocleaning,** an electropolishing technique, is a useful alternative to pickling treatments (Ref 5). Although electrocleaning is not covered under ASTM A 380, it is widely used to remove imperfections from the surface of stainless steel after fabrication. It removes embedded iron particles and similar film defects as does pickling. Unlike pickling, electrocleaning does not roughen the surface, but makes it smoother. A 12 V dc power source with variable current capability is connected to the stainless steel, making it the anode. A copper cathode and an electrolyte--usually phosphoric acid ($H_3PO_4$)--are then used to corrode away the protective film and several layers of the surface in a controlled manner by varying the current and dwell time.

Electrocleaning can be performed in most plating shops by immersion. Localized electrocleaning with field kits is widely practiced to remove heat tint and weld-related defects from the heat-affected zone (see Fig. 3).

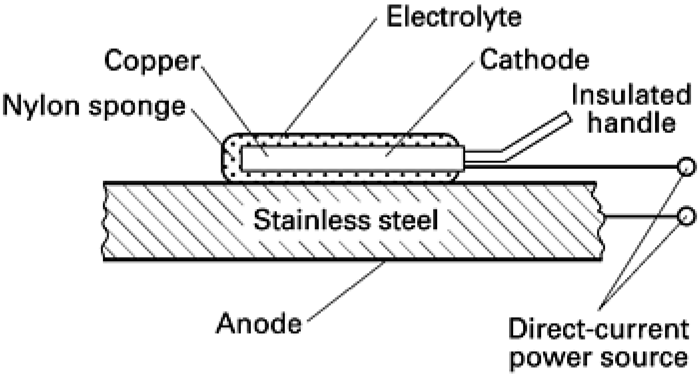

**Fig. 3 Equipment for localized electrocleaning of heat tint from the surface of stainless steel. Source: Ref 5**

**Electropolishing** is the same process as electrocleaning, but is generally performed for a longer time (Ref 5). Electropolishing is used primarily to produce a very smooth, bright, easily cleaned surface with maximum corrosion resistance. It removes the surface layer of a metal by anodic treatment in an acid bath. Conditions for electropolishing of stainless steels in acid electrolytes are given in Table 10.

**Table 10 Conditions for electropolishing in acid electrolytes**

| **Type of metal (and product)** | **Purpose of treatment** | **Bath volume** | | **Installed power** | | **Current density** | | **Polishing cycle, min** | **Daily production** | | | **Operators** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | **No. of parts** | **Area** | | |
| | | **L** | **gal** | **A** | **V** | **A/dm$^2$** | **A/ft$^2$** | | | **m$^2$** | **ft$^2$** | |
| **Sulfuric-phosphoric acid electrolytes** | | | | | | | | | | | | |
| 302 and 430 stainless (job-shop work) | Bright finish | 1150 | 300 | 1500 | 15 | 30 | 300 | 3-8 | 3500 | 25 | 250 | 2 |
| 302 and 202 stainless (plumbingware) | Bright finish | 1150 | 300 | 1500 | 12 | 30 | 300 | 3-4 | 1000-2000 | . . . | . . . | 1 |
| 303 stainless (food-processing equipment) | Bright finish | 2650 | 700 | 2500 | 18 | 20 | 200 | 4-10 | 400-500 | 190-370 | 2000-4000 | 2 |
| Series 300 and 400 stainless (job-shop work) | Various | 2250 | 600 | 3000 | 18 | . . . | . . . | 10(avg) | 25-400 | 5-45 | 50-500 | 2 |
| 304 stainless | Brighten; deburr | 1300 | 350 | 2000 | 12 | 30 | 300 | 4 | 3000 | 55-75 | 600-800 | 1 |
| Stainless steel (aircraft components) | . . . | 2650 | 700 | 3000 | 18 | 25-30 | 250-300 | 5 | 200 | 30 | 300 | 1 |
| 430 stainless | Bright finish | 1500 | 400 | 1500 | 14 | . . . | . . . | 1-2 | 7000 | 75 | 800 | 1 |
| 430 stainless (trim items) | Brighten; deburr | 1500 | 400 | 750 | 18 | . . . | . . . | 3 | 12,000 | 230 | 2500 | 1 |
| 430 stainless (automotive trim) | Bright finish | 3800 | 1000 | 3000 | 18 | 30 | 300 | 4 | 250/h | . . . | . . . | 1 |
| 430 stainless (automotive rain shields) | Bright finish | 3800 | 1000 | 3000 | 18 | 25 | 250 | 5 | 450/h | . . . | . . . | 1 |
| Stainless and carbon steels (job-shop work) | Brighten; deburr | 1500 | 400 | 1500 | 12 | 25-40 | 250-400 | Varies | Varies | . . . | . . . | 1 |
| **Sulfuric-phosphoric-chromic acid electrolytes** | | | | | | | | | | | | |

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 302 stainless (surgical instruments) | Smooth; polish | 3600 | 950 | 3000 | 18 | 30 | 300 | 5 | 5000 | . . . | . . . | 1 |

Electropolishing is applicable to all stainless steel grades, hot or cold finished, cast or wrought. The amount of metal removed is subject to close control, depending on the desired result. The resulting surfaces have a bright, passive finish. The process is most frequently applied to cold-finished surfaces, because they yield a smoother finish than can conventionally be obtained on hot-finished surfaces. As in electroplating, the results depend on the contour and shape of the part. The end-grain surfaces of the free-machining stainless grades, such as types 303 and 416, will appear frosty after electropolishing due to removal of the sulfide inclusions.

Electropolishing can be used as a preliminary brightening operation before final buffing, particularly on drawn parts with burrs, sharp radii, or recessed areas, and it serves to reduce the amount of buffing required. Electropolishing is applied to decorative automotive parts and accessories, conveyor systems for food-handling equipment, animal cages, and pharmacy equipment. It provides an economical finish on many parts that are difficult or impossible to finish by conventional polishing, such as items made from wire.

In contrast to mechanical finishing methods, electropolishing may make inclusions in the material more visible. Some types of inclusions are dissolved out, whereas others remain in relief. Electropolishing has been used as a surface inspection technique to reveal residual foreign material, such as embedded scale and particles of iron, carbide precipitation, and weld defects. The surface obtained by electropolishing is directly related to the original surface quality--the process cannot be used to remove digs, gouges, scratches, and the like.

**Chemical polishing** is another method for providing a smooth and bright surface on stainless steel. Unlike electropolishing, chemical polishing can be done without the use of electricity and without racking of individual parts. Thus, chemical polishing offers significant savings in capital investment and labor. In addition, chemical polishing offers a greater degree of freedom in polishing items with blind holes and other recessed areas. However, it does not produce the high specular reflectivity (brightness) obtained with electropolishing.

Proprietary products for chemical polishing are available on the market. Generally, they are based on combinations of $H_3PO_4$, $HNO_3$, $H_2SO_4$, hydrochloric acid (HCl), organic acids, and special surfactants and stabilizers to promote a high degree of brightness and long bath life. Unlike the $HNO_3$-HF mixtures that are used in chemical cleaning, the proprietary chemical bright dips do not cause severe attack on the grain boundaries or intergranular corrosion.

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## Passivation Treatments

Exposure to air is the natural, primary passivation treatment for stainless steel. This exposure produces a thin, durable chromium oxide film that forms rapidly on the alloy surface and gives stainless steel its characteristic "stainless" quality. Exposure of the surface to water or other oxidizing environments also produces this passivating film. Additional passivation is called for in many specifications to remove light surface contamination from machined stainless steel parts, including shop dirt, iron particles from cutting tools, and machining lubricants. Passivation treatments of stainless steel with $HNO_3$ or mild organic acids are useful mild cleaning operations performed after machining to enhance the protective nature of the natural, air-formed film. Nitric acid treatment enhances the level of chromium in the protective film on stainless steels. DeBold (Ref 6) has published an excellent practical review of $HNO_3$ passivation of stainless steel machined parts.

ASTM A 380 (Ref 1) describes eight $HNO_3$-based cleaning/passivation treatments and four cleaning treatments using other chemicals (Table 11). None of these passivation treatments corrodes or etches the surface. Several are designed to clean bright or polished surfaces by removing loosely adherent foreign matter. The most common treatment is immersion in a 20 to 40% solution of $HNO_3$ at a temperature of 50 to 60 °C (120 to 140 °F).

**Table 11 Acid cleaning and passivation of stainless steel**

| **Alloy** | **Condition** | **Treatment** | | | | |
|---|---|---|---|---|---|---|
| | | **Code** | **Solution, vol%(a)** | **Temperature** | | **Time, min** |
| | | | | **°C** | **°F** | |
| **Part 1: Cleaning with $HNO_3$-HF** | | | | | | |
| *Purpose:* For use after descaling by mechanical or other chemical methods as a further treatment to remove residual particles of scale or products of chemical action (i.e., smut), and to produce a uniform "white pickled" finish | | | | | | |
| 200 and 300 series, 400 series containing 16% Cr or more, and precipitation-hardening alloys (except free-machining alloys) | Fully annealed only | D | 6-25% $HNO_3$ plus $\frac{1}{2}$ to 8% HF(b)(c) | 20-60 | 70-140 | As necessary |
| Free-machining alloys, maraging alloys, and 400 series containing less than 16% Cr | Fully annealed only | E | 10% $HNO_3$ plus $\frac{1}{2}$ to 1 $\frac{1}{2}$% HF(b)(c) | 20 (up to 60 with caution) | 70 (up to 140 with caution) | 1-2 |
| **Part 2: Cleaning/passivation with $HNO_3$solution** | | | | | | |
| *Purpose:* For removal of soluble salts, corrosion products, and free ion and other metallic contamination resulting from handling, fabrication, or exposure to contaminated atmospheres | | | | | | |
| 200 and 300 series, 400 series, precipitation hardening and maraging alloys containing 16% Cr or more (except free-machining alloys)(d) | Annealed, cold rolled, or work hardened, with dull or nonreflective surfaces | F | 20-50% $HNO_3$ | 50-70 | 120-160 | 10-30 |
| | | | | 20-40 | 70-100 | 30-60(c) |
| | Annealed, cold rolled, or work hardened, with bright-machined or polished surfaces | G | 20-40% $HNO_3$ plus 2-6 wt% $Na_2CrSO_7 \cdot 2H_2O$ | 50-70 | 120-155 | 10-30 |
| | | | | 20-40 | 70-100 | 30-60(c) |
| 400 series, maraging and precipitation-hardening alloys containing less than 16% Cr, and high-carbon/straight-chromium alloys (except free-machining alloys)(d) | Annealed or hardened, with dull or nonreflective surfaces | H | 20-50% $HNO_3$ | 45-55 | 110-130 | 20-30 |
| | | | | 20-40 | 70-100 | 60 |
| | Annealed or hardeneith bright-machined or polished surfaces | I(f) | 20-25% $HNO_3$ plus 2-6 wt% $Na_2Cr_2O_7 \cdot 2H_2O$ | 50-55 | 120-130 | 15-30 |
| | | | | 20-40 | 70-100 | 30-60 |

|  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|
| 200, 300, and 400-series free-machining alloys(d) | Annealed or hardened, with bright-machined or polished surfaces | J(f) | 20-50% $HNO_3$ plus 2-6 wt% $Na_2Cr_2O_7 \cdot 2H_2O$(g) | 20-50 | 70-120 | 25-40 |
|  |  | K(e) | 1-2% $HNO_3$ plus 1-5 wt% $Na_2Cr_2O_7 \cdot 2H_2O$ | 50-60 | 120-140 | 10 |
|  |  | L(f) | 12% $HNO_3$ plus 4 wt% $CuSO_4 \cdot 5H_2O$ | 50-60 | 120-140 | 10 |
| Special free-machining 400-series alloys with more than 1.25% Mn or more than 0.40% S(d) | Annealed or hardened, with bright-machined or polished surfaces | M(f) | 40-60% $HNO_3$ plus 2-6 wt% $Na_2Cr_2O_7 \cdot 2H_2O$ | 50-70 | 120-160 | 20-30 |
| **Part 3: Cleaning with other chemical solutions** |  |  |  |  |  |  |
| 200, 300, and 400 series (except free-machining alloys), precipitation hardening and maraging alloys | Fully annealed only | N | 1 wt% citric acid plus 1 wt% $NaNO_3$ | 20 | 70 | 60 |
|  |  | O | 5-10 wt% ammonium citrate | 50-70 | 120-160 | 10-60 |
| Assemblies of stainless and carbon steel (for example, heat exchanger with stainless steel tubes and carbon steel shell) | Sensitized | P | Inhibited solution of 2 wt% hydroxyacetic acid and 1 wt% formic acid | 95 | 200 | 6 h |
|  |  | Q | Inhibited ammonia-neutralized solution of EDTA (ethylene-diamene-tetraacetic acid) followed by hot-water rinse and dip in solution of 10 ppm ammonium hydroxide plus 100 ppm hydrazine | Up to 120 | Up to 250 | 6 h |

Source: Ref 1

(a) Solution prepared from reagents of following weight percent: $HNO_3$, 67; HF, 70.

(b) For reasons of convenience and handling safety, commercial formulations containing fluoride salts may be found useful in place of HF for preparing $HNO_3$-HF solutions.

(c) After acid cleaning and water rinsing, a caustic permanganate solution containing 10 wt% NaOH and 4 wt% $KMnO_4$, 70 to 80 °C (160 to 180 °F) 5 to 60 min, may be used as a final dip for removal of smut, followed by thorough water rinsing and drying.

(d) The purchaser shall have the option of specifying in his purchase documents that all 400-series ferritic or martensitic parts receive additional treatment as follows: Within 1 h after the water rinse following the specified passivation treatment, all parts shall be immersed in an aqueous solution containing 4 to 6 wt% $Na_2Cr_2O_7 \cdot 2H_2O$, at 60 to 70 °C (140 to 160 °F) 30 min. This immersion shall be followed by thorough rinsing with clean water. The parts then shall be thoroughly dried.

(e) Shorter times may be acceptable where established by test and agreed upon by the purchaser.

(f) The high-carbon and free-machining alloys may be subject to etching or discoloration in nitric acid. This tendency can be minimized by the use of high acid concentrations with inhibitors such as $Na_2Cr_2O_7 \cdot 2H_2O$ and $CuSO_4 \cdot 5H_2O$. Oxidizing action increases with increasing concentration of nitric acid; additional oxidizing action is provided by $Na_2Cr_2O_7 \cdot 2H_2O$. Avoid acid cleaning when possible; use mechanical cleaning followed by scrubbing with hot water and detergent, final thorough water rinsing, and drying.

(g) If flash attack (clouding of stainless steel surface) occurs, a fresh (clean) passivating solution or a higher $HNO_3$ concentration will usually eliminate it.

The complete passivation treatment includes degreasing, immersion, and rinsing. Degreasing, preferably in a nonchlorinated solvent, removes organic contaminants from the surface.

**Degreasing.** Neither air nor $HNO_3$ can form or enhance the protective film when grease, oil, fingerprints, or other organic contamination is present on the surface. Parts must be thoroughly degreased prior to any passivation treatment. The water-break test, described in ASTM A 380 (Ref 1), is easy to apply and is effective in detecting residual organic matter that may not have been removed in the degreasing operation. A sheet of water directed over the surface will "break" around oil, grease, and other organic contaminants not completely removed from the surface. Specifications can simply call for no break in the film as it drains from the vertical surface.

**Immersion.** The part is immersed in a passivating solution selected from Table 11 (Part 2 or 3). In addition to the standard $HNO_3$ solution, there are a number of solution variations appropriate for all grades of 200, 300, and 400 series, maraging, precipitation hardening, and free-machining alloys in various heat treatment conditions and surface finishes.

**Rinsing.** Immediate and thorough rinsing in clean water of pH 6 to 8 is mandatory. In many instances neutralization prior to rinsing is helpful. Immersion, neutralization, and rinsing must follow one another without allowing the surface to dry between steps. When passivating stainless steel sheet material, each sheet must be completely dry before it is stacked to avoid marks.

In addition to the cleaning precautions given in ASTM A 380 (Ref 1), different grades of stainless steel should not be mixed in the same passivating bath, as this can initiate corrosion where surfaces come in contact.

Although $HNO_3$ does not normally corrode stainless steel, it will corrode surfaces that are significantly altered. Acid cleaning should not be used for carburized and nitrided stainless steel parts or for improperly heat-treated high-carbon/high-chromium martensitic grades that have not been fully hardened.

**Passivating Free-Machining Steels.** The procedure for passivating free-machining stainless steels is somewhat different from that used for non-free-machining grades; that is because sulfides of sulfur-containing free-machining grades, that are totally or partially removed during passivation, create microscopic discontinuities in the surface of the machined part. Even normally efficient water rinses can leave residual acid trapped in these discontinuities after passivation. This acid can then attack the surface of the part unless it is neutralized or removed. For this reason, a special passivation process is required for free-machining grades.

The alkaline-acid-alkaline (A-A-A) method described in Ref 6 neutralizes trapped acid and is accomplished in less than two hours. The A-A-A method consists of the following steps:

- After degreasing, the parts are soaked for 30 min in a 5% solution of sodium hydroxide at 70 to 80 °C (160 to 180 °F)
- Water rinse
- The parts are then immersed for 30 min in a 20% $HNO_3$ solution containing 22 g/L (3 oz/gal) of sodium dichromate at 50 to 60 °C (120 to 140 °F)
- Water rinse
- Immerse the part for another 30 min in the sodium hydroxide solution at 70 to 80 °C (160 to 180 °F)

- Water rinse and dry (passivation is now complete)

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## References cited in this section

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## Electroplating

Stainless steels may be plated with copper, brass, chromium, nickel, cadmium, and the precious metals for such purposes as:

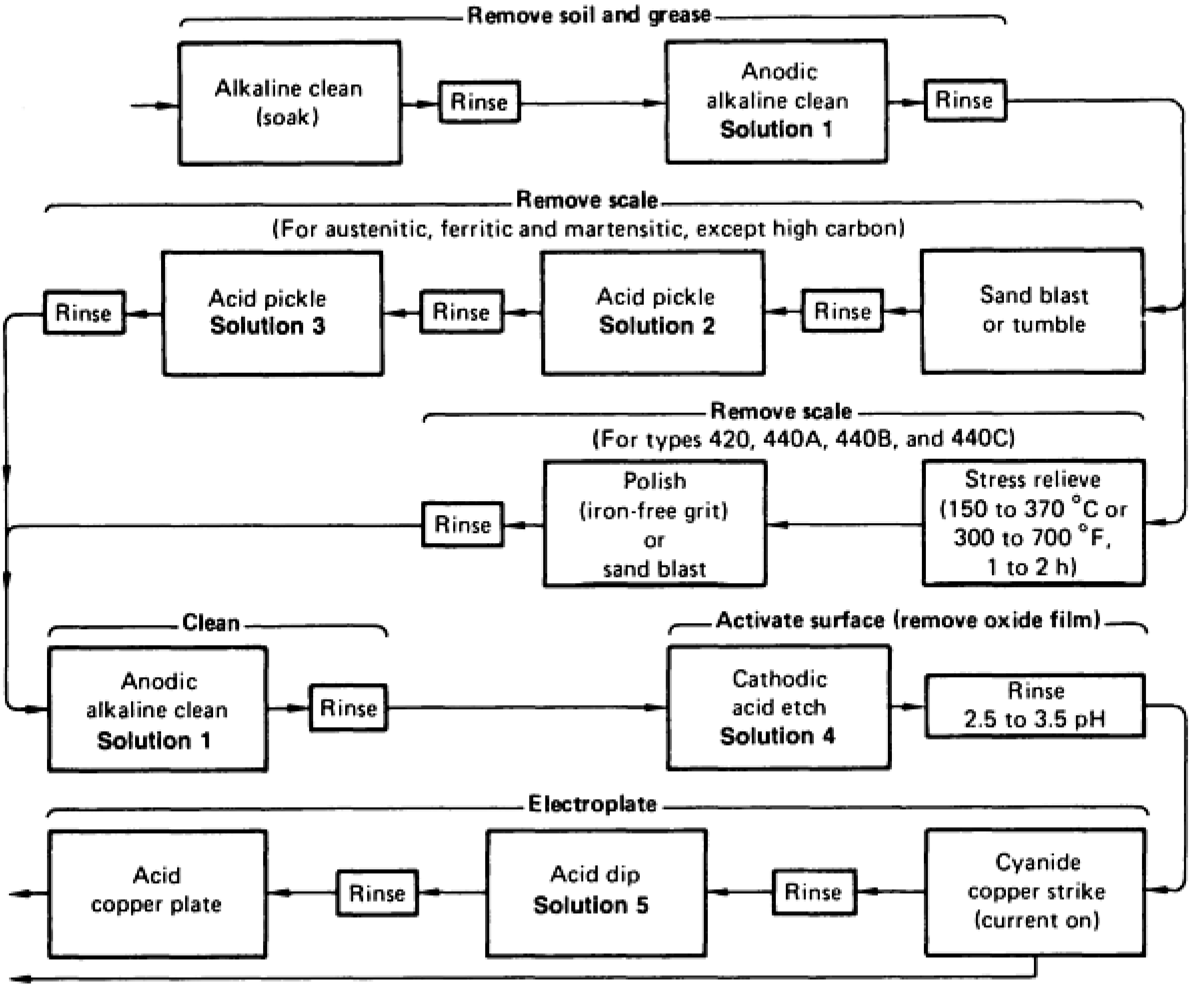
- Color matching
- Lubrication during cold heading, spring coiling, or wire drawing
- Reduction of scaling at high temperature
- Improvement of wettability or of conductance of heat or electricity
- Prevention of galling
- Decorative uses in such applications as jewelry
- Prevention of superficial rusting

Detailed information on plating bath compositions, control of bath composition, bath temperature, plating equipment, process limitations or advantages, and applications for electrodeposits can be found in the articles contained in the Section on "Plating and Electroplating" in this Volume.

Although a stainless steel surface may be clean and scale-free, an adherent electrodeposit cannot be obtained until the surface is activated for removal of its normally ever-present oxide film. Activation, which is performed immediately before plating, may be accomplished by cathodic treatments, immersion treatments, or simultaneous activation-plating treatments. These treatments, together with other procedures necessary for preparing stainless steel for electroplating, are fully described in ASTM B 254 (Ref 7).

Figure 4 summarizes some of the data from ASTM B 254. The same cleaning procedures would be appropriate before electrodeposition of other metals. When preparing stainless steel for electroplating, the following should be considered:

- *Electrocleaning:* When bright plating is desired, the alkalinity, current density, and temperature of the cleaning bath should be kept as low as possible, especially for the high-chromium alloys. To minimize the severity of electrocleaning when a bright finish is desired, a short electropolishing treatment may be used in lieu of electrocleaning, provided that the preliminary cleaning is adequate.
- *Acid pickling:* Freshly prepared pickling baths should be activated by dissolving some iron in them before using the bath; otherwise, the rate of pickling is slow until the bath has dissolved some iron from the steel being treated.
- *Activating:* The activation step is the most important in surface preparation of stainless steel for electroplating. If the simultaneous activation-plating treatment is used, where the anodes are nickel, the nickel content of the solution gradually increases because of the low cathode efficiency. This can be compensated for by removing a portion of the solution and replenishing with HCl. The activation-plating treatment is usually preferred for stainless steel parts that are to be copper plated.
- *Plating:* After activating and rinsing, the work should be entered directly into the electrolyte. When possible, the rinse water should be slightly acid (2.5 to 3.5 pH); the required acidity is usually provided by the dragout of acid from the activation treatment. Stainless steel has much lower electrical conductivity than most other metals, and thus adequate attention should be paid to racking when introducing work into copper electrolyte, to ensure an adequate number of contacts to obtain complete coverage in minimum time.



| **Solution no.** | **Type of solution** | **Composition of solution** | **Operating temperature** | | **Cycle time, min** |
|---|---|---|---|---|---|
| | | | **°C** | **°F** | |
| 1 | Anodic alkaline cleaner[a] | Alkali, as low as possible | [b] | [b] | [b] |
| 2 | Acid pickle | $H_2SO_4$, 8-11% | 65-70 | 150-70 | 10-45 |
| 3 | Acid pickle | $HNO_3$, 6-10 vol%; HF, 1.5 vol% | Room temperature | Room temperature | 10-30 |
| 4 | Cathodic acid etch[c] | $H_2SO_4$, 5-15 vol% | Room temperature | Room temperature | 1-5[d] |

(a) Current density, as low as possible.

(b) As low as possible.

(c) Current density, 54 A/m$^2$ (5 A/ft$^2$).

(d) After subsequent rinse, place parts into copper electrolyte while parts are still wet

**Fig. 4 Electroplating copper on stainless steels**

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## Reference cited in this section

7. "Standard Practice for Preparation of and Electroplating on Stainless Steel," B 254, *Annual Book of ASTM Standards,* ASTM, 1988

## Other Coating Processes (Ref 2)

**Painting.** In the painting of stainless steel surfaces, the main requirement to be satisfied is that of providing a good permanent bond. Stainless steel surfaces are dense, hard, and smooth, particularly when in the cold-rolled or polished condition. For that reason, it is usually advisable to roughen them by means of strong pickling or sandblasting. The latter is advantageous because it can be readily confined to limited areas by masking.

In the transportation industry, acid etching is usually favored as a preliminary step in painting stainless steels. The etchants are solutions of either HCl or HF:

### Solution 1

- 25 parts water by volume
- 75 parts HCl by volume
- 5 parts $HNO_3$ by volume
- 20 wt% $FeCl_3$

### Solution 2

- 10 to 20 vol% $HNO_3$
- 3 to 5 vol% HF
- Remainder water

The stainless steel has either a No. 2D or 2B finish. Paint companies are best qualified to suggest paint types and procedures for prime and finish coats.

Cleanliness is a key element in painting stainless steels. The surface must be clean, and it is good practice to paint only in a clean, dust-free atmosphere. Use thin coats and allow plenty of time to dry between coats.

Sandblasting is best accomplished with clean, hard sand of relatively small grit size driven by an air blast that is entirely free of compressor oil. (Glass beads are sometimes used.) Thin-gage material should be backed up to avoid distortion. Surfaces should be dry and completely free of grease, oil, or any other foreign material before applying the ground coat. More detailed information on the selection and application of various paint types can be found in the article "Painting" in this Volume.

**Surface Blackening.** Stainless steel surfaces can be readily blackened by immersion in a molten salt bath of sodium dichromate. This practice, which is not complicated to set up and operate, is widely used by the automotive industry to blacken stainless steel parts, such as windshield wipers, and it is used by manufacturers of stainless steel solar collector panels.

The process applies a very thin, smooth black oxide film to the surface of all stainless steel types. The film is normally dull black in color, but it can be brightened by the application of oils or waxes. The film shows no tendency to age or lose color in service. It is ductile, will not chip or peel, and is resistant to heating to the normal scaling temperature of the stainless steel. A blackened stainless steel can be deformed moderately without harm, and the film exhibits good resistance to abrasion.

The salt bath operates at approximately 400 °C (750 °F), and dip time varies from 5 to 30 min, followed by a wash-water rinse. Solar panels achieve an ideal blackening in 5 min, while auto trim parts require about 30 min to obtain a deeper black color.

**Coloring.** A proprietary process used for coloring stainless steels involves immersing the material in a hot chromic-sulfuric acid solution, followed by a cathodic hardening treatment in another acidic solution. The reaction of the base material with the hot acid produces a transparent film which in itself is basically colorless, but which shows colors through the phenomenon of light interference. Colors produced, in normal time sequence, are bronze, blue, gold, red, purple, and green, and within this range a wide variety of shades are possible. A black finish is also available. Appearance is also dependent on the nature of the starting surface: matte and satin surfaces produce matte colors; polished surfaces exhibit a high degree of metallic luster. The process is being used throughout the world for architectural applications, furniture, bathtubs, consumer products, and automotive trim.

Different effects can be achieved, for example, by alternating bright polished and satin finished sheets, by selective polishing prior to coloring, and by using cold-embossed colored stainless steel. Masking, screen printing, and photo-resist techniques can be employed to achieve patterned effects and for the reproduction of photographic images. Colored stainless steel can be subjected to considerable deformation without detriment. It can, for example, be drawn, bent through quite sharp angles, and embossed without any deleterious effects or reduction of color intensity. Corrosion resistance of colored stainless is at least as good as that of the untreated material, and exposure tests extending over a number of years have shown no deterioration of color.

**Terne coatings** can be applied to stainless steels by hot dipping sheet in a lead-tin alloy that typically consists of 80% Pb and 20% Sn. Terne coatings were used as early as the 11th century on church roofs in western Europe. Terne-coated stainless steel, however, was introduced only in the 1960s. Since then it has grown in popularity, particularly for architectural (roofing) applications, because of its strength, long life, and attractive patina acquired with age.

The stainless steel that forms the core is usually S30400 or S31600. As well as providing corrosion resistance, the stainless steel offers superior strength and ductility compared to other roofing materials and, because of its high-temperature strength, provides enhanced structural integrity and safety in case of fire.

The terne-coated stainless steel sheet (minimum of 20 μm of coating per side) weathers in one to two years to a uniform gray, the precise shade depending on the sulfur content of the atmosphere. The result is a material with an aged appearance that can blend in with existing roofing or give a new building a distinctive appearance. Because terne coatings are anodic to stainless steel, corrosion resistance can be further improved.

**Thermal Spraying.** Wear-resistant coatings and thermal barrier coating systems have been applied to stainless steel substrates by plasma spraying and high-velocity oxyfuel (HVOF) thermal spray processes. Most of the work has centered around the use of stainless steels, such as S17400 (17-4 PH), in diesel engines. Plasma sprayed thermal barrier coatings on 17-4 PH piston rings include composite zirconia ($ZrO_2$)/NiCrAlY coatings (Ref 8). Wear resistant coatings include $Cr_3C_2$-20% NiCr cermets deposited by the HVOF process and plasma sprayed chromium oxide-based coatings (Ref 9).

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8. R.C. Brink, Material Property Evaluation of Thick Thermal Barrier Coating Systems, *Trans. ASME, Journal*

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9. M.G.S. Naylor, "Development of Wear-Resistant Ceramic Coatings for Diesel Engine Components, Volume 1: Coating Development and Tribological Testing," ORNL/Sub/87-SA581/1, Oak Ridge National Laboratory, June 1992

## Surface Modification

Surface modification is the alteration of surface composition or structure by the use of energy or particle beams. Elements may be added to influence the surface characteristics of the substrate by the formation of alloys, metastable alloys or phases, or amorphous layers. Surface-modified layers are distinguished from conversion or coating layers by their greater similarity to metallurgical alloying versus chemically reacted, adhered, or physically bonded layers.

**Ion implantation** is one of a number of surface modification processes that is emerging as an economical and viable process for improving the near-surface tribological properties of engineering components. In many engineering situations, material selection is often based on a compromise of bulk mechanical properties and near-surface tribological properties, with neither at their optimum values. As a result, there is considerable interest in fabrication processes, such as ion implantation, that make it possible to retain the bulk properties of a given compound yet still achieve desirable tribological properties in near-surface regions.

Ion implantation is a process by which virtually any element in the periodic chart can be injected into near-surface regions of any solid using a beam of high-velocity ions with energies typically ranging from 10 keV up to several MeV. As the ions slow down in the material, they are distributed at depths ranging from a few nanometers to several micrometers, depending on the particle energy, angle of incidence, and substrate composition. Depending on the ion type, mass, energy, dose, deposition temperature, and substrate composition, the chemical, electrical, thermal, microstructural, and crystallographic properties of near-surface regions can be significantly altered to improve the friction and wear performance of the component.

Examples of end-use applications of ion implanted stainless steels are bearing rings and ball bearings made from S44004 (type 440C) that are used in the Space Shuttle (Ref 10). The corrosive wear performance of the bearing rings was improved by implanting chromium plus nitrogen (CrN) ions. Significantly lower friction and wear rates were achieved in the ball bearings via ion implantation with titanium plus carbon (TiC) ions and titanium ions alone.

**Laser surface processing** includes laser transformation hardening, laser melting, laser alloying, laser cladding, and laser melt/particle injection. Of these five method, laser alloying and laser melt/particle injection have been carried out the most on stainless steels. A review of laser surface processing can be found in Ref 11.

***Laser Alloying.*** A technique of localized alloy formation is laser surface melting with the simultaneous, controlled addition of alloying elements in powder form. These alloying elements diffuse rapidly into the melt pool, and the desired depth of alloying can be obtained in a short period of time. By this means, a desired alloy chemistry and microstructure can be generated on the sample surface; the degree of microstructural refinement will depend on the solidification rate.

Laser surface alloying was performed to incorporate molybdenum in type 304 stainless steel (Ref 12). The 304-3Mo material was similar in pitting resistance to type 316 stainless steel. The 304-9Mo material was superior to type 316 stainless steel and showed no pitting up to oxygen evolution potentials. Table 12 shows some of the results for the 304-Mo materials.

**Table 12 Effect of laser surface alloying with molybdenum on pitting potentials of austenitic stainless steels in 0.1 *M* NaCl**

| Sample | Composition, % | | | Pitting potential ($E_{pit}$), (V vs SCE) |
|---|---|---|---|---|
| | Cr | Ni | Mo | |
| Type 304 | 18-20 | 8-10 | 0 | 0.300 |

|  |  |  |  |  |
|---|---|---|---|---|
| Type 316 | 16-18 | 10-14 | 2-3 | 0.550 |
| 304-3Mo | 18.9 | 9.1 | 3.7 | 0.500 |
| 304-9Mo | 19.2 | 11.7 | 9.6 | Did not pit |

***Laser melt/particle injection*** produces an *in situ,* metal-matrix/particulate composite surface layer by mixing, but not melting, the second phase with the substrate. The particulate material is injected with sufficient velocity as a spray into the melt pool formed by the laser beam. If the second phase is hard, such as a carbide, the injected layer can be made to resist wear. Reference 13 describes the processing and properties of a type 304 stainless steel workpiece that was injected with titanium carbide.

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## Surface Hardening

In certain applications, surface hardening is performed to improve the resistance of stainless steel alloys to galling and wear through the formation of hard dispersions. The more soft, tough interior of the alloy remains unaffected, and thus provides impact resistance. The process encompasses a variety of techniques, including nitriding, carburizing, boriding, and flame hardening.

### *Gas Nitriding*

Gas nitriding is a case-hardening process whereby nitrogen is introduced into the surface of an alloy by holding the metal at a suitable temperature in contact with a nitrogenous gas, usually ammonia. Quenching is not required for the production of a hard case. The nitriding temperature for all steels is between 495 and 565 °C (925 and 1050 °F).

Because of the absence of a quenching requirement, with attendant volume changes, and the comparatively low temperatures employed in this process, nitriding produces less distortion and deformation than either carburizing or conventional hardening. Some growth occurs as a result of nitriding, but volumetric changes are relatively small. Although at suitable temperatures all steels are capable of forming iron nitrides in the presence of nascent nitrogen, nitriding results are more favorable in those steels that contain one or more of the major nitride-forming alloying elements. Aluminum is the strongest nitride former, but chromium can approximate the results obtainable with aluminum if the chromium content is high enough.

Because of their chromium content, all stainless steels can be nitrided to some degree. Although nitriding adversely affects corrosion resistance, it increases surface hardness and provides a lower coefficient of friction, thus improving abrasion resistance.

**Austenitic and Ferritic Alloys.** Austenitic stainless steels of the 300 series are the most difficult to nitride; nevertheless, types 301, 302, 303, 304, 308, 309, 316, 321, and 347 have been successfully nitrided. These nonmagnetic alloys cannot be hardened by heat treating; consequently, core material remains relatively soft, and the nitrided surface is limited as to the loads it can support. This is equally true of the nonhardenable ferritic stainless steels. Alloys in this group that have been satisfactorily nitrided include types 430 and 446. With proper prior treatment, these alloys are somewhat easier to nitride than the 300-series alloys.

**Hardenable Alloys.** The hardenable martensitic alloys are capable of providing high core strength to support the nitrided case. Hardening, followed by tempering at a temperature that is at least 15 °C (25 °F) higher than the nitriding temperature, should precede the nitriding operation. Precipitation-hardening alloys, such as 17-4 PH, 17-7 PH, and A-286, also have been successfully nitrided.

**Prior Condition.** Before being gas nitrided, 300-series steels and nonhardenable ferritic steels should be annealed and relieved of machining stresses. The normal annealing treatments generally employed to obtain maximum corrosion resistance are usually adequate. Microstructure should be as nearly uniform as possible. Observance of these prior conditions will prevent flaking or blistering of the nitrided case. Martensitic steels should be in the quenched and tempered condition.

A special pretreatment for 410 stainless steel is hardening from a lower than normal temperature. This results in a very uniform nitrided case with reduced internal stresses. Cracking or spalling of the case is avoided; formation of brittle grain-boundary carbonitrides is suppressed. Austenitizing at 860 °C (1580 °F), followed by tempering at 595 °C (1100 °F), uniformly distributes carbides and provides low residual stress. Case growth is accommodated by a hardness of about 25 HRC.

**Surface Preparation.** The nitriding of stainless steels requires certain surface preparations that are not required for nitriding low-alloy steels. Primarily, the film of chromium oxide that protects stainless alloys from oxidation and corrosion must be removed. This can be accomplished by dry honing, wet blasting, pickling, chemical reduction in a reducing atmosphere, submersion in molten salts, or one of several proprietary processes. Surface treatment must precede placement of the parts in the nitriding furnace. If there is any doubt of the complete and uniform depassivation of the surface, further reduction of the oxide may be accomplished in the furnace by means of a reducing hydrogen atmosphere or halogen-based proprietary agents. Of course, hydrogen must be dry (free of water and oxygen).

Before being nitrided, all stainless parts must be perfectly clean and free of embedded foreign particles. After depassivation, care should be exercised to avoid contaminating stainless surfaces with fingerprints. Sharp corners should be replaced with radii of not less than 1.6 mm ($\frac{1}{16}$ in.).

**Nitriding Cycles.** In general, stainless steels are nitrided in single-stage cycles at temperatures from about 495 to 595 °C (925 to 1100 °F) for periods ranging from 20 to 48 h, depending on the depth of case required. Dissociation rates for the single-stage cycle range from 20 to 35%; a two-stage cycle using 15 to 30% in the first phase and 35 to 45% in the second phase is also used. Thus, except for the prior depassivation of the metal surface, the nitriding of stainless steels is similar to the single-stage nitriding of low-alloy steels.

**Nitriding Results.** Hardness gradients are given in Fig. 5 for types 302, 321, 430, and 446. These data are based on a 48-h nitriding cycle at 525 °C (975 °F), preceded by suitable annealing treatments. A general comparison of the nitriding characteristics of series 300 and 400 steels is presented in Fig. 6; the comparison reflects the superior results that are obtained with series 400 steels, as well as the effects of nitriding temperature on case depth. Data are plotted for single-stage nitriding at temperatures of 525 and 550 °C (975 and 1025 °F). For steels of both series, greater case depths were obtained at the higher nitriding temperature.

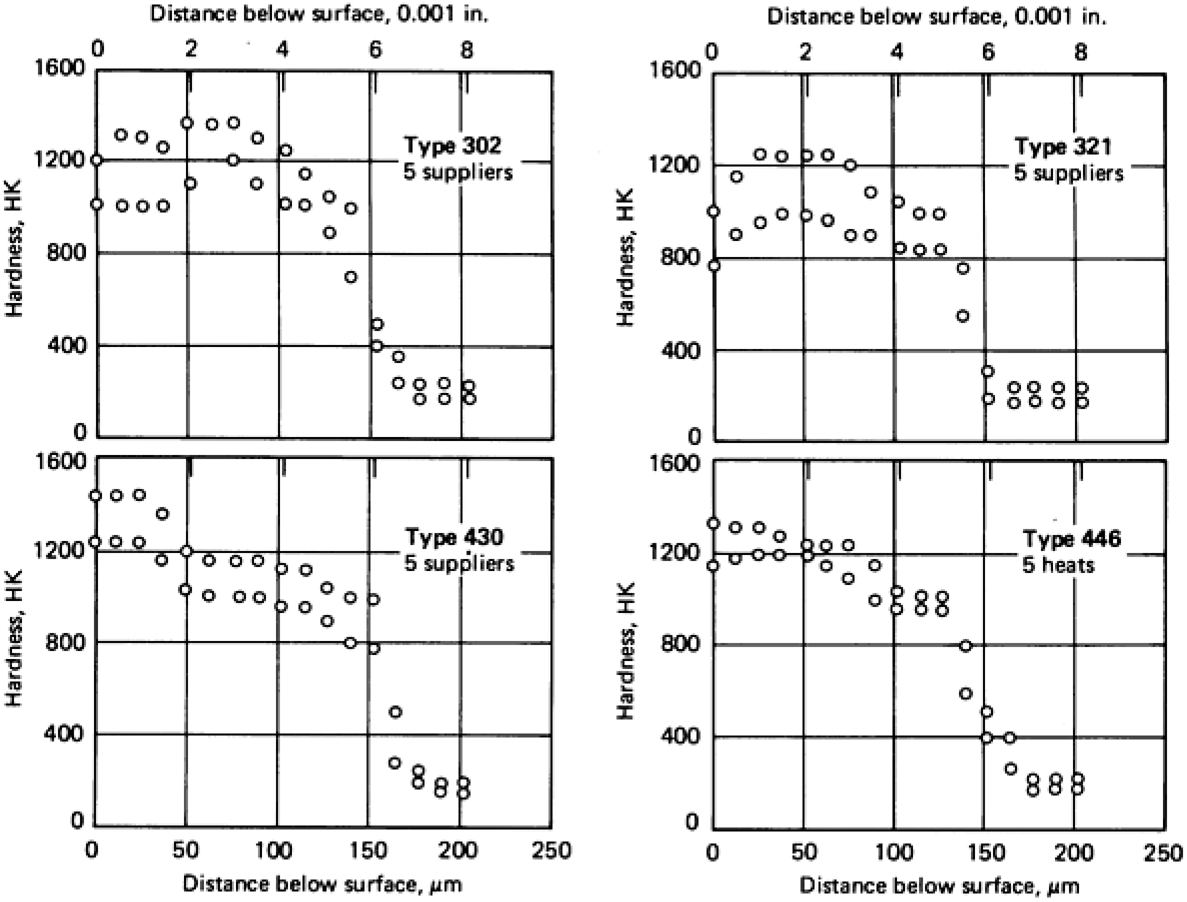


**Fig. 5 Hardness range as a function of case depth for four stainless steels that were annealed prior to nitriding. Annealing temperature: types 302 and 321, 1065 °C (1950 °F); type 430, 980 °C (1800 °F); and type 446, 900 °C (1650 °F)**

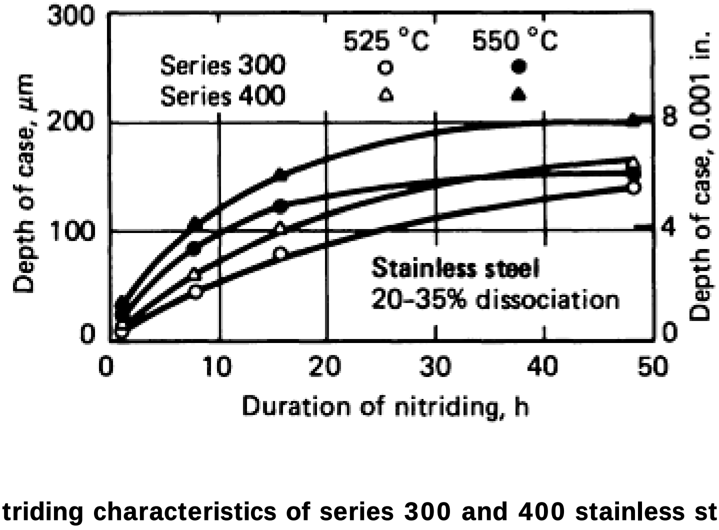


**Fig. 6 Comparison of the nitriding characteristics of series 300 and 400 stainless steels, single-stage nitrided at 525 and 550 °C (975 and 1025 °F)**

**Applications.** Although nitriding increases the surface hardness and wear resistance of stainless steels, it decreases general corrosion resistance by combining surface chromium with nitrogen to form chromium nitride. Consequently, nitriding is not recommended for applications in which the corrosion resistance of stainless steel is of major importance. For example, a hot-air valve made of cast type 347 and used in the cabin-heating system of a jet airplane was nitrided to improve its resistance to wear by the abrading action of a sliding butterfly When the valve remained in the closed position for an extended period, the corrosive effects of salt air froze the valve into position so that it could not be opened.

In contrast, a manufacturer of steam-turbine power-generating equipment has successfully used nitriding to increase the wear resistance of types 422 and 410 stainless steel valve stems and bushings that operate in a high-temperature steam atmosphere. Large quantities of these parts have operated for 20 years of more without difficulty. In a few instances, a light-blue oxide film formed on the valve stem diameter, causing it to "grow" and thus reduce the clearance between stem and bushing; the growth condition, however, was not accompanied by corrosive attack.

Nitrided stainless steel is also being used in the food-processing industry. In one application, nitrided type 321 was used to replace type 302 for a motor shaft used in the aeration of orange juice. Because the unhardened 302 shaft wore at the rubber-sealed junction of the motor and the juice, leaks developed within 3 days. The nitrided 321 shaft ran for 27 days before wear at the seal resulted in leakage. In machinery used in the preparation of dog foods, nitrided type 420 gears have replaced gears made of an unhardened stainless alloy and have exhibited a considerable increase in life.

Modern synthetic fibers, several of which are highly abrasive, have increased the wear of textile machinery. Mechanical parts in textile machines are subjected to high humidity, absence of lubrication, high-speed movements with repeated cycling, and the abrasive action of fibers traveling at high speeds. A shear blade made of hardened (62 to 64 HRC) 1095 steel experienced a normal life of about one million cuts (4 weeks of service) in cutting synthetic fibers at the rate of 90 cuts per minute. In contrast, a nitrided type 410 blade with 0.04 mm (0.0015 in.) case depth showed less wear after completion of five million cuts.

With nitrided stainless steels, the case almost always has lower corrosion resistance than the base material; nevertheless, the corrosion resistance of the case can be adequate for certain applications. For example, nitrided types 302 and 410 stainless steel resist attack from warp conditioner and size in the textile industry but do not resist attack from the acetic acid used in dyeing liquors.

Nitrided stainless steel is not resistant to mineral acids and is subject to rapid corrosion when exposed to halogen compounds. However, a nitrided type 302 piston lasted for more than 5 years in a liquid-ammonia pump; it replaced a piston made of an unnitrided 300-series alloy that lasted approximately 6 months. Nitrided 17-4 PH impellers have performed satisfactorily and without corrosion in various types of hydraulic pumps.

### *Plasma (Ion) Nitriding and Liquid Nitriding*

**Plasma, or ion, nitriding** is a method of surface hardening that uses glow discharge technology to introduce nascent (elemental) nitrogen to the surface of a metal part for subsequent diffusion into the material. In a vacuum, high-voltage electrical energy is used to form a plasma, through which nitrogen ions are accelerated to impinge on the workpiece. This ion bombardment heats the workpiece, cleans the surface, and provides active nitrogen. Ion nitriding provides better control of case chemistry and uniformity and has other advantages, such as lower part distortion than conventional gas nitriding.

The diffusion zone of a nitrided case can best be described as the original core microstructure with some solid solution and precipitation strengthening. In iron-base materials, the nitrogen exists as single atoms in solid solution at lattice sites or interstitial positions until the limit of nitrogen solubility ( !0.4 wt% N) in iron is exceeded. This area of solid-solution strengthening is only slightly harder than the core. The depth of the diffusion zone depends on the nitrogen concentration gradient, time at a given temperature, and the chemistry of the workpiece.

As the nitrogen concentration increases toward the surface, very fine, coherent precipitates are formed when the solubility limit of nitrogen is exceeded. The precipitates can exist both in the grain boundaries and within the lattice structure of the grains themselves. These precipitates, in the form of nitrides, distort the lattice and pin crystal dislocations and thereby substantially increase the hardness of the material. Hardness profiles for various ion-nitrided materials, including stainless steels, are shown in Fig. 7.

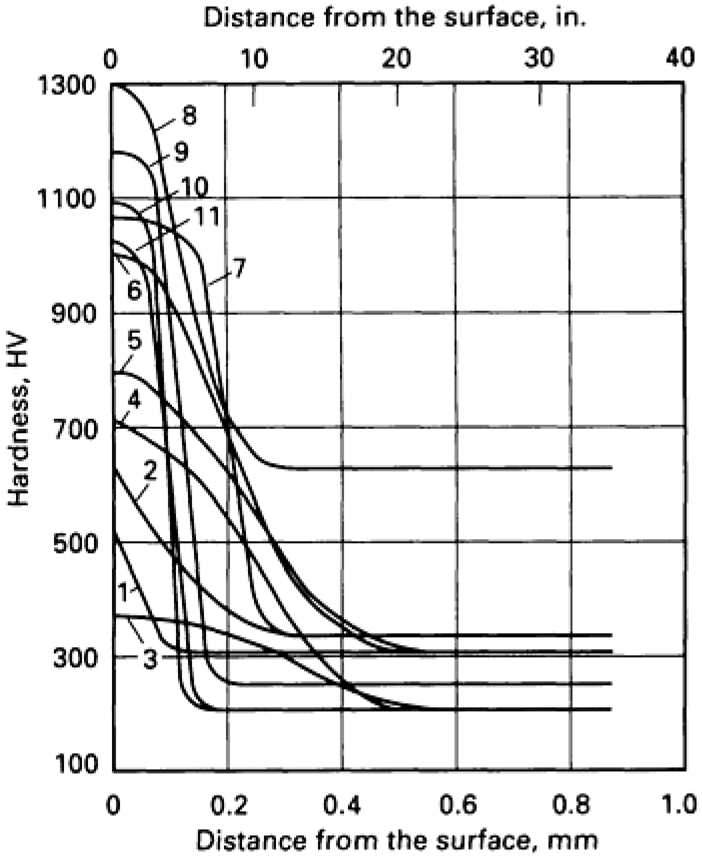


**Fig. 7 Hardness profiles for various ion-nitrided materials. 1, gray cast iron; 2, ductile cast iron; 3, AISI 1040; 4, carburizing steel; 5, low-alloy steel; 6, nitriding steel; 7, 5% Cr hot-work steel; 8, cold-worked die steel; 9, ferritic stainless steel; 10, AISI 420 stainless steel; 11, 18-8 stainless steel**

In most ferrous alloys, the diffusion zone formed by nitriding cannot be seen in a metallograph because the coherent precipitates generally are not large enough to resolve. In stainless steels, however, the chromium level is high enough for extensive nitride formation, which can be seen in etched cross section (Fig. 8).

**Fig. 8 Observable diffusion zone on the unetched (white) portion of an ion-nitrided 416 stainless steel. Nital etched. 500×**

Ion nitriding has a strong advantage over competing processes in the case of stainless steels, particularly austenitic or 300-series materials. The chromium oxide passive layer on the surface represents a barrier to nitriding and must be removed prior to processing. When gas nitriding stainless steels, this passive layer is removed by wet blasting, pickling, or chemical reduction. With ion nitriding, however, this layer can be removed by sputtering in hydrogen in the vessel itself just before introduction of the process gas. With most materials, even the sputtering that occurs naturally during the actual nitriding process is enough to yield good nitriding results.

**Liquid nitriding** is performed in a molten, nitrogen-bearing, fused-salt bath containing either cyanides or cyanates. Unlike liquid carburizing and cyaniding, which employ baths of similar composition, liquid nitriding is a subcritical (that is, below the critical transformation temperature) case-hardening process. Thus, processing of finished parts is possible because dimensional stability can be maintained. Also, liquid nitriding adds more nitrogen and less carbon to ferrous materials than that obtained through higher-temperature diffusion treatments.

Cyanide-free liquid nitriding salt compositions have also been introduced. However, in the active bath, a small amount of cyanide, generally up to 5%, is produced as part of the reaction. This is a relatively low concentration, and these compositions have gained widespread acceptance within the heat treating industry because they contribute substantially to the alleviation of a potential source of pollution.

The wear and gall resistance of stainless steels can be improved by aerated liquid nitriding, a proprietary process (U.S. Patent 3,022,204) in which measured amounts of air are pumped through the molten bath. Immersion in the molten salt at 570 °C (1060 °F) develops a physical compound zone in stainless steels that, depending on treatment time, varies between 0.005 and 0.025 mm (0.0002 and 0.001 in.). Although the hardness of this wear-resistant surface measures 70 to 72 HRC, the surface is tough and ductile (Ref 14).

Liquid nitriding treatments result in some loss in corrosion resistance, because the formation of nitrides and carbides depletes adjacent matrix areas. Corrosion data based on weight loss indicate that liquid-nitrided stainless steels lose approximately 50% of their corrosion resistance; however, these materials remain substantially superior to untreated carbon and low-alloy steels (Ref 14).

Liquid nitriding is one of the few heat treatments that can produce a wear-resistant hard surface, improve fatigue properties, and retain to a significant extent the good corrosion resistance of stainless steels in a single operation. In addition, subsequent quenching is not required, allowing flexibility in design and final machining (Ref 14).

### *Carburizing, Boriding, and Flame Hardening*

**Carburizing** is a case-hardening process in which carbon is dissolved in the surface layers of a steel part at a temperature sufficient to render the material austenitic, followed by quenching and tempering to form a martensitic microstructure. The resulting gradient in carbon content below the surface of the part causes a gradient in hardness, producing a strong, wear-resistant surface layer. In gas carburizing, commercially the most important variant of carburizing, the source of carbon is a carbon-rich furnace atmosphere produced either from gaseous hydrocarbons (e.g., methane, propane, or butane) or from vaporized hydrocarbon liquids.

Stainless steels can be carburized to improve surface hardness and resistance to galling. The availability of substantial amounts of chromium promotes the rapid formation of chromium carbides at the surface, and surface hardness values of 700 to 750 HV have been measured. Precipitation-hardenable stainless steels can be gas carburized to improve resistance to galling. Treatment temperatures up to 1010 °C (1850 °F) may be required (Ref 14).

In austenitic grades, much of the chromium carbide formed migrates and is precipitated in the grain boundaries, promoting susceptibility to intergranular corrosion. Carbide distribution tends to be less segregated in the martensitic grades, but they are also subject to localized corrosion and particularly SCC (Ref 14).

Carburizing is not generally recommended for stainless steels because of the reduction in corrosion resistance brought on by chromium precipitation. Since the precipitated chromium tends to exist at the expense of adjacent areas, localized galvanic cells may develop. In the carburizing process, surface physical properties are obtained at the expense of surface chemical properties (Ref 14).

Because of these disadvantages, most of the carburizing of stainless steel is "accidental" and can be traced to surface contamination. Carbonaceous compounds such as charcoal, coke, oil, and grease can promote carburization under the proper conditions. Molten salt baths that contain cyanide to prevent decarburization may also become carburizing in contact with stainless steels (Ref 14).

**Boriding,** or boronizing, is a thermochemical surface hardening process that involves heating well-cleaned material in the range of 700 to 1000 °C (1300 to 1830 °F), preferably for 1 to 12 h, in contact with a boronaceous solid powder (boronizing compound), paste, liquid, or gaseous medium.

The resultant diffusion zone is known for its low coefficient of friction and high surface hardness, which may reach values of 1800 HV. Case depths of 0.05 mm (0.002 in.) can be achieved with 1 to 5 h treating time (Ref 14). Figure 9 shows the influence of steel composition on abrasive wear resistance. Boriding can considerably enhance the corrosion-erosion resistance of ferrous materials in nonoxidizing dilute acids (Fig. 10) and alkali media, and is increasingly used to this advantage in many industrial applications (Ref 17).

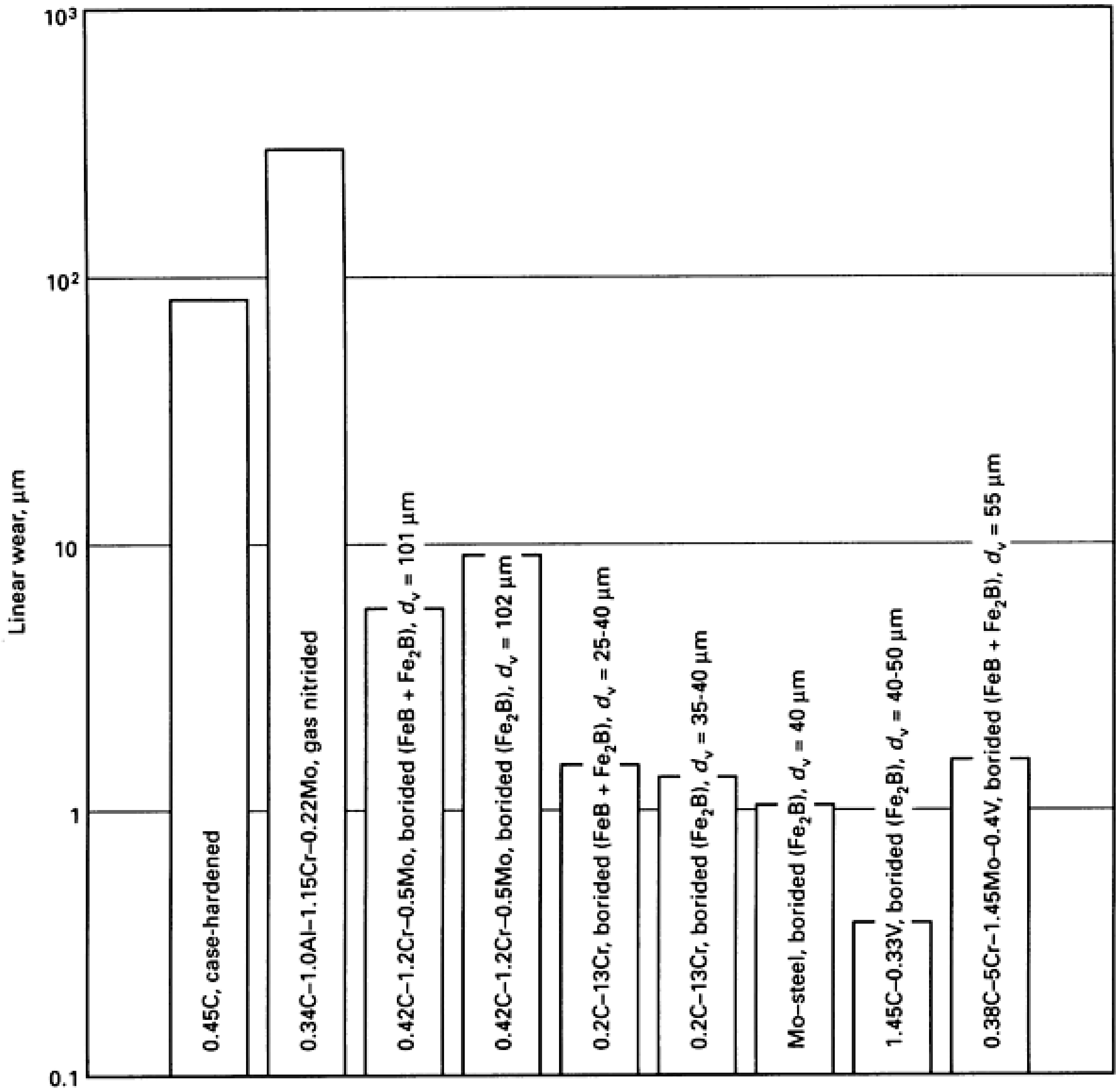
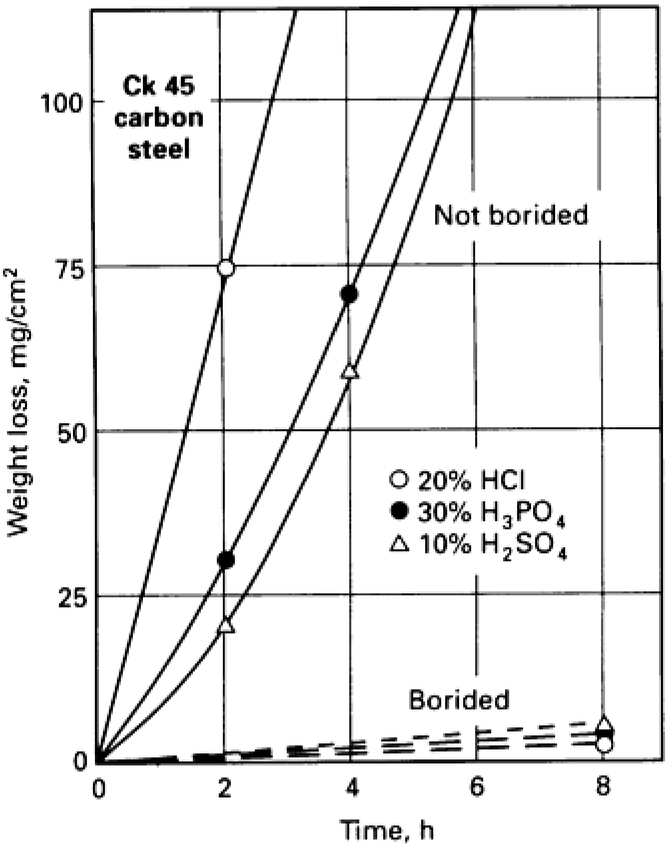
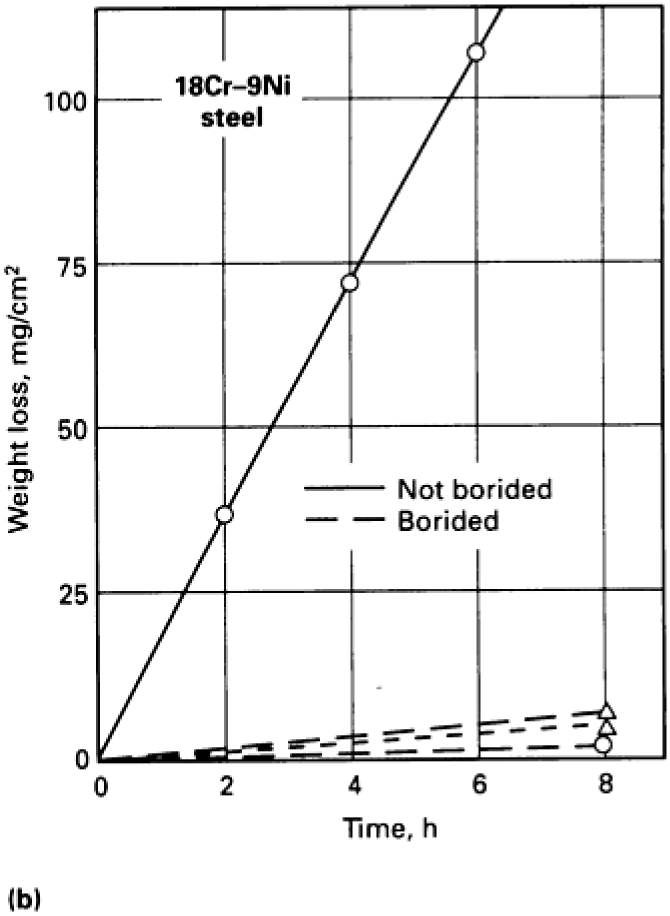


**Fig. 9 Effect of steel composition (nominal values in wt%) on wear resistance under abrasive wear ($d_v$ = thickness of the boride layer). Test conditions: DP-U grinding tester, SiC paper 220, testing time 6 min. Source: Ref 15, 16**


Ck 45
carbon
steel
Not borided
Borided
○ 20% HCl
● 30% $H_3PO_4$
△ 10% $H_2SO_4$
Weight loss, mg/cm²
Time, h
0
25
50
75
100
0
2
4
6
8

(a)


18Cr–9Ni
steel
Not borided
Borided
Weight loss, mg/cm²
Time, h
0
25
50
75
100
0
2
4
6
8

(b)

**Fig. 10 Corroding effect of mineral acids on boronized and nonboronized (a) 0.45% C (Ck 45) steel and (b) 18Cr-9Ni (X10CrNiTi189) steel at 56 °C (130 °F). Source: Ref 17, 18**

Chromium considerably modifies the structure and properties of iron borides. As the chromium content in the base material increases, progressive improvements in the following effects are observed: formation of boron-rich reaction products, decrease in boride depth, and flattening or smoothening of the coating/substrate interface (Ref 19). A reduction of boride thickness has also been noticed in ternary Fe-12Cr-C steels with increasing carbon content (Ref 20).

**Flame hardening** is a heat treating process in which a thin surface shell of a steel part is heated rapidly to a temperature above the critical point of the steel. After the grain structure of the shell has become austenitic (austenitized), the part is quickly quenched, transforming the austenite directly to martensite while leaving the core of the part in its original state.

Flame hardening employs direct impingement of a high-temperature flame or high-velocity combustion product gases. The part is then cooled at a rate that will produce the desired levels of hardness and other properties. The high-temperature flame is obtained by combustion of a mixture of fuel gas with oxygen or air; flame heads are used for burning the mixture. Depths of hardening from about 0.8 to 6.4 mm ($\frac{1}{32}$ to $\frac{1}{4}$ in.) or more can be obtained, depending on the fuels used, the design of the flame head, the duration of heating, the hardenability of the work material, and the quenching medium and method of quenching used.

Hardening by flame differs from true case hardening because the hardenability necessary to attain high levels of hardness is already contained in the steel, and hardening is obtained by localized heating. Although flame hardening is mainly used to develop high levels of hardness for wear resistance, the process also improves bending and torsional strength and fatigue life.

Flame hardening can be applied to martensitic stainless steels. The nature of flame hardening, however--especially the relatively high temperature gradients and higher than normal surface temperatures-- may cause the retention of excessive amounts of austenite in many highly alloyed materials, with possible low hardness and transformation to untempered martensite in service, accompanied by brittleness. Typical hardnesses obtained for martensitic stainless steels by flame heating and quenching in air or oil are given in Table 13.

**Table 13 Response of martensitic stainless steels to flame hardening**

| **Material** | **Typical hardness, HRC, as affected by quenchant** | |
|---|---|---|
| | **Air**(a) | **Oil**(b) |
| 410, 416 | 41-44 | 41-44 |
| 414, 431 | 42-47 | 42-47 |
| 420 | 49-56 | 49-56 |

(a) To obtain the hardness results indicated, those areas not directly heated must be kept relatively cool during the heating process.

(b) Thin sections are susceptible to cracking when quenched with oil.

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## Surface Engineering of Specialty Steels

**J.R. Davis, Davis & Associates**

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## Introduction

SPECIALTY STEELS encompass a broad range of ferrous alloys noted for their special processing characteristics (powder metallurgy alloys), corrosion resistance (stainless steels), wear resistance and toughness (tool steels), high strength (maraging steels), or magnetic properties (electrical steels). Each of these material groups--with the exception of stainless steels, which were discussed in the previous article in this Section--will be reviewed below. Additional information on these materials can be found in Volumes 1 and 2 of the *ASM Handbook*.

## Ferrous Powder Metallurgy Alloys

Powder metallurgy (P/M) in its simplest form consists of compressing metal powders in a shaped die to produce green compacts. These are then sintered, or diffusion bonded, at elevated temperatures in a furnace with a protective atmosphere. During sintering, the constituents usually do not melt, and the compacts become substantially strengthened by the development of bonds between individual particles.

For a specific metal powder and sintering condition, increased compact density results in improved mechanical properties. The density of sintered compacts may be increased by re-pressing. When re-pressing is performed primarily to increase dimensional accuracy rather than density, it is termed sizing. When re-pressing is intended to change the contour of the surface in contact with the punches, it is termed coining. For example, a sintered blank could be coined so that the surface is indented with small slots or letters and numbers. The re-pressing may be followed by re-sintering, which relieves the stresses due to cold work and may further strengthen the compact. More detailed information on consolidation practices for ferrous P/M parts can be found in Ref 1 and 2.

By pressing and sintering only, parts are produced at 80 to 93% of theoretical density. By re-pressing, with or without sintering, the materials may be further densified to 85 to 96% of theoretical density. High-temperature sintering will also produce parts at these high densities. The density of pressed parts is limited by the size and shape of the compact. The most common P/M materials for structural parts are iron-copper-carbon, iron-nickel-carbon, and iron-carbon. Parts made from these materials respond to heat treatment with a defined hardenability band. Iron parts that are low in carbon and high in density can also be case hardened.

### *Designation of Ferrous P/M Materials*

Ferrous P/M materials are customarily designated by the specifications or standards to which they are made, such as those listed in Table 1. Comparable standards are published by ASTM, SAE, and MPIF (Metal Powder Industries Federation).

**Table 1 Compositions of ferrous P/M structural materials**

| **Description** | **Designation**[(a)] | | | **MPIF composition limits and ranges, %**[(b)] | | | | |
|---|---|---|---|---|---|---|---|---|
| | **MPIF** | **ASTM** | **SAE** | **C** | **Ni** | **Cu** | **Fe** | **Mo** |
| P/M iron | F-0000 | B 783 | 853, Cl 1 | 0.3 max | . . . | . . . | 97.7-100 | . . . |
| P/M steel | F-0005 | B 783 | 853, Cl 2 | 0.3-0.6 | . . . | . . . | 97.4-99.7 | . . . |
| P/M steel | F-0008 | B 783 | 853, Cl 3 | 0.6-1.0 | . . . | . . . | 97.0-99.1 | . . . |
| P/M copper iron | FC-0200 | B 783 | . . . | 0.3 max | . . . | 1.5-3.9 | 93.8-98.5 | . . . |
| P/M copper steel | FC-0205 | B 783 | . . . | 0.3-0.6 | . . . | 1.5-3.9 | 93.5-98.2 | . . . |
| P/M copper steel | FC-0208 | B 783 | 864, Gr 1, Cl 3 | 0.6-1.0 | . . . | 1.5-3.9 | 93.1-97.9 | . . . |
| P/M copper steel | FC-0505 | B 783 | . . . | 0.3-0.6 | . . . | 4.0-6.0 | 91.4-95.7 | . . . |
| P/M copper steel | FC-0508 | B 783 | 864, Gr 2, Cl 3 | 0.6-1.0 | . . . | 4.0-6.0 | 91.0-95.4 | . . . |
| P/M copper steel | FC-0808 | B 783 | 864, Gr 3, Cl 3 | 0.6-1.0 | . . . | 6.0-11.0 | 86.0-93.4 | . . . |
| P/M copper steel | . . . | . . . | 864, Gr 4, Cl 3 | 0.6-0.9 | . . . | 18.0-22.0 | 75.1 min | . . . |
| P/M iron-copper | FC-1000 | B 783 | 862 | 0.3 max | . . . | 9.5-10.5 | 87.2-90.5 | . . . |
| P/M prealloyed steel | FL-4205 | B 783 | . . . | 0.4-0.7 | 0.35-0.45 | . . . | 95.9-98.7 | 0.50-0.85 |
| P/M prealloyed steel | FL-4605 | B 783 | . . . | 0.4-0.7 | 1.70-2.00 | . . . | 94.5-97.5 | 0.40-0.80 |
| P/M iron-nickel | FN-0200 | B 783 | . . . | 0.3 max | 1.0-3.0 | 2.5 max | 92.2-99.0 | . . . |
| P/M nickel steel | FN-0205 | B 783 | . . . | 0.3-0.6 | 1.0-3.0 | 2.5 max | 91.9-98.7 | . . . |
| P/M nickel steel | FN-0208 | B 783 | . . . | 0.6-0.9 | 1.0-3.0 | 2.5 max | 91.6-98.4 | . . . |
| P/M iron-nickel | FN-0400 | B 783 | . . . | 0.3 max | 3.0-5.5 | 2.0 max | 90.2-97.0 | . . . |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| P/M nickel steel | FN-0405 | B 783 | . . . | 0.3-0.6 | 3.0-5.5 | 2.0 max | 89.9-96.7 | . . . |
| P/M nickel steel | FN-0408 | B 783 | . . . | 0.6-0.9 | 3.0-5.5 | 2.0 max | 89.6-96.4 | . . . |
| P/M iron-nickel | FN-0700 | . . . | . . . | 0.3 max | 6.0-8.0 | 2.0 max | 87.7-94.0 | . . . |
| P/M nickel steel | FN-0705 | . . . | . . . | 0.3-0.6 | 6.0-8.0 | 2.0 max | 87.4-93.7 | . . . |
| P/M nickel steel | FN-0708 | . . . | . . . | 0.6-0.9 | 6.0-8.0 | 2.0 max | 87.1-93.4 | . . . |
| P/M infiltrated steel | FX-1000 | B 783 | . . . | 0-0.3 | . . . | 8.0-14.9 | 82.8-92.0 | . . . |
| P/M infiltrated steel | FX-1005 | B 783 | . . . | 0.3-0.6 | . . . | 8.0-14.9 | 80.5-91.7 | . . . |
| P/M infiltrated steel | FX-1008 | B 783 | . . . | 0.6-1.0 | . . . | 8.0-14.9 | 80.1-91.4 | . . . |
| P/M infiltrated steel | FX-2000 | B 783 | 870 | 0.3 max | . . . | 15.0-25.0 | 70.7-85.0 | . . . |
| P/M infiltrated steel | FX-2005 | B 783 | . . . | 0.3-0.6 | . . . | 15.0-25.0 | 70.4-84.7 | . . . |
| P/M infiltrated steel | FX-2008 | B 783 | 872 | 0.6-1.0 | . . . | 15.0-25.0 | 70.0-84.4 | . . . |

(a) Designations listed are nearest comparable designations; ranges and limits may vary slightly between comparable designations.

(b) MPIF standards require that the total amount of all other elements be less than 2.0%, except in infiltrated steels, for which the total amount of other elements must be less than 4.0%.

The MPIF designations for ferrous P/M materials, described in detail in Ref 3, include a prefix of one or more letters (the first of which is F to indicate an iron-base material), four numerals, and a suffix. The second letter in the prefix identifies the principal alloying element (if one is specified); the percentage of the element is indicated by the first two digits. The third and fourth digits indicate the amount of carbon in the compacted and sintered part; the code designation 00 indicates less than 0.3%, 05 indicates 0.3 to 0.6%, and 08 indicates 0.6 to 0.9%. The suffix is used to indicate the minimum 0.2% yield strength of as-sintered parts and the minimum ultimate tensile strength of heat-treated materials in units of 1000 psi (6.894 MPa). The letters HT designate heat treated.

Commercially produced iron-base powders often contain controlled amounts of alloying elements other than those specified by any of the designations listed in Table 1. Manganese and molybdenum may be added to improve strength and the response to heat treatment. Sulfur may be added to enhance machinability. Additions of 0.45 to 0.80% P can improve the toughness of the part and reduce magnetic hysteresis losses. These powders are usually identified by the trade name of the producer even though the amounts of alloy additions are small enough that the designations listed in Table 1 could be applied to the powders. Commercially produced iron-base powders usually contain very little carbon because carbon lowers compressibility and the amount of carbon in the finished part is readily controlled by the amount of admixed graphite and the composition of the sintering atmosphere.

### *Deburring P/M Parts (Ref 4)*

Although cleaning and deburring generally are considered different operations, they are often accomplished simultaneously. Therefore, much of the discussion on deburring is applicable to the subsequent section of this article on cleaning.

The inherent porosity in P/M parts demands special considerations in all secondary operations. This is also true for cleaning and deburring; the relatively small size and complex shape of the parts also require special procedures and/or precautions that are not required for wrought or cast parts. The P/M parts shown in Fig. 1 are typical of small, intricate parts that frequently present deburring problems.

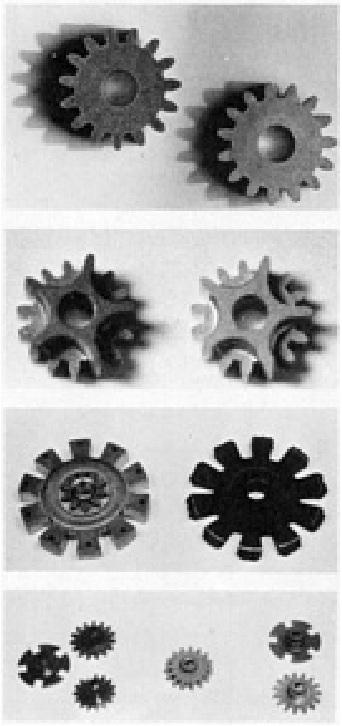

**Fig. 1 Typical shapes of P/M parts that present deburring or cleaning difficulties**

**Deburring Methods.** Due to the nature of the P/M process, burrs typically form on the edges and surfaces of P/M parts. In many simple shapes, deburring is almost automatic--that is, burrs are broken off during handling operations. If parts are surface hardened or steam treated, subsequent deburring may be unnecessary. However, for intricate parts such as those shown in Fig. 1, separate deburring operations generally are required.

The use of liquid deburring methods is not usually suitable, especially if such liquids are corrosive. Thus, acid pickling is not recommended, because acid may be entrapped in the pores, resulting in severe corrosion. Tumbling in a wet medium is used frequently as a deburring method, but removal of the liquid from the pores requires extra drying time. Preferred methods of deburring include:

- Rotary tumbling (self or with abrasive)
- Vibratory
- Abrasive blasting
- Centrifugal or high-energy methods

These methods, which are used for deburring and sometimes for cleaning, are described in the articles "Mechanical Cleaning Systems" and "Mass Finishing Methods" in this Volume. The discussions that follow are unique to P/M parts.

**Rotary Tumbling.** Self-tumbling, tumbling with dry abrasive, and tumbling with abrasive in a liquid medium are suitable for deburring of P/M parts. Wet tumbling is not suitable for deburring P/M parts because of the difficulty of removing the tumbling liquid from the pores of the parts.

During self-tumbling, the workpieces are tumbled in a revolving barrel. This method provides an economical and efficient means of deburring, but is effective only on relatively simple parts. For parts such as those shown in Fig. 1, the internal surfaces and recesses are not completely deburred by this method. For more complete deburring, an abrasive is added. Size of the abrasive is important. At least a portion of the added abrasive should have a mesh size that is smaller than the smallest hole or recess in the workpiece; otherwise, not all surfaces will be reached.

Over-tumbling of P/M parts must be avoided, because it peens the surfaces and may partially close pores (not necessarily desirable). Over-tumbling also may damage gear teeth or other protrusions by removing too much metal or by excessive peening. Tumbling cycles should be based on the minimum time that will provide acceptable deburring.

**Vibratory processing** is similar to rotary tumbling in principle. However, the shaking involved in the vibratory method is faster and provides more uniform results compared to rotary tumbling. As in rotary tumbling, care must be taken to prevent over-tumbling.

**Abrasive blasting,** in which various materials are propelled by air or centrifugal force, offers another method of deburring. For practical reasons, it is used less frequently than tumbling or vibrating. The abrasive must be selected carefully. Coarse shot or grit tends to peen the surfaces and close the pores. Also, abrasive blasting can "hammer" bits of abrasive into the workpiece, thus "charging" it.

Another disadvantage of conventional abrasive blasting is that, especially for large volumes of small workpieces, results are likely to be nonuniform. One type of blasting machine, which tumbles and blasts simultaneously, has been used successfully for deburring of P/M parts. Silica sand or a milder abrasive is suitable and is less likely to damage intricate workpieces. As with other deburring methods, overprocessing must be avoided.

**Centrifugal or High-Energy Methods.** Centrifugal finishing combines rotating action with high centrifugal force, which results in a more severe abrading action than can be obtained by conventional rotary tumbling. This action is obtained by revolving several rotating barrels around the periphery of a large carrier disk.

As a result, the action within one barrel consists of a combination of rotating motion and high centrifugal forces, which provides pressures up to 25 times the weight of the abrasive medium (if used) and the workpiece. As the disk rotates in one direction, the barrels rotate at a faster speed in the opposite direction. This counter movement within the entire mass accomplishes the desired results in a shorter time compared to other abrading processes. An advantage of this process is that it drives the abrasive into relatively inaccessible areas where burr removal may present problems.

## *Cleaning of P/M Parts (Ref 4)*

Some of the deburring methods discussed above also may be considered as methods of cleaning. Frequently, however, methods such as tumbling and blasting are considered as preliminary cleaning operations to be followed by a more thorough cleaning, especially if the parts are to be coated.

**Cleaning Methods.** The inherent porosity in P/M parts imposes restrictions on selection of cleaning method. The use of a cleaning solution that is corrosive to the metal being cleaned is not recommended, because even the most thorough washing is not likely to remove all of the fluid, which presents a corrosion problem. Acid cleaning is therefore not recommended.

Because of porosity, thorough cleaning of P/M parts is more difficult than their wrought counterparts; P/M parts require more attention than is provided in many conventional cleaning systems. Preferred methods are hot caustic washing, ultrasonic degreasing, and electrolytic alkaline cleaning.

**Ultrasonic Degreasing.** Oils, greases, and other shop soil may be removed by vapor degreasing techniques such as vapor phase, vapor-spray-vapor, warm liquid-vapor, or boiling liquid-warm liquid-vapor techniques. For most P/M parts, especially if the degree of soiling is severe and/or part density is low, the boiling liquid-warm liquid-vapor process is preferred. This technique should be used in conjunction with an ultrasonic transducer, which literally shakes all entrapped contaminants out of the pores, resulting in a thorough and safe method of cleaning.

**Electrolytic Alkaline Cleaning.** Ferrous P/M parts can be cleaned, deoxidized, and stripped of nonmetallic coatings by subjecting them to electrolysis in a strongly alkaline aqueous solution. In this method the base metal is not attacked, and the possibility of rusting is minimal. Typical alkaline solutions are comprised of a:

- Source of caustic to aid cleaning
- Chelating agent to detach scale or rust
- Complexing agent to hold relatively large amounts of iron in solution

Electrolytic alkaline cleaning bath compositions and operating conditions are described in the article "Alkaline Cleaning" in this Volume. This cleaning process is well suited to cleaning of P/M parts, because the electrolytic action provides additional energy required to dislodge contaminants from pores or from relatively inaccessible areas.

## *Steam Treating of P/M Parts (Ref 5)*

Ferrous P/M parts have traditionally been steam treated for improved wear resistance, corrosion resistance, and sealing capacity. Here, P/M parts are heated in a specific manner under a steam atmosphere at temperatures between 510 to 595 °C (950 to 1100 °F) to form a layer of black iron oxide (magnetite, or ferrous-ferric oxide, $FeO-Fe_2O_3$) in the surface porosity according to the chemical reaction:

$$3Fe + 4H_2O\ (\text{steam}) \rightarrow Fe_3O_4 + 4H_2(\text{gas}) \qquad \textbf{(Eq 1)}$$

Steam treating cannot be described as a heat treatment because no structural changes occur in the matrix. In this process, magnetite ($Fe_3O_4$) is formed at the interconnecting surface porosity, filling the porosity with a second phase. Magnetite has a microhardness equivalent to HRC 50.

The process itself is straightforward, the primary variables being temperature, time, and steam pressure. Caution must be used to prevent the formation of hydroxides and lower oxides such as ferrous oxide (FeO) and ferric oxide ($Fe_2O_3$), which is red rust.

The recommended procedure for steam treating is:

- Preclean parts to remove any oil or lubricants that may have been absorbed into the porosity from prior machining, sizing, or finishing operations
- Load clean sintered parts in loosely packed baskets and place fixture into a furnace preheated to 315 °C (600 °F)
- Heat parts in air until the center of the load has stabilized at the set temperature
- Introduce superheated steam at a line pressure of 35 to 105 kPa (5 to 15 psi) and allow furnace to purge for at least 15 min
- Increase furnace temperature to desired set point and hold for no longer than 4 h at heat
- Upon completion of cycle, reduce furnace temperature to 315 °C (600 °F). When parts reach this temperature, the steam can be shut off and the parts unloaded

Caution should be used when opening the furnace door after the steam cycle. As shown in Equation 1, hydrogen is produced during this process and can ignite. It is recommended that a nitrogen purge be applied prior to unloading. This process, when correctly applied, can impart improved surface properties, and, depending upon steel composition, increased compressive yield strength.

In all steam-treated P/M steels, the ductility is significantly reduced due to the internal stresses created by the formation of the iron oxide. Care must be taken when treating high-carbon P/M steels because these internal stresses can initiate microcracking and cause severe loss of ductility. Many cases have been reported in which parts were accidentally dropped on the floor after being steam treated, and the parts subsequently shattered like glass. The best recommendation for preventing such an incident is to specify a 0.5% C (max) content on materials that are to be steam treated.

Figure 2(a) shows that transverse rupture strength increases proportionately with sintered density. Upon steam treating, low-carbon P/M steels exhibit a uniform increase in strength, whereas the high-carbon P/M steels show only a small incremental increase in strength.

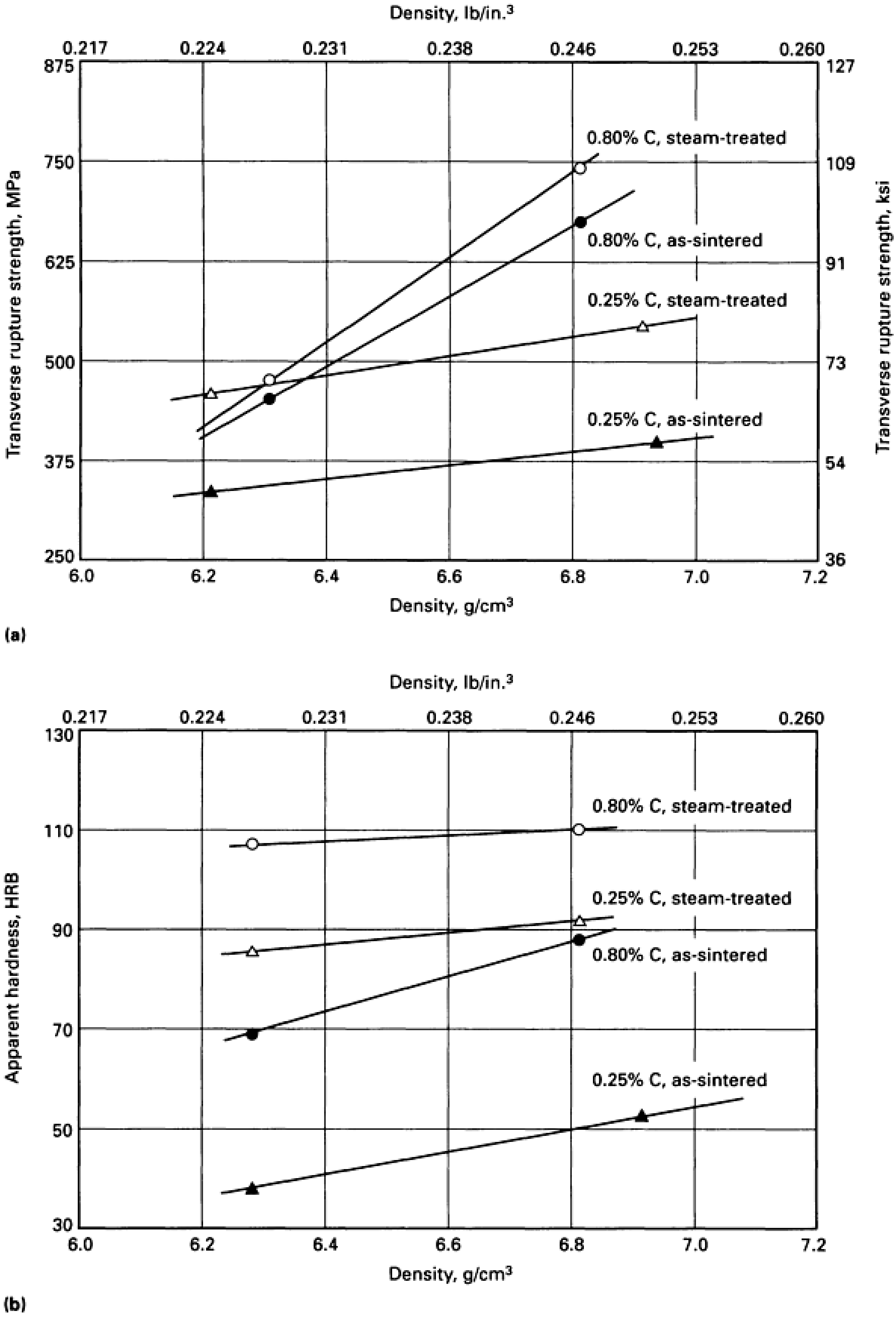

**Fig. 2 Effect of steam treating on the mechanical properties of sintered carbon P/M steels as a function of density. (a) Transverse rupture strength. (b) Apparent hardness. Source: Ref 5**

Apparent hardness also is improved as shown in Fig. 2(b). By filling the porosity with a hard second phase, the P/M steel can offer better support to an indentation hardness test. As with rupture strength, the incremental increase in hardness of high-carbon steels is less than that of low-carbon steels. Additional information on the properties of steam-treated P/M steels can be found in Ref 6.

## *Coating of P/M Parts (Ref 4)*

In addition to the surfaces provided by steam treatment, P/M parts are frequently coated by mechanical means, painting, or electroplating. The blue-black oxide-covered surface produced by exposure to steam is often the final finish for a variety of hardware items. It may also be used as a preliminary coating for a final finishing process, such as painting.

Regardless of the method used for coating, major emphasis must be placed on initial cleaning. If liquid contaminants are allowed to remain in the pores of parts, bleeding occurs, and defective coatings result. Steam treatment provides an excellent paint base.

**Mechanical coating** uses kinetic energy to deposit metallic coatings on parts. This process is also known as mechanical plating, or peen plating, when the coating is less than 25 $\mu$m (1 mil) thick. Coating is accomplished by placing the workpiece, glass beads, water, and the metal plating powder in a tumbling barrel.

Zinc is most commonly used as a plating material, although a wide range of metals and mixtures of metals can be mechanically plated on ferrous metal parts. For example, a mixture of 75% Zn and 25% Sn is commonly used. Metal powders are added to the mixtures to be tumbled. Complete details on the mechanical coating process may be found in the article "Mechanical Plating" in this Volume.

Powder metallurgy parts with densities not less than 83% can be mechanically plated without special considerations for porosity. When density drops below 83%, tests should be conducted to determine whether moisture is entrapped, which is detrimental to the finished parts. Generally, when density is below 83%, parts must be impregnated with wax or resin.

**Painting.** Usually, P/M parts are ideal candidates for coating by painting; the porosity enhances paint adhesion. Furthermore, P/M parts can be painted by spraying, dipping, or the contact transfer method. Air-drying types are suitable only for indoor protective coatings. Baking produces finishes of higher quality that are well suited for outdoor exposure.

Spray painting has several advantages over dipping, including improved control of dimensions and coating quality, and the ability to coat localized areas. However, higher labor costs and more paint loss from overspray are associated with spraying.

For spraying, baking types of alkyds are reduced with solvents to a spraying viscosity of 35 s through a No. 4 Ford Cup. Parts are sprayed and then air dried for 10 min, after which they may be baked for 30 min at a temperature compatible with the type of paint being used. This practice results in a dry film coating 38 to 46 μm (1.5 to 1.8 mils) thick.

In paint dipping, the parts to be coated are placed in baskets or on racks, immersed in the paint, and then allowed to drain. Dipping saves labor and paint, compared to spraying, but general quality of dipped parts is lower, notably because of edge buildup.

Roll painting and lithographing (transfer coating) is a process in which paint is applied to external surfaces of cylindrical P/M parts, followed by the application of lithographing ink. Typically parts are roll coated and oven baked. The initial coating is usually a background color. Numbers of characters, as required, are then roll coated over the background coating, followed by baking dry.

Advantages of this painting procedure include:

- Precision painting can be achieved without applying paint to areas that do not require a coating

- With proper design of parts, areas can be painted with sharply defined edges
- Coating thickness can be closely controlled by varying the number of revolutions the part is permitted to make
- An unlimited number of character forms can be applied at relatively low cost

Principal limitations of the process are:

- Special handling is required
- Internal surfaces are not coated

Types of paint used in general procedures for painting of P/M parts are similar to those used for wrought counterparts, all of which are covered in detail in the article "Painting" in this Volume.

**Electroplating.** Powder metallurgy parts can be electroplated with various metals like their wrought counterparts. Methods used for plating of cast parts generally can be used for very dense parts (95% or more of theoretical). Plating of castings is described in the article "Surface Engineering of Cast Irons" in this Volume. For parts of lower densities, special preparation procedures are required.

During plating of P/M parts, the pores act as thermal pumps. Plating solutions are released from or absorbed by the pores, depending on the temperature differential between the workpiece and the solution. Interconnecting pores entrap solutions, which are then released slowly. Part density should be known before the sequence of cleaning and plating operations begins, and suitable precautions should be taken to prevent solution entrapment.

Entrapped solutions not only cause spotty plating and staining, which may develop within days, but also can cause contamination and depletion of all solutions used in the production process. It is therefore necessary that, if part density is below about 95%, pores must be closed before coating by electroplating.

Methods of closing pores that have proved successful include burnishing, buffing, rolling, heat treating, steam treating, and impregnation. All of these methods, except impregnation, provide varying degrees of closure. Mechanical methods are often excluded because of dimensional tolerances. Consequently, impregnation is the most suitable approach to closing pores.

Infiltration of iron compacts with metals such as copper is common practice and completely solves the porosity problem for subsequent electroplating. However, the cost of metal infiltration usually cannot be justified only to ensure satisfactory electroplating.

Impregnation with plastic seals P/M parts for further processing, such as electroplating. Pressure tightness and frequently an improvement in machining characteristics are added benefits derived from plastic impregnation. The process is not unlike the plastic impregnation process used to attain pressure tightness in porous castings. Optimum results are obtainable with various types of plastic sealants, although the most commonly used are polyester resins and anaerobic sealants.

A typical processing cycle consists of:

- Cleaning thoroughly
- Baking at 120 to 150 °C (250 to 300 °F) to drive off all moisture or solvent
- Applying sealant under vacuum, such as in an autoclave
- Removing excess sealant by means of an emulsion cleaner
- Curing at 120 to 150 °C (200 to 250 °F)
- Tumbling, polishing, or abrasive blasting to remove excess cured sealant

Parts are now ready for routine cleaning and plating cycles, as required by the plating method used. Plating procedures are the same as those used for wrought parts (see the articles contained in the Section "Plating and Electroplating" in this Volume).

### *Case Hardening of P/M Parts (Ref 5)*

Powder metallurgy parts can be case hardened by several processes, although various available processes are not equally suited to every application. Generally the best results (a clear case/core relationship) are obtained with P/M parts with densities exceeding 7.2 g/cm$^3$ (90% of theoretical density). More detailed information on each of the processes described below can be found in *Heat Treating*, Volume 4 of the *ASM Handbook.*

**Carburizing** is normally specified in parts with a large cross-sectional thickness to attain maximum fatigue and impact properties. The material usually specified for carburizing contains hardenability agents such as nickel, molybdenum, and copper with relatively low carbon content. To develop optimum dynamic properties at porosity levels between. 10 to 15%, a combined carbon level of 0.30 to 0.35% is recommended. As porosity is reduced below 10%, combined carbon can be reduced to 0.15 to 0.25% C. Because improved dynamic properties are also associated with high densities, it is recommended that combined carbon be adjusted to a level best suited for re-pressing after sintering.

In wrought steel, carburizing is normally characterized by a surface hardness range and an effective case depth. Microhardness measurements can accurately show the hardness profile in wrought steel but can be erratic when used on P/M steels. With P/M steels, however, subsurface porosity can influence the microhardness readings, resulting in false hardness readings. It is recommended that at least three hardness readings be taken at each level below the surface and averaged to determine effective case depth.

Carburizing of P/M steels is usually done at temperatures between 900 to 930 °C (1650 to 1705 °F). Time cycles are normally short because of the rapid diffusion of carbon through the interconnected porosity. Therefore, atmosphere carbon potentials need to be somewhat higher than those required for wrought steels of similar composition.

**Carbonitriding** is probably the more common case-hardening treatment used on P/M parts. Here process temperatures are lower (800 to 850 °C, or 1470 to 1560 °F) and ammonia additions to approximately 10% are made. Ammonia dissociates on the parts, allowing nitrogen to diffuse into the surfaces. This retards the critical cooling rate upon quenching and provides a more consistent martensite transformation. It also produces a more consistent surface hardness, which improves wear resistance and toughness of the P/M steel. Because lower temperatures can be used, carbonitriding provides better control of distortion compared to carburizing. Care must be taken when adding ammonia, however, since excessive nitrogen diffusion into the internal pore surfaces can cause embrittlement.

Carbonitriding is a shallow case-hardening treatment. Case depths greater than 0.50 mm (0.020 in.) deep are seldom specified. For this reason, cycle times are relatively short, usually on the order of 30 to 60 min. As in neutral hardening, carbon control is a critical aspect of the treatment. Normally carbon potentials of 1.0 to 1.2% are specified to maintain the carbon profile in the part.

**Tempering** is usually required after case hardening when densities exceed 90%. In this case, significantly high stresses that could initiate cracking are developed upon quenching. As porosity increases, this stress level is reduced to a level at which a posttemper is not necessary. However, judgment should be used when deciding whether tempering is required. If a substantial amount of retained austenite is formed upon carbonitriding, a temper is advisable.

If the part has thin cross sections, sharp corners, or undercuts that would act as stress raiser, then tempering would also be advisable. Recommended tempering temperatures for P/M parts range from 105 to 200 °C (220 to 390 °F). Above this temperature, entrained quench oil can ignite, creating a hazardous condition in the furnace. Tempering above 200 °C (390 °F) will result in improved toughness and fatigue properties of the heat-treated P/M steel. However, furnaces will need special adaptations to handle the high volume of smoke created by the ignition of the quench oil.

**Induction Hardening.** Spur gears, bevel gears, splined hubs, and cams are ideal components to utilize P/M production techniques. These parts usually require hard wear-resistant surfaces in some areas, with the retention of the ductility of the sintered matrix in the remainder of the part. Induction hardening is commonly specified for these applications.

This process can be placed in an automated machining line that can reduce handling and be a cost-effective hardening treatment when high volumes of parts are being produced. Because the inductance of P/M materials is typically reduced due to porosity, a higher power setting is normally required to reach a given depth of hardening compared to that used for a wrought material of similar composition. Furthermore, because the heat is rapidly dissipated, a rapid transfer to the quench is mandatory.

As with wrought steels, the response to hardening by induction is dependent upon combined carbon content, alloy content, and surface decarburization. This latter variable can be a major concern with P/M parts. With today's conventional belt-type sintering furnaces using an endogas atmosphere, decarburizing can occur as the parts leave the hot zone and cool slowly through the 1100 to 800 °C (2010 to 1470 °F) temperature range.

In most cases, P/M parts are quenched in a water-based solution containing some type of rust preventative to forestall internal corrosion. In those applications where induction hardening is considered, densities above 90% should be specified. With a decrease in density, the resistivity of the steel increases and permeability decreases. For this reason, integral quench coils using a high-velocity spray quench are generally used to attain maximum surface hardness in the P/M part.

**Nitrocarburizing.** This process is rapidly growing in popularity as a treatment for P/M parts. Here, nitrogen is diffused into the surfaces of the steel in sufficiently high concentration to form a thin layer of $\varepsilon$iron nitride on the surface of the part. This is done at temperatures ranging from 570 to 600 °C (1060 to 1110 °F). At these temperatures no austenite transformation occurs, thereby significantly reducing the dimensional changes and distortion.

The process uses conventional integral quench atmosphere furnaces. The atmosphere usually consists of a 50/50 mixture of endothermic gas and anhydrous ammonia. Control of the nitrided layer thickness, as with the other treatments, is dependent on density. If the nitrided layer is allowed to form on the internal pore surfaces to any significant extent, a volume expansion can occur. For this reason, density of the P/M part should be above 90% of theoretical. This nitrided layer, when properly applied, can reduce the coefficient of friction at the surface of the part and provide improved wear resistance compared to conventional hardening to martensite. This process is best applied to applications where sliding wear and fretting are involved.

Because the hard nitrided layer is relatively thin, this process should not be applied where high indentation or impact loading is involved. The ε nitride layer that is formed can attain a file hardness in excess of HRC 60, depending on the alloy content of the steel. Indentation hardness testing is not recommended when evaluating this process. Since no transformation occurs, the P/M parts can be air cooled without loss of surface hardness. Also, no oil absorption occurs, which leaves the porosity open for impregnation if desired.

Nitrocarburizing also provides improved strength and reduced notch sensitivity in P/M parts. Figure 3 shows the fatigue improvement of two low-carbon P/M steels after nitrocarburizing. A typical nitrocarburized microstructure of an iron-copper-carbon P/M steel is shown in Fig. 4.

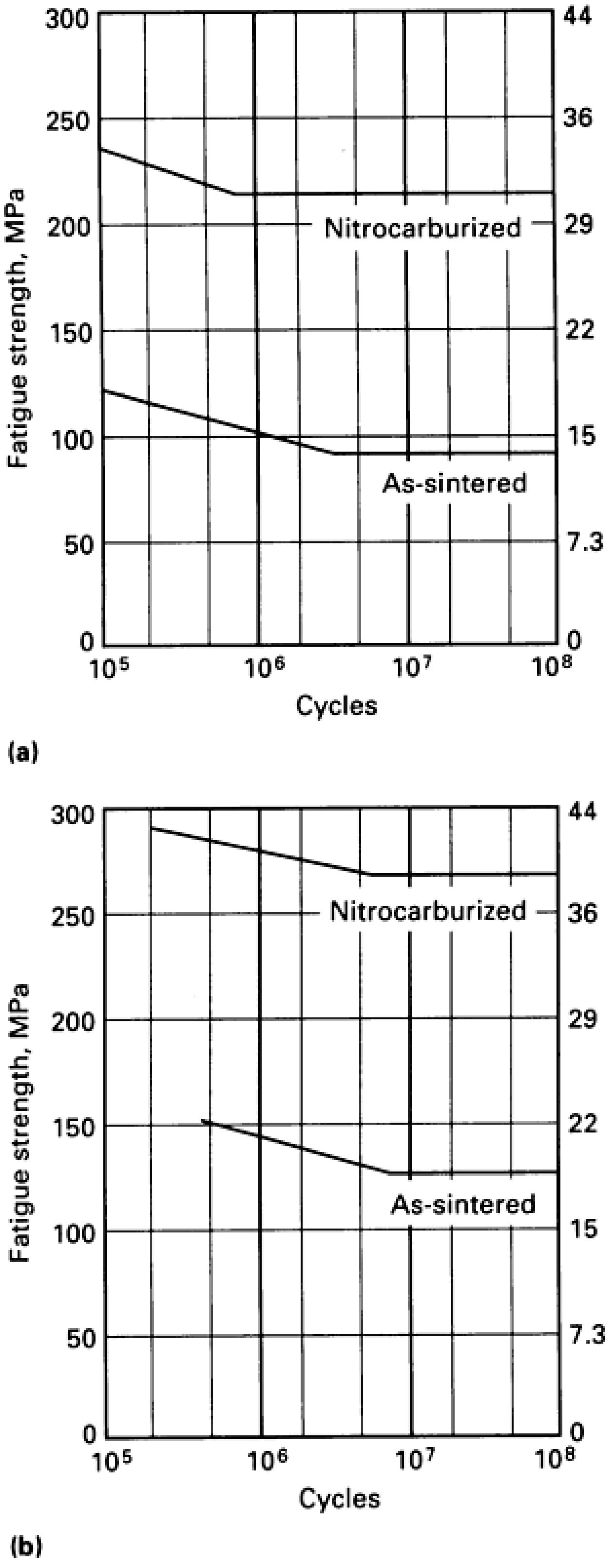

**Fig. 3** Increase in the notched axial fatigue strength of sintered low-carbon P/M steels after nitrocarburizing for 2 h at 570 °C (1060 °F). (a) F-0000 carbon steel. (b) FC-0205 copper-carbon steel. Metal powder density was 7.1 g/cm$^3$ (0.256 lb/in.$^3$). Source: Ref 5

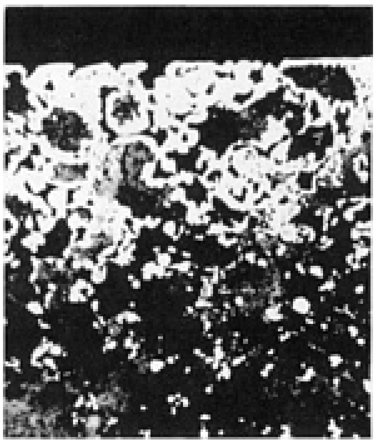

**Fig. 4 Typical microstructure in a sintered ferritic nitrocarburized iron-copper-carbon P/M steel. 100×. Source: Ref 5**

Plasma nitrocarburizing is in essence a variant of the now well-established glow-discharge plasma (ion) nitriding method (see the discussion that follows on ion nitriding). A technical argument against the use of plasma nitrocarburizing has been the effect of retained lubricant on the character and stability of the glow-discharge plasma, thus effecting the reliability of the plasma technology when applied to sintered parts. Lubricants are added to powdered products in order to achieve optimum pressing conditions. A method by which the lubricant can be satisfactorily removed prior to the P/M parts entering the vacuum chamber of the plasma unit is described in Ref 7. Using this method, it is now routinely possible to plasma nitrocarburize in one batch up to 4500 components, such as chain gear wheels, that have been manufactured by P/M. The microstructure of such a plasma nitrocarburized component is shown in Fig. 5. It is interesting to note that detailed examination shows that pores within the material, but close to the surface, also show the presence of the compound layer. The extent of the depth of such nitrocarburized pores is a function of the degree of interconnected porosity of the component, which is, in turn, a function of the pressing conditions.

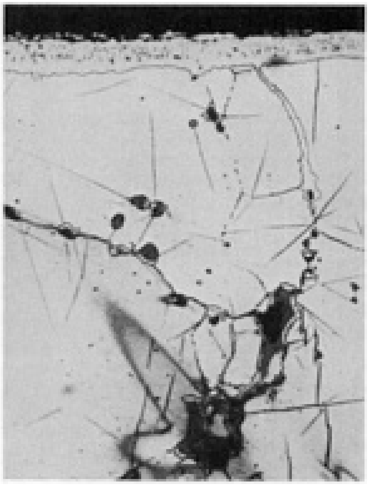

**Fig. 5 Microstructure of a plasma nitrocarburized P/M steel with a compound surface layer thickness of 10 μm. Source: Ref 7**

**Ion Nitriding.** The hardness, wear resistance, and fatigue strength can also be improved by plasma, or ion, nitriding. This is a method of surface hardening using glow discharge technology to introduce nascent (elemental) nitrogen to the surface of a metal part for subsequent diffusion into the material. In a vacuum, high-voltage electrical energy is used to form a plasma, through which nitrogen ions are accelerated to impinge on the workpiece. This ion bombardment heats the workpiece, cleans the surface, and provides active nitrogen. Ion nitriding provides better control of case chemistry and uniformity and has other advantages, such as lower part distortion than conventional gas nitriding.

When ion nitriding of P/M steels, precleaning is more critical than with wrought alloys because of the porosity characteristic. A baking operation should precede the ion nitriding of P/M parts in order to break down or release agents and/or to evaporate any cleaning solvents.

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## Tool Steels

A tool steel is any steel used to make tools for cutting, forming, or otherwise shaping a material into a final part or component. These complex alloy steels, which contain relatively large amounts of tungsten, molybdenum, vanadium, manganese, and/or chromium, make it possible to meet increasingly severe service demands. In service, most tools are subjected to extremely high loads that are applied rapidly. The tools must withstand these loads a great number of times without breaking and without undergoing excessive wear or deformation. In many applications, tool steels must provide this capability under conditions that develop high temperatures in the tool. Most tool steels are wrought products, but precision castings can be used in some applications. The powder metallurgy process is also used in making tool steels. It provides, first, a more uniform carbide size and distribution in large sections and, second, special compositions that are difficult or impossible to produce in wrought or cast alloys.

### Tool Steel Classifications

Tool steels are classified according to their composition, applications, or method of quenching. Each group is identified by a capital letter; individual tool steel types are assigned code numbers. Table 2 gives composition limits for the tool steels most commonly used. More detailed information on tool steels, including their processing, properties, and applications, can be found in Ref 8 and 9.

**Table 2 Composition limits of principal types of tool steels**

| **Designations** | | | **Composition(a), %** | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **AISI** | **SAE** | **UNS** | **C** | **Mn** | **Si** | **Cr** | **Ni** | **Mo** | **W** | **V** | **Co** |
| **Molybdenum high-speed steels** | | | | | | | | | | | |
| M1 | M1 | T11301 | 0.78-0.88 | 0.15-0.40 | 0.20-0.50 | 3.50-4.00 | 0.30 max | 8.20-9.20 | 1.40-2.10 | 1.00-1.35 | . . . |

| Designations | | | Composition(a), % | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| AISI | SAE | UNS | C | Mn | Si | Cr | Ni | Mo | W | V | Co |
| M2 | M2 | T11302 | 0.78-0.88; 0.95-1.05 | 0.15-0.40 | 0.20-0.45 | 3.75-4.50 | 0.30 max | 4.50-5.50 | 5.50-6.75 | 1.75-2.20 | . . . |
| M3, class 1 | M3 | T11313 | 1.00-1.10 | 0.15-0.40 | 0.20-0.45 | 3.75-4.50 | 0.30 max | 4.75-6.50 | 5.00-6.75 | 2.25-2.75 | . . . |
| M3, class 2 | M3 | T11323 | 1.15-1.25 | 0.15-0.40 | 0.20-0.45 | 3.75-4.50 | 0.30 max | 4.75-6.50 | 5.00-6.75 | 2.75-3.75 | . . . |
| M4 | M4 | T11304 | 1.25-1.40 | 0.15-0.40 | 0.20-0.45 | 3.75-4.75 | 0.30 max | 4.25-5.50 | 5.25-6.50 | 3.75-4.50 | . . . |
| M6 | . . . | T11306 | 0.75-0.85 | 0.15-0.40 | 0.20-0.45 | 3.75-4.50 | 0.30 max | 4.50-5.50 | 3.75-4.75 | 1.30-1.70 | 11.00-13.00 |
| M7 | . . . | T11307 | 0.97-1.05 | 0.15-0.40 | 0.20-0.55 | 3.50-4.00 | 0.30 max | 8.20-9.20 | 1.40-2.10 | 1.75-2.25 | . . . |
| M10 | . . . | T11310 | 0.84-0.94; 0.95-1.05 | 0.10-0.40 | 0.20-0.45 | 3.75-4.50 | 0.30 max | 7.75-8.50 | . . . | 1.80-2.20 | . . . |
| M30 | . . . | T11330 | 0.75-0.85 | 0.15-0.40 | 0.20-0.45 | 3.50-4.25 | 0.30 max | 7.75-9.00 | 1.30-2.30 | 1.00-1.40 | 4.50-5.50 |
| M33 | . . . | T11333 | 0.85-0.92 | 0.15-0.40 | 0.15-0.50 | 3.50-4.00 | 0.30 max | 9.00-10.00 | 1.30-2.10 | 1.00-1.35 | 7.75-8.75 |
| M34 | . . . | T11334 | 0.85-0.92 | 0.15-0.40 | 0.20-0.45 | 3.50-4.00 | 0.30 max | 7.75-9.20 | 1.40-2.10 | 1.90-2.30 | 7.75-8.75 |
| M36 | . . . | T11336 | 0.80-0.90 | 0.15-0.40 | 0.20-0.45 | 3.75-4.50 | 0.30 max | 4.50-5.50 | 5.50-6.50 | 1.75-2.25 | 7.75-8.75 |
| M41 | . . . | T11341 | 1.05-1.15 | 0.20-0.60 | 0.15-0.50 | 3.75-4.50 | 0.30 max | 3.25-4.25 | 6.25-7.00 | 1.75-2.25 | 4.75-5.75 |
| M42 | . . . | T11342 | 1.05-1.15 | 0.15-0.40 | 0.15-0.65 | 3.50-4.25 | 0.30 max | 9.00-10.00 | 1.15-1.85 | 0.95-1.35 | 7.75-8.75 |
| M43 | . . . | T11343 | 1.15-1.25 | 0.20-0.40 | 0.15-0.65 | 3.50-4.25 | 0.30 max | 7.50-8.50 | 2.25-3.00 | 1.50-1.75 | 7.75-8.75 |

| **Designations** | | | **Composition(a), %** | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **AISI** | **SAE** | **UNS** | **C** | **Mn** | **Si** | **Cr** | **Ni** | **Mo** | **W** | **V** | **Co** |
| M44 | . . . | T11344 | 1.10-1.20 | 0.20-0.40 | 0.30-0.55 | 4.00-4.75 | 0.30 max | 6.00-7.00 | 5.00-5.75 | 1.85-2.20 | 11.00-12.25 |
| M46 | . . . | T11346 | 1.22-1.30 | 0.20-0.40 | 0.40-0.65 | 3.70-4.20 | 0.30 max | 8.00-8.50 | 1.90-2.20 | 3.00-3.30 | 7.80-8.80 |
| M47 | . . . | T11347 | 1.05-1.15 | 0.15-0.40 | 0.20-0.45 | 3.50-4.00 | 0.30 max | 9.25-10.00 | 1.30-1.80 | 1.15-1.35 | 4.75-5.25 |
| **Tungsten high-speed steels** | | | | | | | | | | | |
| T1 | T1 | T12001 | 0.65-0.80 | 0.10-0.40 | 0.20-0.40 | 3.75-4.00 | 0.30 max | . . . | 17.25-18.75 | 0.90-1.30 | . . . |
| T2 | T2 | T12002 | 0.8-0.90 | 0.20-0.40 | 0.20-0.40 | 3.75-4.50 | 0.30 max | 1.00 max | 17.50-19.00 | 1.80-2.40 | . . . |
| T4 | T4 | T12004 | 0.70-0.80 | 0.10-0.40 | 0.20-0.40 | 3.75-4.50 | 0.30 max | 0.40-1.00 | 17.50-19.00 | 0.80-1.20 | 4.25-5.75 |
| T5 | T5 | T12005 | 0.75-0.85 | 0.20-0.40 | 0.20-0.40 | 3.75-5.00 | 0.30 max | 0.50-1.25 | 17.50-19.00 | 1.80-2.40 | 7.00-9.50 |
| T6 | . . . | T12006 | 0.75-0.85 | 0.20-0.40 | 0.20-0.40 | 4.00-4.75 | 0.30 max | 0.40-1.00 | 18.50-21.00 | 1.50-2.10 | 11.00-13.00 |
| T8 | T8 | T12008 | 0.75-0.85 | 0.20-0.40 | 0.20-0.40 | 3.75-4.50 | 0.30 max | 0.40-1.00 | 13.25-14.75 | 1.80-2.40 | 4.25-5.75 |
| T15 | . . . | T12015 | 1.50-1.60 | 0.15-0.40 | 0.15-0.40 | 3.75-5.00 | 0.30 max | 1.00 max | 11.75-13.00 | 4.50-5.25 | 4.75-5.25 |
| **Chromium hot-work steels** | | | | | | | | | | | |
| H10 | . . . | T20810 | 0.35-0.45 | 0.25-0.70 | 0.80-1.20 | 3.00-3.75 | 0.30 max | 2.00-3.00 | . . . | 0.25-0.75 | . . . |
| H11 | H11 | T20811 | 0.33-0.43 | 0.20-0.50 | 0.80-1.20 | 4.75-5.50 | 0.30 max | 1.10-1.60 | . . . | 0.30-0.60 | . . . |
| H12 | H12 | T20812 | 0.30-0.40 | 0.20-0.50 | 0.80-1.20 | 4.75-5.50 | 0.30 max | 1.25-1.75 | 1.00-1.70 | 0.50 max | . . . |

| Designations | | | Composition[(a)], % | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **AISI** | **SAE** | **UNS** | **C** | **Mn** | **Si** | **Cr** | **Ni** | **Mo** | **W** | **V** | **Co** |
| H13 | H13 | T20813 | 0.32-0.45 | 0.20-0.50 | 0.80-1.20 | 4.75-5.50 | 0.30 max | 1.10-1.75 | . . . | 0.80-1.20 | . . . |
| H14 | . . . | T20814 | 0.35-0.45 | 0.20-0.50 | 0.80-1.20 | 4.75-5.50 | 0.30 max | . . . | 4.00-5.25 | . . . | . . . |
| H19 | . . . | T20819 | 0.32-0.45 | 0.20-0.50 | 0.20-0.50 | 4.00-4.75 | 0.30 max | 0.30-0.55 | 3.75-4.50 | 1.75-2.20 | 4.00-4.50 |
| **Tungsten hot-work steels** | | | | | | | | | | | |
| H21 | H21 | T20821 | 0.26-0.36 | 0.15-0.40 | 0.15-0.50 | 3.00-3.75 | 0.30 max | . . . | 8.50-10.00 | 0.30-0.60 | . . . |
| H22 | . . . | T20822 | 0.30-0.40 | 0.15-0.40 | 0.15-0.40 | 1.75-3.75 | 0.30 max | . . . | 10.00-11.75 | 0.25-0.50 | . . . |
| H23 | . . . | T20823 | 0.25-0.35 | 0.15-0.40 | 0.15-0.60 | 11.00-12.75 | 0.30 max | . . . | 11.00-12.75 | 0.75-1.25 | . . . |
| H24 | . . . | T20824 | 0.42-0.53 | 0.15-0.40 | 0.15-0.40 | 2.50-3.50 | 0.30 max | . . . | 14.00-16.00 | 0.40-0.60 | . . . |
| H25 | . . . | T20825 | 0.22-0.32 | 0.15-0.40 | 0.15-0.40 | 3.75-4.50 | 0.30 max | . . . | 14.00-16.00 | 0.40-0.60 | . . . |
| H26 | . . . | T20826 | 0.45-0.55[(b)] | 0.15-0.40 | 0.15-0.40 | 3.75-4.50 | 0.30 max | . . . | 17.25-19.00 | 0.75-1.25 | . . . |
| **Molybdenum hot-work steels** | | | | | | | | | | | |
| H42 | . . . | T20842 | 0.55-0.70[(b)] | 0.15-0.40 | . . . | 3.75-4.50 | 0.30 max | 4.50-5.50 | 5.50-6.75 | 1.75-2.20 | . . . |
| **Air-hardening medium-alloy cold-work steels** | | | | | | | | | | | |
| A2 | A2 | T30102 | 0.95-1.05 | 1.00 max | 0.50 max | 4.75-5.50 | 0.30 max | 0.90-1.40 | . . . | 0.15-0.50 | . . . |
| A3 | . . . | T30103 | 1.20-1.30 | 0.40-0.60 | 0.50 max | 4.75-5.50 | 0.30 max | 0.90-1.40 | . . . | 0.80-1.40 | . . . |

| Designations | | | Composition[(a)], % | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **AISI** | **SAE** | **UNS** | **C** | **Mn** | **Si** | **Cr** | **Ni** | **Mo** | **W** | **V** | **Co** |
| A4 | . . . | T30104 | 0.95-1.05 | 1.80-2.20 | 0.50 max | 0.90-2.20 | 0.30 max | 0.90-1.40 | . . . | . . . | . . . |
| A6 | . . . | T30106 | 0.65-0.75 | 1.80-2.50 | 0.50 max | 0.90-1.20 | 0.30 max | 0.90-1.40 | . . . | . . . | . . . |
| A7 | . . . | T30107 | 2.00-2.85 | 0.80 max | 0.50 max | 5.00-5.75 | 0.30 max | 0.90-1.40 | 0.50-1.50 | 3.90-5.15 | . . . |
| A8 | . . . | T30108 | 0.50-0.60 | 0.50 max | 0.75-1.10 | 4.75-5.50 | 0.30 max | 1.15-1.65 | 1.00-1.50 | . . . | . . . |
| A9 | . . . | T30109 | 0.45-0.55 | 0.50 max | 0.95-1.15 | 4.75-5.50 | 1.25-1.75 | 1.30-1.80 | . . . | 0.80-1.40 | . . . |
| A10 | . . . | T30110 | 1.25-1.50[(c)] | 1.60-2.10 | 1.00-1.50 | . . . | 1.55-2.05 | 1.25-1.75 | . . . | . . . | . . . |
| **High-carbon, high-chromium cold-work steels** | | | | | | | | | | | |
| D2 | D2 | T30402 | 1.40-1.60 | 0.60 max | 0.60 max | 11.00-13.00 | 0.30 max | 0.70-1.20 | . . . | 1.10 max | 1.00 max |
| D3 | D3 | T30403 | 2.00-2.35 | 0.60 max | 0.60 max | 11.00-13.50 | 0.30 max | . . . | 1.00 max | 1.00 max | . . . |
| D4 | . . . | T30404 | 2.05-2.40 | 0.60 max | 0.60 max | 11.00-13.00 | 0.30 max | 0.70-1.20 | . . . | 1.00 max | . . . |
| D5 | D5 | T30405 | 1.40-1.60 | 0.60 max | 0.60 max | 11.00-13.00 | 0.30 max | 0.70-1.20 | . . . | 1.00 max | 2.50-3.50 |
| D7 | D7 | T30407 | 2.15-2.50 | 0.60 max | 0.60 max | 11.50-13.50 | 0.30 max | 0.70-1.20 | . . . | 3.80-4.40 | . . . |
| **Oil-hardening cold-work steels** | | | | | | | | | | | |
| O1 | O1 | T31501 | 0.85-1.00 | 1.00-1.40 | 0.50 max | 0.40-0.60 | 0.30 max | . . . | 0.40-0.60 | 0.30 max | . . . |
| O2 | O2 | T31502 | 0.85-0.95 | 1.40-1.80 | 0.50 max | 0.35 max | 0.30 max | 0.30 max | . . . | 0.30 max | . . . |

| **Designations** | | | **Composition(a), %** | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **AISI** | **SAE** | **UNS** | **C** | **Mn** | **Si** | **Cr** | **Ni** | **Mo** | **W** | **V** | **Co** |
| O6 | O6 | T31506 | 1.25-1.55(c) | 0.30-1.10 | 0.55-1.50 | 0.30 max | 0.30 max | 0.20-0.30 | . . . | . . . | . . . |
| O7 | . . . | T31507 | 1.10-1.30 | 1.00 max | 0.60 max | 0.35-0.85 | 0.30 max | 0.30 max | 1.00-2.00 | 0.40 max | . . . |
| **Shock-resisting steels** | | | | | | | | | | | |
| S1 | S1 | T41901 | 0.40-0.55 | 0.10-0.40 | 0.15-1.20 | 1.00-1.80 | 0.30 max | 0.50 max | 1.50-3.00 | 0.15-0.30 | . . . |
| S2 | S2 | T41902 | 0.40-0.55 | 0.30-0.50 | 0.90-1.20 | . . . | 0.30 max | 0.30-0.60 | . . . | 0.50 max | . . . |
| S5 | S5 | T41905 | 0.50-0.65 | 0.60-1.00 | 1.75-2.25 | 0.35 max | . . . | 0.20-1.35 | . . . | 0.35 max | . . . |
| S6 | . . . | T41906 | 0.40-0.50 | 1.20-1.50 | 2.00-2.50 | 1.20-1.50 | . . . | 0.30-0.50 | . . . | 0.20-0.40 | . . . |
| S7 | . . . | T41907 | 0.45-0.55 | 0.20-0.80 | 0.20-1.00 | 3.00-3.50 | . . . | 1.30-1.80 | . . . | 0.20-0.30(d) | . . . |
| **Low-alloy special-purpose tools steels** | | | | | | | | | | | |
| L2 | . . . | T61202 | 0.45-1.00(b) | 0.10-0.90 | 0.50 max | 0.70-1.20 | . . . | 0.25 max | . . . | 0.10-0.30 | . . . |
| L6 | L6 | T61206 | 0.65-0.75 | 0.25-0.80 | 0.50 max | 0.60-1.20 | 1.25-2.00 | 0.50 max | . . . | 0.20-0.30(d) | . . . |
| **Low-carbon mold steels** | | | | | | | | | | | |
| P2 | . . . | T51602 | 0.10 max | 0.10-0.40 | 0.10-0.40 | 0.75-1.25 | 0.10-0.50 | 0.15-0.40 | . . . | . . . | . . . |
| P3 | . . . | T51603 | 0.10 max | 0.20-0.60 | 0.40 max | 0.40-0.75 | 1.00-1.50 | . . . | . . . | . . . | . . . |
| P4 | . . . | T51604 | 0.12 max | 0.20-0.60 | 0.10-0.40 | 4.00-5.25 | . . . | 0.40-1.00 | . . . | . . . | . . . |

| **Designations** | | | **Composition(a), %** | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **AISI** | **SAE** | **UNS** | **C** | **Mn** | **Si** | **Cr** | **Ni** | **Mo** | **W** | **V** | **Co** |
| P5 | . . . | T51605 | 0.10 max | 0.20-0.60 | 0.40 max | 2.00-2.50 | 0.35 max | . . . | . . . | . . . | . . . |
| P6 | . . . | T51606 | 0.05-0.15 | 0.35-0.70 | 0.10-0.40 | 1.25-1.75 | 3.25-3.75 | . . . | . . . | . . . | . . . |
| P20 | . . . | T51620 | 0.28-0.40 | 0.60-1.00 | 0.20-0.80 | 1.40-2.00 | . . . | 0.30-0.55 | . . . | . . . | . . . |
| P21 | . . . | T51621 | 0.18-0.22 | 0.20-0.40 | 0.20-0.40 | 0.20-0.30 | 3.90-4.25 | . . . | . . . | 0.15-0.25 | 1.05-1.25Al |
| **Water-hardening tool steels** | | | | | | | | | | | |
| W1 | W108, W109, W110, W112 | T72301 | 0.70-1.50(e) | 0.10-0.40 | 0.10-0.40 | 0.15 max | 0.20 max | 0.10 max | 0.15 max | 0.10 max | . . . |
| W2 | W209, W210 | T72302 | 0.85-1.50(e) | 0.10-0.40 | 0.10-0.40 | 0.15 max | 0.20 max | 0.10 max | 0.15 max | 0.15-0.35 | . . . |
| W5 | . . . | T72305 | 1.05-1.15 | 0.10-0.40 | 0.10-0.40 | 0.40-0.60 | 0.20 max | 0.10 max | 0.15 max | 0.10 max | . . . |

(a) All steels except group W contain 0.25 max Cu, 0.03 max P, and 0.03 max S; group W steels contain 0.20 max P, and 0.025 max S. Where specified, sulfur may be increased to 0.06 to 0.15% to improve machinability of group H, M, and T steels.

(b) Available in several carbon ranges.

(c) Contains free graphite in the microstructure.

(d) Optional.

(e) Specified carbon ranges are designated by suffix numbers.

**High-speed steels** are tool materials developed largely for use in high-speed metal cutting applications. There are two classifications of high-speed steels; molybdenum high-speed steels, or group M, which contain from 0.75 to 1.52% C and 4.50 to 11.0% Mo, and tungsten high-speed steels, or group T, which have similar carbon contents but high (11.75 to 21.00%) tungsten contents. Group M steels constitute more than 95% of all high-speed steel produced in the United States.

**Hot-work steels (group H)** have been developed to withstand the combinations of heat, pressure, and abrasion associated with punching, shearing, or forming of metals at high temperatures. Group H steels usually have medium carbon contents (0.35 to 0.45%) and combined chromium, tungsten, molybdenum, and vanadium contents of 6 to 25%. H steels are divided into chromium hot-work steels, tungsten hot-work steels, and molybdenum hot-work steels.

**Cold-work steels** are restricted in application to those uses that do not involve prolonged or repeated heating above 205 to 260 °C (400 to 500 °F). There are three categories of cold-work steels: air-hardening steels, or group A; high-carbon, high-chromium steels, or group D; and oil-hardening steels, or group O.

**Shock-resisting, or group S, steels** contain manganese, silicon, chromium, tungsten, and molybdenum, in various combinations; carbon content is about 1.50%. Group S steels are used primarily for chisels, rivet sets, punches, and other applications requiring high toughness and resistance to shock loading.

**The low-alloy special purpose, or group L, tool steels** contain small amounts of chromium, vanadium, nickel, and molybdenum. Group L steels are generally used for machine parts and other special applications requiring good strength and toughness.

**Mold steels, or group P,** contain chromium and nickel as principal alloying elements. Because of their low resistance to softening at elevated temperatures, group P steels are used almost exclusively in low-temperature die casting dies and in molds for injection or compression molding of plastics.

**Water-hardening, or group W, tool steels** contain carbon as the principal alloying element (0.70 to 1.50% C). Group W steels, which also have low resistance to softening at elevated temperatures, are suitable for cold heading, coining, and embossing tools, woodworking tools, metal-cutting tools, and wear-resistant machine tool components.

## *Surface Treatments for Tool Steels (Ref 10)*

Most surface treatments are employed to increase surface hardness and/or wear resistance, minimize adhesion (reduce friction), or improve the corrosion resistance of the tool steel base. The processes discussed below are described in greater detail elsewhere in this Volume or in *Heat Treating*, Volume 4 of the *ASM Handbook*.

**Carburizing.** The processes of case hardening and carburizing are of limited use in tool steel applications, because of the relatively high carbon contents of the tool steels. Carburizing can be accomplished in many ways, and essentially consists of heating the final machined tool into the austenite region in the presence of carbonaceous solids, liquids, or gases.

Low-carbon plastic mold steels (P type) are often carburized after hubbing or machining of the cavity in the mold. In this application, the tool steel is intentionally lean in carbon content to improve hubbing or machining, and must be carburized in order to have sufficient surface hardness for the end use.

**Nitriding** is a frequently used surface treatment that increases surface hardness, adds to the corrosion resistance of the tool, and reduces friction. Basically, the process involves heating the finished tool in the presence of a nitrogen-containing liquid or gas and allowing nitrogen to diffuse into the tool. Gas nitriding is usually accomplished at a lower temperature (about 527 °C, or 980 °F) and longer time (10 to 90 h) than liquid nitriding, which occurs at temperatures ranging from 538 to 552 °C (1000 to 1025 °F) for 2 to 4 h. A nitrided depth that ranges from 13 to 76 $\mu$m (0.0005 to 0.003 in.) is desired.

Because of decreased wear and die pickup, cold-extrusion punches experience a two to three-fold improvement in life. Nitriding is often used whenever mold wash is a problem in the die casting of zinc or aluminum alloys. Galling of sheet metal working dies can be alleviated by nitriding these dies before use.

Steels that will be nitrided should contain one or more of the nitride-forming elements (chromium, vanadium, or aluminum) in order to prevent the easy spalling and chipping that results when iron nitride is formed. Commonly nitrided tool steels include H11, H12, H13, A2, O2, and the high-speed tool steels.

**Ion or plasma nitriding** has many of the same characteristics of liquid or gas nitriding. This process relies on a nitrogen gas being ionized by glow discharge conditions between the tool (carbide) and the furnace wall or shield (anode).

The primary advantages are the reductions in time and temperature, which save money and reduce the distortion and softening of prehardened tools. Usually, treatment times vary between 0.5 and 36 h.

**Boriding.** In this process, boron atoms from a solid, liquid, gas, or plasma atmosphere surrounding the finished part are diffused into the surface, creating a hard, water-resistant iron boride layer. Metal-to-metal wear testing demonstrated a three-fold improvement in wear resistance of borided O1 and O2 tool steels and over a two-fold increase in A2 tool steel (Ref 11). Borided A2 tool steel showed twice the life of uncoated O2 tool steel in a deep-drawing operation in which low-carbon steel cups were manufactured (Ref 11). An H13 roller designed to flange milk cans was borided and produced three times as many cans before it wore out (Ref 12).

Boriding takes place at temperatures as low as 600 °C (1100 °F), but usual practice involves a period from 1 to 6 h at temperatures from 800 to 900 °C (1470 to 1650 °F) (Ref 11, 12). The resultant layer is between 13 and 130 μm (0.0005 and 0.005 in.), and tends to be dull because of the microroughness of the surface. This high process temperature requires that the boron treatment act as the austenitization step, or else the process must be followed by reaustenitization. This necessarily limits the process to applications where tolerances of about 25 μm (0.001 in.) can be tolerated.

**Carbide Coating by Toyota Diffusion Process.** Good surface covering and strongly bonding carbide coatings, such as VC, NbC, and $Cr_7C_3$, can be formed on die steel surfaces by a coating method developed at Toyota Central Research and Development Laboratory, Inc. of Japan.

In the Toyota Diffusion (TD) process, metal dies to be treated are degreased, immersed in a carbide salt bath for a specific time period, quenched for core hardening, tempered, and washed in hot water for the removal of any residual salt. The borax salt bath contains compounds (usually ferroalloys) with carbide-forming elements such as vanadium, niobium, and chromium. The bath temperature is selected to conform to the hardening temperature of the die steel. For example, the borax bath temperature would be between 1000 and 1050 °C (1830 and 1920 °F) for H13 die steel.

The carbide layer is formed on the die surface through a chemical reaction between carbide-forming elements dissolved in the fused borax and carbon in the substrate. The carbide layer thickens due to reaction between the carbide-forming element atoms in the salt bath and the carbon atoms diffusing into the outside surface layer from the interior of the substrate.

The thickness of the carbide layer is varied by controlling the bath temperature and immersion time. An immersion time of 4 to 8 h is needed for H13 steel to produce carbide layers with satisfactory thickness (5 to 10 μm) for die-casting applications. Dies are then removed from the bath and cooled in oil and salt or air for core hardening followed by tempering.

Coated tool steels, such as H12 and H13 steels, exhibit high hardness and excellent resistance to wear, seizure, corrosion, and oxidation. In addition, resistance to cracking, flaking, and heat checking is claimed. Hardness of the coating depends on layer composition: 3500 HV for vanadium carbide, 2800 HV for niobium carbide, and 1700 HV for chromium carbide.

**Oxidation** is a well-established process used for high-speed steel cutting tools. Increases in tool life of up to 100% are mostly due to a decrease in friction, because of the hard oxide coating and the ability of the porous oxide to entrap lubricant and draw it to the tool-workpiece interface. Steam oxidation of a finished tool is accomplished either by exposure to steam at a temperature of about 566 °C (1050 °F) or by treating in liquid sodium hydroxide and sodium nitrate salts at approximately 140 °C (285 °F) for periods of time ranging from 5 to 20 min. These treatments result in a black oxidized layer that is less than 5 μm (0.0002 in.) thick and will not peel, chip, nor crack, even when the tool is bent or cut. Tool life improvements due to steam oxidation are listed in Tables 3 and 4.

**Table 3 Machining tool life improvements due to steam oxidation**

| Tool | Application | Tool life | |
|---|---|---|---|
| | | Before steam treating | After steam treating |
| M2 broachers | Cutting AISI 1010 latch | 20 h per grind | 70 h per grind |

| | | | |
|---|---|---|---|
| M2 drills | Drilling Bakelite plastic insulating blocks | 10 holes | 25 holes |
| | Phenolic terminal plates | 1700 holes per grind | 8500 holes per grind |
| | Drilling AISI 4030 steel 25 mm (1 in.) thick | 17 holes | 81 holes |
| M7 end mill tools | Cutting 8740 steel forgings | 30 pieces | 200 pieces |
| A6 hobs | Cutting teeth on AISI 3140 forged gear | . . . | 62.2% increased life |
| M2 milling cutters | Two slots in 1020 steel | 150 cuts per grind | 306 cuts per grind |
| | Slotting 1020 steel bars | 2000 per grind | 7000 per grind |
| M2 saw blades | Cutting 75 mm (3 in.) rods, austenitic steel | 100% endurance at 0.52 m/s (102 sfm) | 120% endurance at 0.57 m/s (112 sfm) |
| M2 taps | Cutting SAE 52100 steel | 1800 pieces | 3000 pieces |

Source: Ref 13

**Table 4 Effect of steam oxidation on tool life in forming various carbon steel nuts and bolts**

| **Tool** | **Application** | **Tool life** | |
|---|---|---|---|
| | | **Before steam treating**[(a)] | **After steam treating**[(b)] |
| M2 4th station punch | Castle nut 1030 material | 21,000 nuts | 42,000 nuts |
| M2 4th station punch | Slotted insert nut 1030 material | 22,000 nuts | 38,000 nuts |
| M2 4th station punch | Castle nut 1030 material | 29,000 nuts | 80,000 nuts |
| M2 3rd station punch | Castle nut 1110 material | 20,000 nuts | 35,000 nuts |
| M2 4th station punch | Castle nut 1110 material | 15,000 nuts | 35,000 nuts |
| M2 trim die | Bolt head 1335 material | 7,000 bolts | 16,000 bolts |

(a) Hardened and triple tempered.

(b) Hardened, triple tempered and steam treated.

**Bright Finish.** Most high-speed cutting tools are finished with a ground or mechanically polished surface that would be categorized as a bright finish. Bright finished tools are often preferred to tools with an oxide finish for machining nonferrous work material. The smooth or bright finish tends to resist galling, a type of welding or buildup associated with many nonferrous alloys. However, work materials of ferrous alloys tend to adhere to similar, iron-base tools having a bright finish. This buildup on the cutting edges leads to increased frictional heat, poor surface finish, and increased load at the cutting edge.

**Plating.** Three different kinds of plating are used on tool steels. Cadmium plating is used for appearance purposes and to reduce corrosion of the tool. It also has some usefulness in preventing adhesion. Nickel plating is commonly used for appearance purposes and to prevent corrosion.

The most commonly practiced tool steel plating process is hard chromium plating. Plating thickness varies between 2 and 13 μm (0.0001 and 0.0005 in.) and, because it is very hard, it prolongs life by increasing abrasive wear resistance. More important than plating hardness is its very low friction coefficient, which effectively prevents adhesive wear.

However, hard chromium plating is not without problems. Tool steels may be hydrogen embrittled when plated, and the plating has a tendency to spall and flake. These wear debris can actually accelerate abrasive wear.

**Chemical vapor deposition (CVD),** a process conducted in a vacuum chamber, relies on a deposition from reacted gas onto the tool steel surface. Many different materials can be used as coatings. Chromium, $Al_2O_3$, TiC, CrC, $Fe_4N$, and TiN are commonly used, and other materials are being studied. This process utilizes high temperatures, usually above 800 °C (1472 °F), which means that tool steels must be tempered after the CVD coating is applied. The most popular wear-resistant coatings are TiC and TiN, which are used to coat high-speed, cold-work die and hot-work die tool steels. These coatings commonly range in thickness from 2 to 20 μm (0.0001 to 0.001 in.). Using CVD coating with TiC and TiN, the primary mechanism of wear reduction is the extremely high hardness, which leads to excellent abrasion resistance, although some decrease in friction coefficient can often be realized. The chlorine content of the coating must carefully be maintained at a level below 5% to avoid degradation of the wear resistance (Ref 14).

Tool steels that can be successfully CVD coated include the AISI A, S, D, H, M, and T steel types. The lower-alloyed S type and all of the W and O types are either very difficult or impossible to properly coat, because of their low austenitization temperatures.

**Physical vapor deposition (PVD),** which is also conducted in a vacuum chamber, can be accomplished in several different ways. The process relies on plasma-aided precipitation of either TiC or TiN onto tool steel at temperatures ranging from 200 to 550 °C (400 to 1025 °F) (Ref 14). This temperature range is much more suitable for the coating of high-speed tool steels than the temperatures required for CVD.

Tool steel wear is reduced in about the same proportions (2 to 6 times less wear), whether the TiC or TiN is applied by CVD or PVD. TiN coatings on H13 pins reduced the friction coefficient in pin-on-disk tests from 0.7 to less than 0.2 (Ref 15). Modified ASTM G65-10 abrasive wear testing of D3 steel showed that wear of the TiN-coated samples was between 4 and 23% of the uncoated samples, depending on their initial surface roughness (Ref 15). This result led Sundquist et al. to propose that increases in tool life that are due to TiN coating can only be expected when the surface roughness is less than the coating thickness (Ref 15). Specific examples of the use of PVD coatings for improving the life of high-speed steel tools are listed in Table 5.

**Table 5 Increased tool life attained with PVD coated cutting tools**

| Cutting tool | Coating | Workpiece material | Workpieces machined before resharpening |
|---|---|---|---|

| **Type** | **High-speed tool steel, AISI type** | | | **Uncoated** | **Coated** |
|---|---|---|---|---|---|
| End mill | M7 | TiN | 1022 steel, 35 HRC | 325 | 1200 |
| End mill | M7 | TiN | 6061-T6 aluminum alloy | 166 | 1500 |
| End mill | M3 | TiN | 7075T aluminum alloy | 9 | 53 |
| Gear hob | M2 | TiN | 8620 steel | 40 | 80 |
| Broach insert | M3 | TiN | Type 303 stainless steel | 100,000 | 300,000 |
| Broach | M2 | TiN | 48% nickel alloy | 200 | 3400 |
| Broach | M2 | TiN | Type 410 stainless steel | 10,000-12,000 | 31,000 |
| Pipe tap | M2 | TiN | Gray iron | 3000 | 9000 |
| Tap | M2 | TiN | 1050 steel, 30-33 HRC | 60-70 | 750-800 |
| Form tool | T15 | TiC | 1045 steel | 5000 | 23,000 |
| Form tool | T15 | TiN | Type 303 stainless steel | 1840 | 5890 |
| Cutoff tool | M2 | TiC-TiN | Low-carbon steel | 150 | 1000 |
| Drill | M7 | TiN | Low-carbon steel | 1000 | 4000 |
| Drill | M7 | TiN | Titanium alloy 662 layered with D6AC tool steel, 48-50 HRC | 9 | 86 |

Source: Ref 16

**Ion implantation** is a process by which atoms of virtually any element can be injected into the near-surface region of any solid. The implantation process involves forming a beam of charged ions of the desired element and then accelerating them at high energies towards the surface of the solid, which is held under high vacuum. The atoms penetrate into the solid to a depth of 0.25 to 25 nm (2.5 to 250 Å). This process differs from coating processes in that it does not produce a discrete coating; rather, it alters the chemical composition near the surface of the solid. The most common element implanted in tool steels in order to improve tribological properties, specifically adhesive and sliding wear, is nitrogen.

Examples of ion implantation in metal forming and cutting applications are listed in Table 6. Ion implantation of titanium and carbon has also improved the service life of stamping and cutting tools.

**Table 6 Examples of ion implantation in metalforming and cutting applications**

| Part | Part material | Process | Work material | Ion | Energy, keV | Benefit |
|---|---|---|---|---|---|---|
| Tool inserts | TiN-coated tool steel | Machining | 4140 | N | 80 | 3× life |
| Taps | HSS | Tapping | 4140 | N | 80 | 3× life |
| | HSS | Tapping | 4130 | N | 80 | 5× life |
| | HSS | Tapping | 4140 | N | 50 | 10× life |
| | M35 | Tapping | . . . | $N_2$ | 200 | 4× life |
| | M7 | Tapping | . . . | N | 100 | 2× life |
| Cutting blade | M2 | Cutting | 1050 | N | 100 | 2× life |
| | M2 | Cutting | SAE 950 | N | 100 | 4× life |
| Dies | D2 | Forming | 321 SS | N | 80 | 2× life |
| | M2 | Forming | Steel | N | 100 | 2-12× life |
| | M2 | Forming | 1020 | N | 100 | Negligible effect |
| | D6 | Forming | $TiO_2$ and rubber | N | 100 | 6× life |
| Molds | D2 | Forming | Polymers | N | 50 | 5× life |
| Rollers | H13 | Rolling | Steel | N | 100 | 5× life |

Note: HSS, high-speed steel; SS, stainless steel.

**Laser surface processing methods,** such as laser melting, have also been applied to tool steels. Hsu and Molian (Ref 18) reported that the tool life of laser-melted M2 steel tool bits was from 200 to 500% higher than if they were conventionally hardened using catastrophic failure criterion (Fig. 6). For laser-melted M35 steel tool bits, the tool life was from 20 to 125% higher than if they were conventionally hardened using flank wear failure criterion (Fig. 6). High-alloy martensite, fine austenite grain size, and finely dispersed carbides all contributed to high hardness, good toughness, and low coefficient of friction.

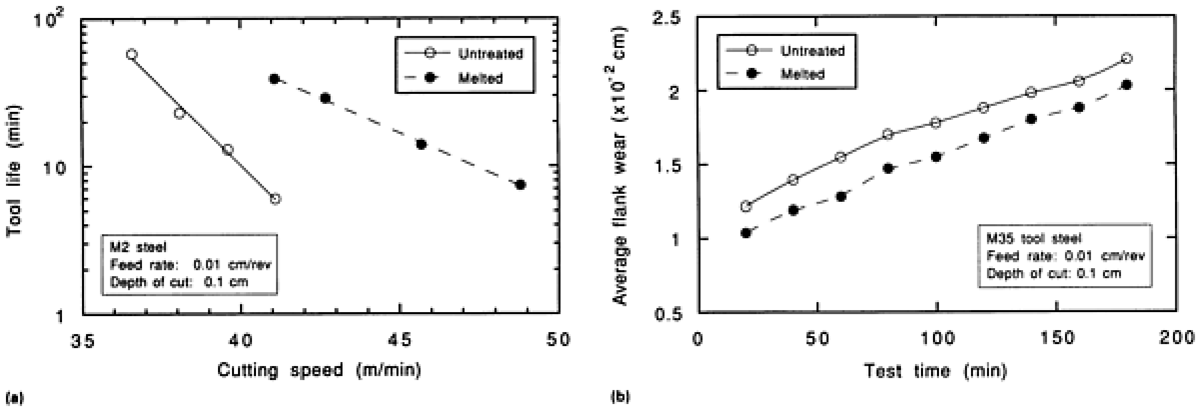

**Fig. 6 Tool life of conventionally heat-treated and laser-melted tool bits. (a) M2 tool steel. (b) M35 tool steel. Source: Ref 18**

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## Maraging Steels (Ref 19)

Maraging steels comprise a special class of high-strength steels that differ from conventional steels in that they are hardened by a metallurgical reaction that does not involve carbon. Instead, these steels are strengthened by the precipitation of intermetallic compounds at temperatures of about 480 °C (900 °F). The term maraging is derived from martensite age hardening and denotes the age hardening of low-carbon, iron-nickel lath martensite matrix. The physical metallurgy and properties of maraging steels are described in Ref 19.

Commercial maraging steels are designed to provide specific levels of yield strength from 1030 to 2420 MPa (150 to 350 ksi). Some experimental maraging steels have yield strengths as high as 3450 MPa (500 ksi). These steels typically have very high nickel, cobalt, and molybdenum contents and very low carbon contents. Carbon, in fact, is an impurity in these steels and is kept as low as commercially feasible in order to minimize the formation of titanium carbide (TiC), which can adversely affect strength, ductility, and toughness.

Table 7 lists the chemical compositions of the more common grades of maraging steel. The nomenclature that has become established for these steels is nominal yield strength (ksi units) in parentheses. Thus, for example, 18Ni (200) steel is normally age hardened to a yield strength of 1380 MPa (200 ksi). The first three steels in Table 7--18Ni (200), 18Ni (250), and 18Ni (300)--are the most widely used and most commonly available grades. The 18Ni (350) grade is an ultrahigh-strength variety made in limited quantities for special applications. Two 18Ni (350) compositions have been produced (see the footnote in Table 7). The 18Ni (Cast) grade was developed specifically as a cast composition.

## Table 7 Nominal compositions of commercial maraging steels

| **Grade** | **Composition, %**[(a)] | | | | | |
|---|---|---|---|---|---|---|
| | **Ni** | **Mo** | **Co** | **Ti** | **Al** | **Nb** |
| **Standard grades** | | | | | | |
| 18Ni(200) | 18 | 3.3 | 8.5 | 0.2 | 0.1 | . . . |
| 18Ni(250) | 18 | 5.0 | 8.5 | 0.4 | 0.1 | . . . |
| 18Ni(300) | 18 | 5.0 | 9.0 | 0.7 | 0.1 | . . . |
| 18Ni(350) | 18 | 4.2[(b)] | 12.5 | 1.6 | 0.1 | . . . |
| 18Ni(Cast) | 17 | 4.6 | 10.0 | 0.3 | 0.1 | . . . |
| 12-5-3(180)[(c)] | 12 | 3 | . . . | 0.2 | 0.3 | . . . |
| **Cobalt-free and low-cobalt bearing grades** | | | | | | |
| Cobalt-free 18Ni(200) | 18.5 | 3.0 | . . . | 0.7 | 0.1 | . . . |
| Cobalt-free 18Ni(250) | 18.5 | 3.0 | . . . | 1.4 | 0.1 | . . . |
| Low-cobalt 18Ni(250) | 18.5 | 2.6 | 2.0 | 1.2 | 0.1 | 0.1 |

(a) All grades contain no more than 0.03% C.

(b) Some producers use a combination of 4.8% Mo and 1.4% Ti, nominal.

(c) Contains 5% Cr

A number of cobalt-free maraging steels and a low-cobalt bearing maraging steel have recently been developed. The driving force for the development of these particular alloys was the cobalt shortage and resultant price escalation of cobalt during the late 1970s and early 1980s. The nominal compositions for these alloys are also listed in Table 7.

### Surface Treatments for Maraging Steels (Ref 19)

**Cleaning.** Grit blasting is the most efficient technique for removing oxide films formed by heat treatment. Maraging steels can be chemically cleaned by pickling in sulfuric acid or by duplex pickling in hydrochloric acid and then in nitric acid plus hydrofluoric acid (see Tables 7 and 11 in the article "Surface Engineering of Stainless Steels" in this Volume). As with conventional steels, care must be taken to avoid overpickling. The sodium hydride cleaning of maraging steels should be avoided to minimize problems with crack formation. Grease and oils can be removed by cleaning in trichloroethane-type solutions.

**Nickel Plating.** Maraging steels can be nickel plated in chloride baths provided that proper surface-activation steps are followed. Heavy chromium deposits can be plated on top of nickel electrodeposits. Maraging steels are less susceptible to hydrogen embrittlement during plating than conventional quenched and tempered steels of comparable hardness. They are not immune to hydrogen, however, and baking after plating is recommended. Baking should be done at temperatures of about 150 to 205 °C (300 to 400 °F) for periods of 3 to 10 h, depending on size and baking temperature. Baking cannot be combined with age hardening, because considerable hydrogen remains in the steel after heat treating at the higher temperatures.

**Nitriding.** Considerable surface hardening can be achieved by nitriding maraging steels in dissociated ammonia. Hardness levels equivalent to 65 to 70 HRC can be achieved at depths of up to 0.15 mm (0.006 in.) after nitriding for 24 to 48 h at 455 °C (850 °F). Nitriding at this temperature allows age hardening to occur during nitriding; therefore, the two processes can be accomplished simultaneously. Salt bath nitriding for 90 min at 540 °C (1000 °F) has been done successfully. Such treatment must be very carefully controlled to avoid excessive overaging. Both the fatigue strength and the wear resistance (Fig. 7) of maraging steels are improved by nitriding.

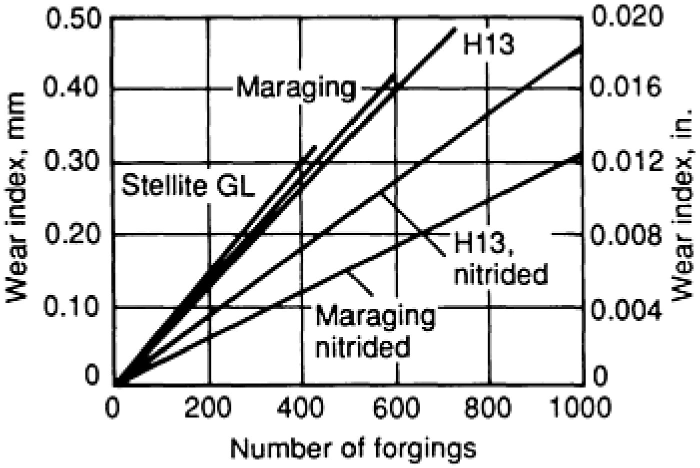

**Fig. 7 Relative wear rates of nitrided and non-nitrided tool steels and maraging steels used in extrusion forging**

Maraging steels can also be surface hardened by ion nitriding. Ozbaysal and Inal (Ref 20) have demonstrated that the surface hardening of maraging steels without a reduction in core hardness is possible using the ion nitriding process. Their studies on 18Ni(250), 18Ni(300), and 18Ni(350) showed that the highest surface hardness and the highest core hardness for all three grades were achieved by nitriding at approximately 440 °C (825 °F). Figure 8 shows the surface and core hardness as functions of ion nitriding time and temperature for 300-grade maraging alloy.

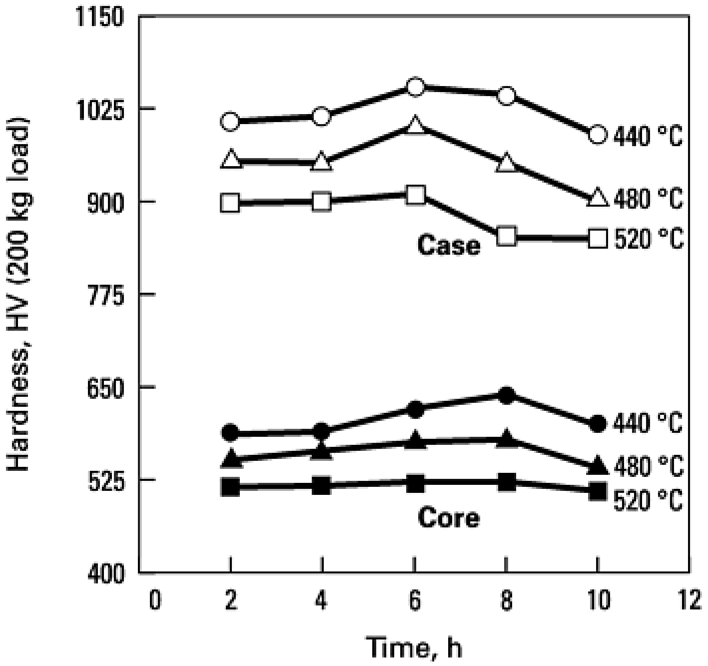

**Fig. 8 Surface (case) and core hardness as functions of ion nitriding time and temperature for 18Ni (300) maraging steel. Source: Ref 20**

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## Electrical Steels (Ref 21)

Electrical steels are flat-rolled silicon-containing alloys used for soft magnetic applications such as components (magnetic cores) for motors, generators, and transformers. The beneficial effects of silicon additions to iron include:

- Increase of electrical resistivity
- Suppression of the γ loop enabling desirable grain growth
- Development of preferred orientation grain structure

The addition of silicon also reduces magnetocrystalline anisotropy energy, and at ~6.5% Si content reduces the magnetostriction constants to nearly zero. High-permeability and low hysteresis losses can therefore be attained at the 6.5Si-Fe composition. On the negative side, the addition of silicon to iron lowers magnetic saturation, lowers Curie temperature, and seriously decreases mechanical ductility. At silicon levels above ~4%, the alloy becomes brittle and difficult to process by cold-rolling methods; thus, few commercial steels contain more than ~3.5% Si.

The commercial grades of silicon steel in common use are made mostly in electric or basic oxygen furnaces. Continuous casting and/or vacuum degassing (V-D) may be employed. Flat-rolled silicon-iron sheet and strip has low sulfur content, typically below 0.25%, with better grades below 0.01%. Carbon contents are frequently less than 0.04%. Manganese may be present up to approximately 0.70%. Residual elements such as chromium, molybdenum, nickel, copper, and phosphorus may also be present. The major alloying addition is silicon plus up to 0.6% Al (optional). These alloys are not generally sold on the basis of their composition, but rather are sold based upon controlled magnetic properties, particularly ac core losses.

Electrical sheet grades are divided into two general classifications, (1) oriented steels and (2) nonoriented steels. The oriented steels are given mill treatments designed to yield exceptionally good magnetic properties in the rolling, or lengthwise, direction of the steel. Nonoriented grades are made with a mill treatment that yields a grain structure, or texture, of a random nature and, therefore, the magnetic properties in the rolling direction of the steel are not significantly better than those in the transverse direction. Subdivisions of these steels include semiprocessed grades and the fully processed grades. The former must be given a heat treatment by the purchaser. Fully processed grades are process annealed by the manufacturer.

Table 8 gives examples of properties specified by ASTM and American Iron and Steel Institute (AISI) for standard grades of nonoriented and oriented electrical steel. The AISI designations were adopted in 1946 to eliminate the wide variety in nomenclature formerly used. When originally adopted, the AISI designation number approximated ten times the maximum core loss,* in watts per pound, exhibited by 29 gage (0.36 mm, or 0.014 in.) samples when tested at a flux density of 1.5 T (15 kG) and a magnetic circuit frequency of 60 Hz. Note that fully processed M-36 tested as 0.36 mm (0.14 in.) strip now has a maximum allowable core loss of 4.2 W/kg (1.9 W/lb), not an approximate level of 7.9 W/kg (3.6 W/lb). Low core loss is obtained with higher silicon contents, larger grain size optimization, lower impurity levels, thinner gages, and insulating coatings.

### Table 8 Properties of selected electrical steels

| **AISI type (approximate equivalent)** | **Nominal (Si + Al) content, %** | **Thickness** | | **ASTM designation** | **Maximum core loss at 60 Hz and *B* = 1.5 T (15 kG)** | |
|---|---|---|---|---|---|---|
| | | **mm** | **in.** | | **W/kg** | **W/lb** |
| **Nonoriented** | | | | | | |
| Semiprocessed (ASTM A 683)[(a)] | | | | | | |
| M-47 | 1.10 | 0.64 | 0.025 | 64S350 | 7.71 | 3.50 |
| | 1.10 | 0.47 | 0.019 | 47S300 | 6.61 | 3.00 |
| M-45 | 1.70 | 0.64 | 0.025 | 64S280 | 6.17 | 2.80 |
| | 1.70 | 0.47 | 0.019 | 47S250 | 5.51 | 2.50 |
| M-43 | 2.00 | 0.64 | 0.025 | 64S260 | 5.73 | 2.60 |
| | 2.00 | 0.47 | 0.019 | 47S230 | 5.07 | 2.30 |
| M-36 | 2.40 | 0.64 | 0.025 | 64S230 | 5.07 | 2.30 |
| | 2.40 | 0.47 | 0.019 | 47S200 | 4.41 | 2.00 |

| | | | | | | |
|---|---|---|---|---|---|---|
| M-27 | 2.70 | 0.64 | 0.025 | 64S213 | 4.69 | 2.13 |
| | 2.70 | 0.47 | 0.019 | 47S188 | 4.14 | 1.88 |
| . . . | 3.00 | 0.64 | 0.025 | 64S194 | 4.28 | 1.94 |
| . . . | 3.00 | 0.47 | 0.019 | 47S178 | 3.92 | 1.78 |
| Fully processed (ASTM A 677)[(b)] | | | | | | |
| . . . | 0.50 | 0.64 | 0.025 | 64F600 | 13.22 | 6.00 |
| . . . | 0.80 | 0.47 | 0.019 | 47F450 | 9.92 | 4.50 |
| M-47 | 1.05 | 0.64 | 0.025 | 64F470 | 10.36 | 4.70 |
| | 1.05 | 0.47 | 0.019 | 47F380 | 8.38 | 3.80 |
| M-45 | 1.85 | 0.64 | 0.025 | 64F340 | 7.49 | 3.40 |
| | 1.85 | 0.47 | 0.019 | 47F290 | 6.39 | 2.90 |
| M-43 | 2.35 | 0.64 | 0.025 | 64F270 | 5.95 | 2.70 |
| | 2.35 | 0.47 | 0.019 | 47F230 | 5.07 | 2.30 |
| M-36 | 2.65 | 0.64 | 0.025 | 64F240 | 5.29 | 2.40 |
| | 2.65 | 0.47 | 0.019 | 47F205 | 4.52 | 2.05 |
| | 2.65 | 0.36 | 0.014 | 36F190 | 4.19 | 1.90 |
| M-27 | 2.8 | 0.64 | 0.025 | 64F225 | 4.96 | 2.25 |
| | 2.8 | 0.47 | 0.019 | 47F190 | 4.19 | 1.90 |
| | 2.8 | 0.36 | 0.014 | 36F180 | 3.97 | 1.80 |
| M-22 | 3.2 | 0.64 | 0.025 | 64F218 | 4.80 | 2.18 |
| | 3.2 | 0.47 | 0.019 | 47F185 | 4.08 | 1.85 |

| | | | | | | |
|---|---|---|---|---|---|---|
| | 3.2 | 0.36 | 0.014 | 36F168 | 3.70 | 1.68 |
| M-19 | 3.3 | 0.64 | 0.025 | 64F208 | 4.58 | 2.08 |
| | 3.3 | 0.47 | 0.019 | 47F174 | 3.83 | 1.74 |
| | 3.3 | 0.36 | 0.014 | 36F158 | 3.48 | 1.58 |
| M-15 | 3.5 | 0.47 | 0.019 | 47F168 | 3.70 | 1.68 |
| | 3.5 | 0.36 | 0.014 | 36F145 | 3.20 | 1.45 |
| **Oriented** | | | | | | |
| Fully processed (ASTM A 876)(c) | | | | | | |
| M-6 | 3.15 | 0.35 | 0.014 | 35G066 | 1.45 | 0.66 |
| | 3.15 | 0.35 | 0.014 | 35H094 | 2.07(d) | 0.94 |
| M-5 | 3.15 | 0.30 | 0.012 | 30G058 | 1.28 | 0.58 |
| | 3.15 | 0.30 | 0.012 | 30H083 | 1.83(d) | 0.83 |
| M-4 | 3.15 | 0.27 | 0.011 | 27G051 | 1.12 | 0.51 |
| | 3.15 | 0.27 | 0.011 | 27H074 | 1.63(d) | 0.74 |
| . . . | 3.15 | 0.23 | 0.009 | 23G046 | 1.01 | 0.46 |
| . . . | 3.15 | 0.23 | 0.009 | 23H071 | 1.56(d) | 0.71 |
| . . . | 3.15 | 0.27 | 0.011 | 27P066 | 1.45(d) | 0.66 |
| . . . | 3.15 | 0.30 | 0.012 | 30P070 | 1.54(d) | 0.70 |

(a) Refer to ASTM A 683-84 and companion specification A 683M-84 (metric) for detailed information.

(b) Refer to ASTM A 677-84 and companion specification A 677M-83 (metric) for detailed information.

(c) Refer to ASTM A 876-87 and companion specification A 876M-87 for detailed information.

(d) $B$ (magnetic induction) = 1.7 T (17 kG).

The AISI designations are still in common use, but the newer ASTM designations provide more specific information regarding the grade identified. A typical ASTM designation is 47S200. The first two digits of the ASTM designation indicate the thickness in mm (×100). Following these digits is a letter (C, D, F, S, G, H, or P) that indicates the material type and the respective magnetic test conditions. The last three digits provide an indication of the maximum allowable core loss in units of either (watts/kg) × 100, or (watts/lb) × 100. If the core-loss value is expressed in watts/kg, the grade designation takes the suffix M, indicating an ASTM metric standard. Several ASTM flat-rolled products specifications are written in English and metric versions, such as A 677-84 and its companion metric specification A 677M-83.

## Surface Treatments for Electrical Steels

The purpose of the core metal in a motor, generator, or transformer is to offer the best path for the magnetic lines of flux, and its success in this respect is measured by its permeability. Cores are usually composed of a larger number of thin metal laminations that are fabricated by punching from thin sheets of metal, and which are subsequently assembled to form a core.

Interlaminar insulation is necessary for high electrical efficiency in the magnetic core, whether the application is static or rotating. For small cores used in fractional-horsepower motors, an oxide surface on the laminations may insulate the core adequately. Insulations of AISI types C-1, C-2, C-3, C-4, and C-5 are used for more rigorous requirements. Table 9 describes the characteristics of these various core coatings.

**Table 9 Types of core plate coatings used for lowering core losses in electrical steels**

| Core plate, designation | Description |
|---|---|
| C-1 | An organic enamel or varnish coating sometimes used for cores not immersed in oil. It enhances punchability and is resistant to ordinary operating temperatures. It will not withstand stress-relief annealing. |
| C-2 | An inorganic insulation consisting of a glass-like film formed during the high-temperature annealing of electrical steel, particularly grain-oriented electrical steel, as the result of the reaction of an applied coating of MgO and silicates in the surface of the steel. This insulation is intended for air-cooled or oil-immersed cores. It will withstand stress-relief annealing and has sufficient interlamination resistance for wound cores of narrow-width strip such as in distribution transformers. It is not intended for stamped lamination because it is abrasive to dies. |
| C-3 | An enamel or varnish coating intended for air-cooled or oil-immersed cores. C-3 enhances punchability and is resistant to normal operating temperatures. It will not withstand stress-relief annealing. |
| C-4 | Consists of a chemically treated or phosphated surface useful for air-cooled or oil-immersed cores. It will withstand stress-relief annealing in relatively neutral atmospheres. |
| C-5 | An inorganic insulation similar to C-4 but with ceramic fillers (such as colloidal silica) added to increase the electrical insulation properties. C-5 can be used in air-cooled or oil-immersed cores and will endure stress-relief annealing. |

Source: ASTM A 345

**Organic-Type Insulation.** Types C-1 and C-3 are organic and cannot be successfully applied to laminations before annealing. They are unsuitable for electrical equipment operated at high temperatures or for power transformers with certain types of coolants. However, they improve the punchability of the sheet steel.

**Inorganic-Type Insulation.** Inorganic types C-4 and C-5 are used when insulation requirements are severe and when annealing temperatures up to 790 °C (1450 °F) must be withstood. Typical values of interlaminar resistance for these two types are between 3 and 100 Ω· cm/lamination under a pressure of 2070 kPa (300 psi). These coatings also can be made to impart residual tensile stresses in the steel substrate, which can improve magnetic properties.

Core insulation must be sufficiently thin and uniform so as to have no more than 2.0% effect on the lamination factor (solidity of the core). To calculate the required insulation for most operations at power frequency, the square of the resistivity, in ohm-centimeters per lamination, should at least equal the square of the width of the magnetic path, in inches. This usually ensures a negligible interlaminar loss that is less than 1.0% of the core loss.

**Ceramic Films.** Japanese electrical steel producers have reported significant improvement in core loss as a result of ion plating of TiN and CrN ceramic coatings (Ref 22). Application of these ceramic films on chemically polished grain-oriented electrical steel sheet increased the magnetic flux density by 0.004 to 0.015 T (0.04 to 0.15 kG) and lowered the core loss by 0.12 to 0.20 W/kg (0.05 to 0.09 W/lb). By laser domain refining (see discussion below), it was possible to further improve the core loss by 0.04 to 0.09 W/kg (0.02 to 0.04 W/lb). Using this dual ceramic film/laser treatment, electrical steels with original core losses of 0.88 W/kg (0.4 W/lb) were improved to an ultralow core loss of 0.55 W/kg (0.25 W/lb), which corresponds to an improvement of about 40% (Ref 22).

**Laser Magnetic Domain Refinement.** Core loss improvements of 2 to 14% can be achieved by rapid scanning (typically 100 m/s, or 325 ft/s) a high-powered focused laser beam across the surface (transverse to the rolling direction) of grain-oriented glass-coated (Si-Mg-P-Al glass) 3% silicon-irons (Ref 23). There is no flame, spark, or smoke generated during this process, which is also referred to as laser scribing, and the material/coating shows no visible surface change. The improvement in core loss is due to a thermal shock imparted to the microstructure which causes slip plane dislocations to form, thereby producing new magnetic domain wall boundaries (Ref 23). By adjusting the spacing of the scanned laser lines, the energy lost due to moving domain walls back and forth under the action of the applied ac field in the transformer is minimized. The laser lines restrict the length of the domains and also act to control the width of the domains. Thus by adjusting the spacing of the laser lines, the domain sizes can be controlled, i.e., refined. Figure 9 illustrates the improvement in core loss as a function of applied field strength for a 0.26 mm (0.0104 in.) thick silicon steel sheet.

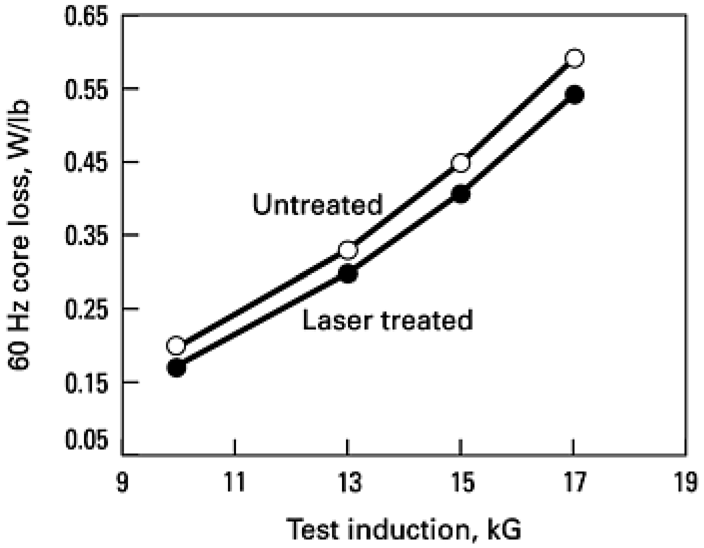

**Fig. 9 Effect of laser scribing on the core loss of a high-permeability grain-oriented electrical steel. Source: Ref 23**

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* The term *core loss,* as applied to electrical steel, is a quantitative measure of the rate at which electrical energy is converted to thermal energy during 50 or 60 cycle ac magnetization. Core loss is separated into two components: hysteresis loss and eddy current loss.

# Surface Engineering of Heat-Resistant Alloys

**Revised by F.S. Pettit, University of Pittsburgh**

## Introduction

HEAT-RESISTANT ALLOYS (solid-solution-strengthened or precipitation-hardened nickel-, iron-, or cobalt-base alloys) are often referred to as superalloys, because of their strength, oxidation resistance, and corrosion resistance at elevated service temperatures (650 to 1205 °C, or 1200 to 2200 °F). The surfaces of parts made from these alloys must be cleaned of contaminants, of which there are several types.

Shop soils, such as oil, grease, and cutting fluids, must be removed by solvents or soaps. The article "Solvent Cold Cleaning and Vapor Degreasing" in the Section "Surface Cleaning" of this Volume describes those contaminants and the procedures that must be used to remove them. The Section "Environmental Protection Issues" contains articles that provide guidelines for selecting appropriate solvents or suitable alternatives.

The removal of metallic contaminants, tarnish, and scale resulting from hot-working or heat-treating operations on nickel-, cobalt-, and iron-base heat-resistant alloys is described in this article; a brief description of applicable finishing and coating processes is also provided. For additional information on heat-resistant alloys, see Volume 1 of the *ASM Handbook.*

## Metallic Contaminant Removal

Parts made from heat-resistant alloys can accumulate traces of other metals on their surfaces after contacting cutting tools, forming dies, and heat-treating fixtures. Although metal contamination is not always harmful, its presence can be highly deleterious in certain cases. For example, Inconel X-750 may be unaffected by traces of zinc from drawing dies, but even the smallest particle of aluminum will readily alloy with the Inconel at elevated temperatures and degrade the corrosion resistance and mechanical integrity of the affected areas. Copper is another example of a metal that may affect some nickel-base alloys when they are subsequently exposed to high temperatures. Therefore, all surface contaminants should be removed from heat-resistant alloys before they are heat treated or subjected to service at elevated temperatures.

In operations such as cutting and forming, the use of lubricants can either prevent or sharply reduce metal contamination. This is the preferred practice, because lubricants can be removed easily and cheaply, if they have not been baked or fired.

When contamination is unavoidable, testing is recommended to determine the seriousness of the contamination. After heat-treating operations, metallographic examination can be conducted to detect alloy diffusion, and bend or hardness tests can be conducted to detect embrittlement. For example, lead can be detected by the yellow precipitate that forms when a test solution of chromic acid (10 wt%), sodium chlorate (1.5 wt%), and water (88.5 wt%) is applied to the suspected surface at temperatures ranging from 21 to 60 °C (70 to 140 °F).

**Mechanical removal methods** used for metallic contaminants include dry or wet abrasive blasting with metal-free abrasives, polishing with ceramic materials, and wet tumbling. The shape of a part, the required surface finish, the allowable loss of gage, and residual stress considerations will determine the suitability of these mechanical methods.

**Chemical removal methods,** however, are used more often than mechanical methods to remove metallic contaminants. A typical procedure for chemically removing iron, zinc, and thin films of lead is to first perform vapor degreasing or alkaline cleaning, and then immerse the parts in a 1:1 solution (by volume) of nitric acid (1.41 sp gr) and water for 15 to 30 min at approximately 35 °C (95 °F). Water rinsing, followed by drying, completes the process.

Another procedure that has been successful in removing brass, lead, zinc, bismuth, and tin from nickel-base and cobalt-base alloys involves vapor degreasing or alkaline cleaning, followed by soaking at room temperature in a solution of nitric acid (54 g/L, or 7.22 oz/gal), acetic acid (150 to 375 g/L, or 20 to 50 oz/gal), and hydrogen peroxide (19 to 64 g/L, or 2.5 to 8.5 oz/gal). Depending on the severity of the contamination, the soaking time can vary from 20 min to 4 h, as determined by visual observation of the reaction. After this treatment, parts must be rinsed thoroughly in water and dried. When possible, a test specimen should be immersed for the maximum time anticipated and then examined for chemical attack before the first load of parts is processed.

Nickel-base alloys should be acid etched to prepare for subsequent nondestructive inspection. The etching process removes smeared metal that may be present as a thin surface layer after machining and/or blast cleaning. The parts can be etched by immersing them in a bath containing hydrochloric acid (80%), hydrofluoric acid (13%), and nitric acid (7%) to remove the disturbed or smeared layer. This bath may leave smut that must be removed by a second bath containing iron chloride (22%), hydrochloric acid (75%), nitric acid (2%), and water. After being rinsed and dried, the parts can undergo visual and penetrant inspections. The extent of etching depends on the depth or thickness of the smeared layer. All of this layer should be removed. However, overetched parts will retain excessive amounts of penetrant.

## Tarnish Removal

Tarnish, which is a thin oxide film, does not always have a harmful effect on the end use of parts made from heat-resistant alloys. In fact, it can even be useful, such as when it functions as a bond for paint, a barrier to prevent diffusion from another alloy, or a retardant to further oxidation. However, other functional requirements can necessitate the removal of tarnish from parts. Tarnish should always be removed before welding or brazing.

Abrasive cleaning methods, such as those used to remove metallic contaminants, are also used to remove tarnish. The applicability of these methods is determined by part shape, required surface finish, and allowable loss of gage or dimension.

However, abrasive cleaning can remove some metal and degrade surface finishes. Therefore, flash pickling is used more often than abrasive cleaning to remove tarnish. A typical flash-pickling formula uses nitric acid (1.41 sp gr; 23 vol%), hydrofluoric acid (1.26 sp gr; 4 vol%), and water (73 vol%). Parts are immersed in this solution for 1 to 5 min at approximately 52 °C (125 °F). Warming the parts in hot water before flash pickling speeds tarnish removal. Water rinsing and drying must follow pickling.

## Oxide and Scale Removal

The most widely used methods for removing oxides or scale from heat-resistant alloys, in order of decreasing preference based on economic considerations, are acid pickling, abrasive cleaning by tumbling or blasting, and descaling in molten salt. Alkaline scale conditioning is helpful in modifying the scale to facilitate its removal by these methods. When extremely heavy oxide layers must be removed, grinding is an appropriate preliminary operation. Combinations of two or more methods are often used. Before these removal methods are discussed, the characteristics of the various products that need to be removed are described.

Oxide films will form on parts that are heated in reducing atmospheres, out of contact with air. Sometimes, these oxides can be removed by immersing the parts for 5 to 15 min in a tarnish-removing, flash-pickling bath, such as that with the formulation given above. However, most heat-resistant alloys form a tenacious coating in the presence of carbon monoxide or water because of their high content of oxide-forming metals, such as nickel, cobalt, and chromium. The resulting oxides vary widely with alloy composition and furnace atmosphere. Usually, pickling is required for their removal. Scale conditioners are useful.

Scale develops on hot-forged, hot-formed, or heat-treated parts that are processed in air. Usually, scale is tenacious and occurs in all gradations, including thick layers that result from heating in an oxidizing furnace using high-sulfur fuels. The scale that forms under such conditions has a dull, spongy appearance. Fine cracks may be present, and patches of scale may break from the surface. The underlying metal is rough and cannot be corrected by pickling. In these extreme conditions, grinding or abrasive blasting to sound metal, followed by flash pickling, is recommended.

Scale conditioning is used to soften, modify, or reduce scale to promote easier and more uniform acid pickling, but is seldom required to remove discolorations or thin interference coatings. A scale-conditioning bath consists of a highly alkaline aqueous solution, sometimes containing complexing and chelating compounds. The main purpose of these agents is to solubilize the scale as much as possible. The performance of a particular chelating agent depends on the affinity of the compound for the metal ions present, the pH of the scale-conditioning solution, and the physical and chemical composition of the scale. Typical multicycle descaling operations, including scale conditioning, are defined in Tables 1 and 2.

### Table 1 Procedure for removing scale from heat-resistant alloys

| **Operation** | **Time, min** | **Temperature** | | **Solution** | **Concentration** |
|---|---|---|---|---|---|
| | | **°C** | **°F** | | |
| **Precleaning cycle** | | | | | |
| Vapor degreasing | 5-10 | 87-88 | 185-190 | Stabilized trichloroethylene | . . . |
| Emulsion cleaning | 10-20 | 54-66 | 130-150 | Emulsion cleaner | 20 vol% |
| **Scale-conditioning cycle** | | | | | |
| Alkaline chelating | 15-30 | 125-135 | 260-275 | Caustic solution containing alkanol amines and aliphatic hydroxy acids | . . . |
| Alkaline oxidizing | 60-120 | 95-105 | 205-220 | Potassium permanganate | 5 wt% |
| | | | | Sodium hydroxide | 20 wt% |
| | | | | Water | Remainder |
| **Pickling cycle** | | | | | |
| Acid pickling | 5-30 | 49-60 | 120- | Hydrofluoric acid | 4 wt% |

### Table 2 Procedure for removing scale from Inconel alloys

| **Operation** | **Time** | **Temperature** | | **Solution**[(a)] | **Concentration**[(a)] |
|---|---|---|---|---|---|
| | | **°C** | **°F** | | |

| | | | | | |
|---|---|---|---|---|---|
| Alkaline conditioning | 1-2 h | 96-105 | 205-220 | Sodium hydroxide | 20 wt% |
| | | | | Potassium permanganate | 5 wt% |
| Rinse | 15-30 s | Not heated | Not heated | Water quench and water spray | . . . |
| Acid pickling | 5-10 min | 60-71 | 140-160 | Sulfuric acid (1.83 sp gr) | 7.5 vol% |
| | | | | Hydrochloric acid (1.16 sp gr) | 12 vol% |
| Rinse | 15-30 s | Not heated | Not heated | Water | . . . |
| Acid pickling | 10-20 min | 60-71 | 140-160 | Nitric acid (1.41 sp gr) | 20 vol% |
| Rinse | 15-30 s | Not heated | Not heated | Water | . . . |
| Acid pickling | 5-60 min[b] | 49-54 | 120-130 | Hydrofluoric acid (1.26 sp gr) | 3.7 vol% |
| | | | | Nitric acid (1.41 sp gr) | 22 vol% |
| Rinse | 15-30 s | Not heated | Not heated | Water | . . . |

(a) Undefined remainder is water.

(b) Type of oxide will determine immersion time required; until immersion time is established, inspect frequently to avoid overpickling.

Minimal scale removal occurs during treatment in the alkaline scale-conditioning bath. Further treatment in highly alkaline solutions containing a strong oxidizing material, such as potassium permanganate, is often necessary. The scale on heat-resistant alloys sometimes contains carbon and incompletely burned and polymerized residues, as well as metallic oxides. These organic components react with the oxygen that is released by the alkaline oxidizing bath.

**Acid Pickling.** After the scale is conditioned, it is subjected to acid pickling, during which most of the high-temperature scale either breaks away from or becomes so loosely attached to the parts that pressure rinsing with water completes the descaling. The acid pickle is usually a dilute nitric acid or a hydrofluoric-nitric acid solution. In addition to removing scale, pickling solutions that contain nitric acid will remove many surface contaminants through oxidation. However, because the acid solution attacks the base metal, it is necessary to limit the pickling time to prevent excessive metal loss or metal surface roughening.

Parts made from alloys that are high in aluminum and titanium, such as M252 and René 41, must undergo a special procedure before welding or brazing. When parts are in the solution-treated condition and descaling is required, they are treated in a scale-conditioning solution, as previously described, after which they are immersed in a solution of nitric acid (30 wt%) and hydrofluoric acid (3 wt%) for 5 to 10 min. Alloys in the aged condition are descaled anodically in an acid solution. A solution made for this procedure should contain sulfuric acid (75 wt%) and hydrofluoric acid (3 wt%). It should be operated using a current density of 215 to 430 A/mm$^2$ (20 to 40 A/ft$^2$) and graphite cathodes. The material should be immersed in the electrolytic cleaning bath for 3 to 12 min, and the operation will be complete when the amperage drops to nearly zero. Sodium sulfite (1.6 wt%) is used to reactivate the solution after a period of operation.

Alloys that contain less than approximately 12% Cr, unstabilized austenitic stainless steels, and martensitic and ferritic stainless steels can experience high metal loss or intergranular attack by acids during pickling. When the susceptibility of a material to these problems is unknown, it is safer to perform mechanical descaling than acid pickling. In one specific instance, acid descaling was proven to cause intergranular attack and a subsequent loss of ductility in aged René 41.

Weld areas typically differ, in terms of composition and structure, from the base metal and react differently to conditioning and pickling cycles. Weld areas or heat-affected zones are often susceptible to selective attack during pickling. Although inhibitors can eliminate or reduce this selective attack, it is preferable to use abrasive or other mechanical descaling methods, rather than acid pickling, to remove scale from welded parts, unless a safe pickling procedure has been found for a given application.

Hydrogen embrittlement does not occur in nickel-, cobalt-, or austenitic iron-base alloys as a result of aqueous descaling.

**Abrasive blasting** with dry aluminum oxide can be used to remove oxide and scale from all types of wrought and cast heat-resistant alloys. Silicon carbide is more expensive than aluminum oxide and is seldom used. Silica (silicon dioxide, or sand) has a limited application because of its lack of cutting ability. It is sometimes used to clean refractory metal forgings prior to pickling. Grit sizes as coarse as No. 30 (0.59 mm, or 0.023 in.) are recommended for cleaning forgings and castings. Finer grits, such as Nos. 90 and 100 (0.17 and 0.15 mm, or 0.0065 and 0.0059 in., respectively), are used for general blasting.

Metallic shot and grit should not be used to descale heat-resistant alloys unless their use is followed by pickling to remove metal contamination. For parts that must be welded or brazed, or that have highly tenacious scales produced by furnace atmospheres, pickling after dry abrasive cleaning is recommended, regardless of the abrasive used.

Wet abrasive blasting, also referred to as vapor honing, is also used to clean heat-resistant alloys. This process uses Nos. 200 to 1250 silica abrasive particles (0.074 to 0.010 mm, or 0.0029 to 0.0004 in.) mixed with water to produce a slurry that removes loose scale, discoloration, and soils. Metal loss is not excessive when normal pressures and exposure times are used.

When spherical beads made of high-quality optical crown glass are used as the abrasive, stock loss is minimized. Bead sizes of 0.038 to 0.074 mm (0.0015 to 0.0029 in.) are generally used, and blasting pressures are kept below 410 kPa (60 psi) to prevent the beads from fracturing.

Surfaces that have been wet blasted are usually suitable for welding, brazing, electroplating, and final inspection processes. Further cleaning is seldom necessary. Exceptions are alloys with a high titanium and aluminum content, which require the special procedure discussed in the section "Acid Pickling" in this article.

Most of the general advantages and limitations associated with the abrasive cleaning of steel will also apply to heat-resistant alloys. However, there is a risk of contamination from either metallic abrasives or abrasives that have been used to clean parts made from metals of widely different compositions. For example, heat-resistant alloys should not be blasted with abrasive material that has been used to clean low-alloy steel, aluminum, copper, or magnesium. However, abrasives used to clean titanium and corrosion-resistant steels have been used to clean heat-resistant alloys without serious contamination. The flash pickling of these alloys after abrasive cleaning provides additional assurance that no harmful surface contamination remains. Detailed information on equipment and procedures for dry and wet blasting is provided in the Section "Finishing Methods" in this Volume.

**Wet tumbling** by the barrel or vibratory method can be used to descale heat-resistant alloys if the shape and size of the parts are suitable. The removal of burrs and sharp edges is accomplished in the same operation. Shop soils are also removed, thus eliminating the need for preliminary degreasing.

Parts are tumbled or vibrated in a mixture of acid descaling compound and metal-free abrasives and then subjected to a neutralizing cycle. Precautions regarding metal contamination are similar to those noted above for abrasive blasting.

Pickling is required after tumbling and before resistance welding to remove residual smut, which can cause poor-quality weldments. There is less need for pickling prior to fusion welding, unless an inspection of the weldments reveals porosity or inclusions that are a result of pickup from the tumbling process.

**Wire brushing** is sometimes used to remove very light scale or surface discoloration. All brushes used on heat-resistant alloys must have stainless steel bristles.

**Salt-bath descaling** is an effective first step in removing scale from heat-resistant alloys. The process is generally more expensive than acid pickling, particularly if production is intermittent, because of the cost of maintaining the bath during idle time. The electrolytic salt bath used to descale heat-resistant alloys contains fused caustic soda, rather than sodium hydride. The parts and the tank are alternately negative and positive poles of a direct current circuit.

This fused caustic soda bath, which contains oxidizing salts such as sodium nitrate, is operated at 425 to 540 °C (800 to 1000 °F). It is slightly more effective than the sodium hydride bath on high-chromium alloys, such as type 310 stainless steel, and cobalt-chromium-nickel-base alloys, such as L-605. Processing steps are similar. Parts are immersed in the oxidizing bath for 5 to 15 min, quenched in water, soaked in a solution of 5 to 10% sulfuric acid at 70 °C (160 °F) for 1 to 5 min, and then dipped in a solution of 15 to 20% nitric acid and 2 to 4% hydrofluoric acid at 54 to 60 °C (130 to 140 °F) for 2 to 15 min.

A typical sequence for sodium hydride descaling and pickling is given in Table 3. Equipment details and other information on salt-bath descaling are provided in the Section "Surface Cleaning" in this Volume.

### Table 3 Procedure for sodium hydride descaling and acid pickling of heat-resistant alloys

| Operation | Time | Temperature | | Solution[a] | Concentration, vol %[a] |
|---|---|---|---|---|---|
| | | °C | °F | | |
| Sodium hydride descale | 1-2 h | 370-390 | 700-730 | Sodium hydroxide | . . . |
| Quench | 15-30 s | Not heated | Not heated | Water | . . . |
| Neutralizing rinse | 1-3 min | RT to 60 | RT to 140 | Sulfuric acid | 2-10 |
| Brightening pickle | 5-15 min | 54-60 | 130-140 | Hydrofluoric acid<br>Nitric acid | 2-4<br>15-20 |
| Rinse | 15-30 s | Not heated | Not heated | Water | . . . |
| High-pressure spray wash | [b] | Not heated | Not heated | Water[c] | . . . |

(a) Governed by shape of part.

(b) 1 min on parts with accessible surfaces.

(c) Water pressure of 690 kPa (100 psi)

## Applicable Finishing and Coating Processes

Many finishing operations that are commonly used for steel and other metals are not required for the heat-resistant alloys for several reasons. First, these alloys are inherently resistant to corrosion in a wide range of environments. Second, the applications of parts made from these alloys do not typically require a polished finish.

The oxide coating that is obtained during processing is frequently of value to heat-resistant alloys that are subjected to elevated temperatures in service. Consequently, the dense, tenacious oxide that develops on formed or machined finished parts during final heat treatment is allowed to remain as protection against further oxidation.

**Polishing** of heat-resistant alloys is sometimes used to obtain a desired surface finish, as well as to remove light scale or oxide from parts that are to be welded or brazed. Silicon carbide in various grit sizes is commonly used to prepare surfaces for brazing.

Surfaces are usually prepared for welding by polishing with No. 90 grit aluminum oxide, set up with sodium silicate on a cloth wheel. Discoloration can be removed by polishing with No. 120 grit aluminum oxide, used with a greaseless compound and a cloth wheel. Buffing is seldom required for the finishing of heat-resistant alloys.

**Electroplating.** Chromium, copper, nickel, and silver are sometimes electroplated on heat-resistant alloys in order to:

- Prepare for brazing
- Deposit brazing metal
- Provide antigalling characteristics
- Repair expensive parts or correct dimensional discrepancies

Conventional nickel plating processes are often used to assist in brazing. Deposits can vary in thickness from 2.5 to 25 $\mu$m (0.1 to 1 mil). Alloys that contain titanium or aluminum will require the thicker deposits.

Silver and copper are the metals most often deposited as actual brazing materials. Some brazing alloys are deposited as separate layers of their various constituent metals on a weight-percentage basis. Plate thickness depends on the amount of metal needed for brazing.

Electrodeposited silver or nickel is used in special applications for antigalling purposes. Either nickel or chromium can be used to repair worn parts or build up dimensions. Procedures and electrolytes for plating these metals are described in the Section "Plating and Electroplating" in this Volume.

**Ceramic coatings** are frequently applied to heat-resistant alloys to increase the oxidation resistance of parts exposed to extremely high temperatures, such as gas turbine and missile components. Several types of ceramics are currently used, and some serve as thermal barriers, as well. The article "Ceramic Coatings and Linings" in this Volume describes the relevant procedures.

**Diffusion coatings** of aluminum, chromium, silicon, or combinations thereof, also are used to protect heat-resistant alloy parts from high-temperature corrosion and to prolong part life. The coating of engine exhaust valves with aluminum is a common example. Procedures for diffusion coating are described in the Section "Vacuum and Controlled-Atmosphere Coating and Surface Modification" in this Volume.

**Shot peening** is currently used to improve the mechanical properties of compressor blades, turbine-blade dovetails, and latter-stage turbine-blade airfoils by introducing favorable patterns of residual stress. Although all turbine-blade dovetails are peened with steel shot, glass beads are sometimes favored over metallic shot in other shot-peening applications. The advantages of glass beads are that they:

- Pose no risk of metal contamination
- Remove virtually no metal
- Are available in smaller sizes than metallic shot and can therefore be used to peen areas that are difficult to reach when using metallic shot

However, glass beads are not equivalent to metal shot for improving mechanical properties. Details on peening are given in the Section "Finishing Methods" in this Volume.

## Cleaning and Finishing Problems and Solutions

The complex oxides and scale that form on heat-resistant alloys often create production problems and require the use of special procedures to obtain the desired surfaces. The examples described below, all of which are drawn from actual production experience, identify cleaning and finishing problems and the procedures used to solve them.

**Example 1.** After heat treatment, turbine combustion chambers made from Hastelloy X sheet exhibited irregular scale adherence, variations in surface finish, and loss of formability. An investigation disclosed that residual shop soils, such as lubricants, marking inks, and handprints, remained on the parts despite the solvent cleaning and vapor degreasing to which the parts were subjected before being heat treated. These soils were decomposing during heat treatment and causing carbon diffusion.

The substitution of electrolytic alkaline cleaning for the methods previously used eliminated the difficulty. In this procedure, parts were immersed for 5 min in a bath compounded to Federal Specification P-C-535 and operated at 82 to 93 °C (180 to 200 °F) using 6 to 8 V. Parts were anodic in the electrical circuit. The scale was easily removed by subjecting the heat-treated parts to a 5 min immersion in a room-temperature acid pickling bath composed of 70% nitric acid (20 to 30 vol%), 60% hydrofluoric acid (10 to 15 vol%), and water (55 to 70 vol%).

**Example 2.** The descaling of alloys A-286 and S-816 was inadequate when this procedure was used:

- Descale in an oxidizing salt bath at 480 to 495 °C (900 to 925 °F) for 25 min, and then quench in cold water
- Immerse in a solution of sulfuric acid (23 vol%) for 10 to 15 min, and then rinse with cold water
- Immerse in a solution of 25% nitric acid and 3% hydrofluoric acid for 2 min, and then rinse in cold water
- Immerse in 30% nitric acid for 5 min, rinse in cold water, rinse in hot water, and then dry

However, changing the procedure to the following proved to be successful:

- Descale in an oxidizing salt bath at 480 to 495 °C (900 to 925 °F) for 10 min, and then quench in cold water
- Immerse in 23% sulfuric acid for 5 min, and then rinse in cold water
- Immerse for 1 min in a solution of 25% nitric acid and 3% hydrofluoric acid, rinse in cold water, rinse in hot water, and then dry
- Reimmerse in oxidizing salt bath at 480 to 495 °C (900 to 925 °F) for 10 min, and then quench in cold water
- Immerse for 30 s in solution of 25% nitric acid and 3% hydrofluoric acid, and then rinse in cold water
- Immerse for 5 min in 30% nitric acid, rinse in cold water, rinse in hot water, and then dry

**Example 3.** Excessive zinc contamination of formed parts made from 19-9 DL alloy was traced to the contamination of drawing lubricants that had been stored too closely to zinc dies that were being finished by sanding. The zinc was removed from the parts by chemicals (see the section "Chemical Removal Methods" in this article). A recurrence of this problem was prevented by improved housekeeping and by direct instructions to personnel.

**Example 4.** It was not feasible to broach turbine disks made from D-979 alloy in the solution-treated and aged condition. The disks were first broached in the solution-treated condition, and then the surfaces were protected by a flash of nickel (Wood's plating) and a subsequent overlay of copper, so that they could undergo aging at temperatures higher than 730 °C (1350 °F) in a reducing gas atmosphere. After aging, the plated copper and nickel were removed from the disks by the procedures given in Tables 4 and 5.

**Table 4 Procedure for stripping copper plate**

| | |
|---|---|
| Composition of bath | |
| Chromic oxide, g/L (oz/gal) | 360 (48) |
| Sulfuric acid (concentrated), mL/L | 39-55 (5-7) |
| Water | Remainder |
| Temperature | Room temperature |
| Time | Varies with thickness of plate |

**Table 5 Procedure for stripping nickel plate**

| | |
|---|---|
| Composition of bath | |
| Sodium cyanide, g/L (oz/gal) | 90 (12) |
| Nitroaromatics, g/L (oz/gal) | 60 (8) |
| Water | Remainder |
| Temperature, °C (°F) | 49-66 (120-150) |
| Time | Varies with thickness of plate |

Stripping the chemicals and using a light vapor blast to remove smut resulted in clean, dimensionally unaltered parts and had no detrimental effect on mechanical properties. The procedures defined in Tables 4 and 5 were based on the available facilities. A cheaper and faster method would be to strip the copper and nickel in a nitric acid solution (50 vol%) at room temperature.

**Example 5.** Conventional salt-bath descaling and pickling failed to remove all annealing scale from stampings made from 19-9 DL, Hastelloy X, Inconel 600, and Inconel X-750. The sequence of operations performed on these stampings was either to form, degrease, remove metal contamination, anneal, and descale, or to immerse in molten salt and then pickle. The difficulty was traced to the open-hearth, gas-fired annealing furnaces. It was found that the atmosphere was reducing while the burners were on, and that a thin, tight scale was produced.

A satisfactory remedy was to adjust the burners to bring the oxygen content to 3%. The resulting scale was loose and easily removed by the usual descaling and pickling procedures.

**Example 6.** Jet-engine combustion liners made from Hastelloy X require three in-process anneals. Forming without first removing scale required expensive carbide dies, and the resulting liners were unacceptable. The problem was solved by installing a salt-bath descaling line. The following cycle was satisfactory for descaling:

- Immerse in an oxidizing salt bath at 480 °C (900 °F) for 10 to 20 min, and then rinse, first in cold water and then in water at 82 °C (180 °F)

- Immerse in a solution of 24% hydrochloric acid for 2 to 10 min, and then rinse in cold running water
- Immerse in nitric-hydrofluoric acid for 2 to 10 min, rinse in cold running water, hose off, and then dry

**Example 7.** Small cracks appeared in welded 19-9 DL tubing (1.3 mm, or 0.050 in. wall) after annealing. The processing sequence was to form tubing from flat stock, degrease, perform an automatic seam weld, anneal, and descale. The tubing was formed on dies of zinc alloy, but was not dezinced before being welded. Small amounts of zinc on the surface near the weld melted during welding. This initiated zinc diffusion, and the residual stresses around the weld were sufficient to crack the embrittled material. The problem was solved by pickling the tubing in 20% nitric acid to remove the zinc before welding.

## Surface Engineering of Aluminum and Aluminum Alloys

### Introduction

ALUMINUM OR ALUMINUM ALLOY products often have various types of finishes applied to their surfaces to enhance appearance or improve functional properties. This article discusses the methods employed in the cleaning, finishing, and coating of aluminum.

### Acknowledgements

The information in this article is largely taken from:

- Cleaning and Finishing of Aluminum and Aluminum Alloys, *Metals Handbook,* 9th ed., Vol 5, American Society for Metals, 1982, p 571-610
- Porcelain Enameling, *Metals Handbook,* 9th ed., Vol 5, American Society for Metals, 1982, p 509-525
- Shot Peening, *Metals Handbook,* 9th ed., Vol 5, American Society for Metals, 1982, p 138, 140-145

### Abrasive Blast Cleaning

One of the simplest and most effective methods for cleaning aluminum surfaces is by blasting with dry nonmetallic or metallic abrasives. Although this method is normally associated with the cleaning of aluminum castings, it is also used to prepare surfaces of other product forms for subsequent finishes, such as organic coatings. In addition to cleaning, blasting is used to produce a matte texture for decorative purposes.

Abrasive blasting is an efficient means of removing scale, sand, and mold residues from castings. Because castings typically are thick, they generally suffer no distortion from the process. Blast cleaning of parts with relatively thin sections is not recommended, because such parts are readily warped by the compressive stresses that blasting sets up in the surface; coarse abrasives can wear through thin aluminum sections. Typical conditions for dry blasting with silica abrasive are given in Table 1.

**Table 1 Conditions for abrasive blast cleaning of aluminum products with silica**

| Grit size | Mesh | Nozzle diameter | | Nozzle to work[(a)] | | Air pressure | |
|---|---|---|---|---|---|---|---|
| | | mm | in. | mm | in. | kPa | psi |
| 20-60 | Coarse | 10-13 | $\frac{3}{8}-\frac{1}{2}$ | 300-500 | 12-20 | 205-620 | 30-90 |
| 40-80 | Medium | 10-13 | $\frac{3}{8}-\frac{1}{2}$ | 200-350 | 8-14 | 205-620 | 30-90 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 100-200 | Fine | 6-13 | $\frac{1}{4}$-$\frac{1}{2}$ | 200-350 | 8-14 | 205-515 | 30-75 |
| Over 200 | Very fine | 13 | $\frac{1}{2}$ | 200-300 | 8-12 | 310 | 45 |

(a) Nozzle approximately 90° to work

Washed silica sand and aluminum oxide are most commonly used for abrasive blast cleaning of aluminum alloys. Steel grit is sometimes used and, because of the fragmenting characteristics of silica, is often preferred. It also has a longer life, which lowers cleaning costs. However, when an aluminum surface is blasted with grit, steel particles become embedded, and unless they are removed by a subsequent chemical treatment, they will rust and stain the surface. It is good practice to remove particle contamination with a nitric acid pickle to prevent degradation of corrosion resistance. A 20-min soak in 50% nitric acid solution at ambient temperature will dissolve embedded or smeared iron particles, but it will not remove silica or aluminum oxide. When aluminum is blasted with No. 40 or 50 steel grit, a 9.5 mm ($\frac{3}{8}$ in.) diameter nozzle and air pressure at about 276 kPa (40 psi) are commonly used. Organic materials such as plastic pellets and crushed walnut shells also are used to blast clean aluminum, often for the removal of carbonaceous matter.

Stainless steel shot is sometimes used for cleaning aluminum surfaces. Shot blasting is used as a preliminary operation for developing a surface with a hammered texture. An attractive finish is produced when this textured surface is bright dipped and anodized. In addition, the varying degrees of matte texture that can be produced by blasting offer many decorative possibilities. Blasting is often used to produce the maximum diffuseness of the reflectivity of a surface. For example, aluminum army canteens are blasted as a final finish to reduce glare. Glass bead blasting offers another approach to cleaning and producing diffuse surfaces.

Sandblasting with a fine abrasive produces a fine-grain matte finish on wrought or cast aluminum products. For plaques, spandrels, and related decorative architectural applications, sandblasting the background and polishing or buffing the raised portions of the surface produces an effect known as highlighting.

The matte finish produced by abrasive blasting is highly susceptible to scratching and to staining from fingerprints. Therefore, matte-finish surfaces usually are protected by an anodic coating or clear lacquer. Anodizing is the more popular protective treatment, because it does not alter the original texture of a surface. Clear lacquers smooth out roughened surfaces and produce various degrees of gloss, which may be undesirable. Anodizing of a blasted aluminum surface results in a gray color because of embedded abrasive particles in the surface. This color frequently is nonuniform because of variations in blasting conditions, such as nozzle-to-work distance, direction or movement of the nozzle, and air pressure.

Blasting conditions can be closely controlled by the use of specially designed equipment. Uniform movement of the work on conveyors, established nozzle movement, constant velocity of the abrasive, and controlled size of grit contribute to better color uniformity of subsequently anodized surfaces.

The nonuniform appearance that results from blasting can be corrected by bleaching prior to anodizing. Bleaching is done by deep etching in a solution of 5% sodium hydroxide at 40 to 65 °C (100 to 150 °F) to remove metal that contains embedded abrasive. Some trial and error may be necessary to determine etching time for specific conditions. If the surface is not etched enough, a mottled appearance may result. Embedded abrasive can also be removed with a solution of nitric acid and fluoride used at room temperature.

Care should be exercised when selecting the aluminum or aluminum alloy to be sandblasted. For example, alloy 1100, which contains 99% Al, provides a transparent anodic finish; alloys rich in manganese, silicon, and copper, on the other hand, are colored when anodized. Alloy segregation can occur in high-magnesium alloys, and pitting will result unless special pretreatments are used. Table 2 lists several typical applications for abrasive blast cleaning of aluminum products, indicating the type and size of abrasive used and typical production rates.

### Table 2 Applications for abrasive blast cleaning of aluminum products

Automatic rotary equipment with five nozzles was used for blasting of all parts except the cake pan, for which a hand-operated single-nozzle setup was used.

| **Product** | **Size** | | **Abrasive** | | **Pieces, h** |
|---|---|---|---|---|---|
| | **mm** | **in.** | **Type** | **Mesh size** | |
| **Blasting to prepare for organic coating** | | | | | |
| Cake pan | 280 by 380 by 51 | 11 by 15 by 2 | Alumina | 100 | 60 |
| Frying pan | 250 mm diam | 10 in. diam | Alumina | 100 | 260 |
| Griddle | 6775 $mm^2$ | 10.5 $in.^2$ | Alumina | 100 | 225 |
| Sauté pan | 200 mm diam | 8 in. diam | Alumina | 100 | 250 |
| **Blasting for appearance produced** | | | | | |
| Army canteen(a) | . . . | . . . | Steel | 80 | 420 |
| Cocktail-shaker body(b) | 100 mm diam by 180 | 4 in. diam by 7 | Steel | 80 | 375 |

(a) 1 qt army canteen blasted for reduction of light reflectivity.

(b) Blasted for decorative effect

**Wet blasting** mixes a fine abrasive with water to form a slurry that is forced through nozzles directed at the part. Abrasive grits from 100 to 5000 mesh may be used. Wet blasting is generally employed when a fine-grain matte finish is desired for decorative purposes.

An attractive two-tone finish on appliance trim can be obtained by contrasting a buffed finish with a wet-blasted finish. Aluminum firearm components and eyeglass parts such as frames and temples often are wet-blasted to produce fine matte finishes. In these applications, anodic coatings, either plain or colored, are used to protect without distorting the intended surface texture.

Typical wet blasting procedures are listed in Table 3. Wet blasting is also used to prepare surfaces for organic or electroplated coatings. Ultrafine glass bead blasting is an alternative to wet blasting.

### Table 3 Conditions for wet blasting of aluminum-base materials

At a nozzle-to-work distance of 75 to 100 mm (3 to 4 in.) and an operating pressure of 550 kPa (80 psi)

| Operation | Abrasive | |
|---|---|---|
| | Type | Mesh size |
| Deburr and clean | Alumina | 220 |
| Blend and grind | Silica flour | 325 |
| Lap and hone | Glass | 1000 |
| | Diatomite | 625-5000 |

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## Barrel Finishing

Barrel finishing is a low-cost method of smoothing sharp edges, imparting a matte finish, and preparing surfaces for anodizing, painting, or plating. Many small aluminum stampings, castings, and machined parts are cleaned, deburred, and burnished by barrel finishing. In most instances, the main objective is deburring and/or burnishing, with cleaning being an accidental benefit of the treatment. Deburring sometimes is the final barrel operation, but more often it is followed by burnishing to obtain a smoother finish or one that is better suited to anodizing or plating. Parts that have only been deburred are often painted. Burnished parts are frequently anodized for protection.

Small aluminum parts are sometimes tumbled dry in media such as pumice and hardwood pegs, hardwood sawdust, or crushed walnut shells to remove burrs and improve the finish. However, this method is relatively inefficient compared to the more widely used wet process.

All aluminum alloys can be safely finished by wet barrel methods. Limitations imposed by workpiece size and shape are essentially the same as for steel and other metals. There are two general areas in which wet barrel finishing of aluminum parts is more critical than in processing similar parts made of steel. First, there is danger of surface contamination by ferrous metals, caused by the use of either a steel barrel or a steel medium. Second, the pH of the compounds is more critical when processing aluminum, because the metal is susceptible to etching by both acids and alkalis, and because gas generated during chemical attack can build up pressure in the barrel and cause serious accidents. Barrels must be vented when processing aluminum. Compounds that are nearly neutral (pH of about 8) are recommended, although some alloys can be safely processed in compounds having a pH as high as 9.

Barrels used for aluminum are basically the same as those used for processing steel. However, barrels made of steel or cast iron should be lined with rubber or similar material to prevent contamination. A preferred practice is to use specific barrels exclusively for processing aluminum.

**Deburring** is done by tumbling the work in a nonlubricating compound that contains abrasives. In most instances, media also are used to cushion the workpieces and increase the abrasive action. Synthetic detergents mixed with granite fines or limestone chips are usually preferred as the compound for deburring aluminum; aluminum oxide and silicon carbide are not desirable because they leave a smudge that is difficult to remove. High water levels, completely covering the mass, are used during deburring to assist in maintaining fluidity of the mass and to help prevent the medium from becoming glazed and losing cutting action. Deburring can also be accomplished by using vibratory units with synthetic abrasives.

**Barrel burnishing** is used to produce a smooth, mirrorlike finish on aluminum parts. Bright dipping immediately prior to burnishing aids in producing desired results. Other preliminary treatments also are helpful in specific instances, particularly for cast aluminum parts. One of these pretreatments entails etching the castings for 20 s in an alkaline solution at 80 °C (180 °F) and then dipping them for 2 to 3 s in a solution consisting of 3 parts by volume nitric acid (36° Bé) and 1 part hydrofluoric acid at 20 to 25 °C (70 to 75 °F).

The principle of barrel burnishing is to cause surface metal to flow, rather than to remove metal from the surface. Burnishing compounds must have lubricating qualities; soaps made especially for burnishing are usually used and are readily obtainable. Many of them have a pH of about 8, although more acidic materials can be used.

When burnishing aluminum, the pH of the burnishing compound must be closely controlled. This is accomplished by frequent titration of the compound, followed by the addition of small amounts of borax or boric acid as needed. Steel balls and shapes are the most commonly used burnishing media. Several examples of conditions used in barrel finishing applications are detailed in Table 4. Note that deburring and burnishing are sometimes accomplished in a single operation.

**Table 4 Conditions for wet barrel finishing of aluminum products**

| **Product** | **No. of pieces per** | | **No. of pieces per load** | **Cycle time, min** | **Barrel speed, rev/min** |
|---|---|---|---|---|---|
| | **kg** | **lb** | | | |
| **Clean, deburr and brighten**[(a)] | | | | | |
| Percolator spout | 60 | 130 | 630 | 20 | 33 |
| Measuring spoon | 20 | 50 | 750 | 20 | 33 |
| Flame guard | 40 | 90 | 1500 | 15 | 33 |
| Leg | 35 | 80 | 2700 | 30 | 33 |
| Toy spoon | 80 | 180 | 5000 | 17 | 33 |
| Handle | 105 | 225 | 5800 | 25 | 33 |
| **Deburr and brighten**[(b)] | | | | | |
| Die cast handles | 11 | 25 | 600 | 120 | 15 |
| **Burnish to high gloss**[(c)] | | | | | |

(a) Rubber-lined steel, single-compartment drum, 560 mm (22 in.) diam, 760 mm (30 in.) long. Processing cycle: load drum with medium (20 kg or 50 lb of 3-mm or $\frac{1}{8}$ -in. steel balls per load), parts, and compound (154 g or 5.5 oz of burnishing soap per load); cover load with water (66 °C or 150 °F); rotate drum for specified time; unload, rinse, separate parts from medium; tumble-dry parts in sawdust for 4 min.

(b) Rubber-lined steel, double-compartment drum; each component 740 mm (29 in.) long, 915 mm (36 in.) in diameter. Processing cycle: load deburring compartment with parts, compound (2 kg or 5 lb of burnishing soap), and medium (365 kg or 800 lb of No. 4 granite chips), using hoist; cover load with cold tap water; rotate drum for 1 h; unload, and rinse with cold water; separate parts and medium, and transfer parts to burnishing compartment; add burnishing compound (0.9 kg or 2 lb of burnishing soap) and medium (680 kg or 1500 lb of 3-mm or $\frac{1}{8}$ -in. steel balls); cover load with water (71 °C or 160 °F) and rotate drum for 1 h; separate parts and medium, and rinse parts in hot water and then in cold water; spin dry in a centrifugal hot-air dryer.

(c) Single-compartment drum, 1.5 m (5 ft) long, 1.2 m (4 ft) in diameter. Processing cycle: load drum with parts (parts are fixtured, to prevent scratching), medium (2040 to 2270 kg or 4500 to 5000 lb of steel balls 3, 6, and 8 mm or $\frac{1}{8}$, $\frac{1}{4}$, and $\frac{5}{16}$ in. in diameter, and 2 and 3 mm or $\frac{1}{16}$ and $\frac{1}{8}$ in. steel diagonals), and compound (5 kg or 12 lb of alkaline burnishing soap. pH 10); cover load with cold tap water; rotate drum for 22 $\frac{1}{2}$ min in one direction, then 22 $\frac{1}{2}$ min in reverse direction; rinse and unload; dip-rinse parts, and hand wipe

**Self-tumbling** is an effective means of cleaning, deburring, or burnishing small aluminum parts. Procedures for self-tumbling are basically the same as those for other methods of barrel finishing, except that the parts themselves serve as the medium. Compounds for self-tumbling of aluminum should be of nearly neutral pH, and oxides should be removed from the aluminum parts before tumbling. The size and shape of the parts usually determine whether self-tumbling is suitable. Interior surfaces receive little or no action during self-tumbling.

**Vibratory finishing** is a newer method used for deburring and burnishing metal parts. When applied to aluminum parts, compounds and media are subject to the same restrictions as discussed previously for conventional barrel finishing.

## Polishing and Buffing

Because aluminum is more easily worked than many other metals, few aluminum parts require polishing prior to buffing for final finish. In some instances, polishing may be required for the removal of burrs, flash, or surface imperfections. Usually, buffing with a sisal wheel prior to final buffing is sufficient.

**Polishing.** Most polishing operations can be performed using either belts or setup wheels. Setup wheels may be superior to belts for rough polishing when canvas wheels in a relatively crude setup can be used. For fine polishing work, a specially contoured wheel may be more satisfactory than a belt. Setup wheels have two main disadvantages in comparison with belts: wheels may be costly; and time, skill, and equipment are necessary for setting up wheels. (The actual time required may be as short as 10 min, but this time is spread over several hours because of intermediate drying steps.) Inventory thus becomes an important factor when several wheels with different types of abrasives or grit sizes are needed. Considerable operator skill is required for wheel polishing, whereas unskilled labor can be used for belt polishing. Flap wheels have been used to replace setup wheels for many applications. The use of flap wheels tends to overcome the above-mentioned disadvantages. Typical conditions for polishing aluminum parts are discussed in the following examples.

The conditions for wheel polishing die cast aluminum soleplates for steam irons are as follows:

| | |
|---|---|
| Type of polishing wheel | Felt |
| Setup time | 10 min |
| Wheel speed | 180-2000 rev/min |
| Lubricant | Tallow grease stick |

The medium-hard felt polishing wheel is 350 to 400 mm (14 to 16 in.) in diameter, with a 125 mm (5 in.) face. The surface of the wheel is double coated with 240-mesh alumina abrasive bonded with hide glue. Setup time, spread out over several hours of operation, totals 10 min. The polishing wheel can cover 34 to 43 m/s (6600 to 8400 sfm).

The soleplates are made of alloy 380.0 and the sides are polished to remove holes or other surface defects. Buffing follows to produce the required mirror finish. The polishing conditions given in the list above are based on a production rate of 115 pieces/h per wheel. Each wheel has a service life of 5000 to 6000 pieces.

Table 5 gives the conditions and sequence of operations for belt polishing of die-cast steam-iron soleplates made of aluminum alloy 380.0. Ten polishing heads are used to produce a bright finish on the soleplate sides and bottom.

### Table 5 Conditions of belt polishing for bright finishing aluminum die-cast soleplates

| **Operation** | **Area polished** | **Polishing head, No.** | **Type** | **Contact wheel** | | | **Belt**[(a)] | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | **Size** | | **Hardness, durometer** | **Size** | | **Abrasive mesh size** | **Life, pieces** |
| | | | | **mm** | **in.** | | **mm** | **in.** | | |
| 1 | Side | 1, 2 | Plain face | 50 by 380 | 2 by 15 | 60 | 50 by 3050 | 2 by 120 | 280[(b)] | 600 |
| 2 | Side | 3, 4 | Plain face | 50 by 380 | 2 by 15 | 60 | 50 by 3050 | 2 by 120 | 320[(b)] | 600 |
| 3 | Bottom | 5 | Serrated[(c)] | 150 by 380 | 6 by 15 | 45 | 150 by 3050 | 6 by 120 | 120[(b)] | 1200 |
| 4 | Bottom | 6 | Serrated[(c)] | 150 by 380 | 6 by 15 | 45 | 150 by 3050 | 6 by 120 | 150[(b)] | 2000 |
| 5 | Bottom | 7 | Serrated[(c)] | 150 by 380 | 6 by 15 | 45 | 150 by 3050 | 6 by 120 | 220[(b)] | 2000 |
| 6 | Bottom | 8 | Serrated[(c)] | 150 by 380 | 6 by 15 | 45 | 150 by 3050 | 6 by 120 | 280[(b)] | 2000 |
| 7 | Bottom | 9 | Plain face | 150 by 380 | 6 by 15 | 60 | 150 by 3050 | 6 by 120 | 320[(b)] | 2000 |

(a) Belt speed for all operations was 35 m/s (6900 sfm). All belts were cloth; bond, resin over glue.

(b) Aluminum oxide abrasive.

(c) 45° serration, 13 mm ($\frac{1}{2}$ in.) land, 10 mm ($\frac{3}{8}$ in.) groove.

(d) Silicon carbide abrasive

**Buffing.** Selection of a buffing procedure depends mainly on cost, because it is usually possible to obtain the desired results by any one of several different methods. For example, depending on the application, hand buffing might call for the use of equipment ranging from simple, light-duty machines to heavy-duty, variable-speed, double-control units. These machines represent a wide range in capital investment.

Automatic buffing requires custom-made machinery or special fixtures on standard machinery. The size and complexity of the machinery are determined by the required production rates and by the size or shape of the workpieces. High production requires more stations, heavier equipment, and more power. The configuration of the part may be so simple that one buff covers the total area to be finished, or it may be so complex as to require the use of many buffs set at angles and advanced toward the workpiece by cam action.

For cut and color work, buffs are bias types with a thread count of 86/93. For severe cut-down, treated cloth is used with the same thread count. The final color work is accomplished using a buff with very little pucker and a low thread count of 64/64 (see Table 6). A number of procedures that have proved successful for high-luster buffing of specific aluminum parts are summarized in Table 6; others are described in the following examples.

**Table 6 Equipment and operating conditions for high-luster buffing of aluminum products**

| Product | Size | | Type of buffing machine | Type | Buffing wheel | | | | | | | | | | Production, pieces per hour |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Diameter | | | | | | Thread count | Wheel speed | | Type of compound | |
| | | | | | Overall | | Center | | Ply | | | | | | |
| | mm | in. | | | mm | in. | mm | in. | mm | in. | | m/s | sfm | | |
| Biscuit pan | 340 by 240 | $13\frac{1}{4}$ by 9 | Semiautomatic | Bias | 360 | 14 | 125 | 5 | 410 | 16 | 86/93 | 40 | 8250 | Bar | 205 |
| Burner ring | 75 diam by 20 | 3 diam by $\frac{3}{4}$ | Continuous rotary(a) | Radial, vented | (b) | (b) | 30 | $1\frac{1}{8}$ | 510 | 20 | 64/64 | (c) | (c) | Liquid | 297 |
| Cake-carrier base | 270 diam by 20 | $11\frac{1}{4}$ diam by $1\frac{3}{16}$ | Continuous rotary(a) | Bias | Two 360 | Two 14 | 125 | 5 | 460 | 16 | 86/93 | 50 | 9550 | Liquid | 278 |
| | | | | Bias | Two 330 | Two 13 | 75 | 3 | 50 | 2 | 64/68 | 45 | 8850 | Liquid | . . . |
| Cake pan | 350 by 241 by 65 | 14 by $9\frac{1}{2}$ by $2\frac{1}{2}$ | Hand buffing (handles) | Bias | 330 | 13 | 75 | 3 | 50 | 2 | 64/68 | 40 | 7650 | Bar | 438 |
| | | | Semiautomatic (sides) | Bias | 360 | 14 | 125 | 5 | 410 | 16 | 86/93 | 40 | 8250 | Bar | 200 |
| Cake pan | 200 by 203 by 50 | 8 by 8 by 2 | Semiautomatic | Bias | 360 | 14 | 125 | 5 | 410 | 16 | 86/93 | 40 | 8250 | Bar | 127 |

| | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Cup | 60 diam by 65 | 2$\frac{3}{8}$ diam by 2$\frac{1}{2}$ | Semiautomatic | Bias | 360 | 14 | 125 | 5 | 410 | 16 | 86/93 | 40 | 8250 | Bar | 450 |
| Pan bottom | 280 by 280 | 11$\frac{1}{8}$ square | Semiautomatic | Bias | 360 | 14 | 125 | 5 | 410 | 16 | 86/93 | 40 | 8250 | Bar | 106 |
| Pan cover | 285 by 285 | 11$\frac{1}{4}$ square | Semiautomatic(d) | Bias (sides) | 360 | 14 | 125 | 5 | 410 | 16 | 86/93 | 40 | 8250 | Bar | 95 |
| | | | | Loose, vented (top) | (e) | (e) | 50 | 2 | 510 | 20 | 64/64 | (f) | (f) | Bar | 95 |
| Toy pitcher | 65 diam by 90 | 2$\frac{1}{2}$ diam by 3$\frac{1}{2}$ | Continuous rotary(g) | Bias | 360 | 14 | 125 | 5 | 410 | 16 | 64/68 | 50 | 9550 | Liquid | 817 |
| Toy tumbler | 50 diam by 65 | 1$\frac{7}{8}$ diam by 2$\frac{1}{2}$ | Continuous rotary(g) | Bias | 360 | 14 | 125 | 5 | 410 | 16 | 64/68 | 50 | 9550 | Liquid | 864 |

(a) Five-spindle machine; four buffing heads, one load-unload station.

(b) Each of the four wheels used had one 330 mm (13 in.) and three 360 mm (14 in.) sections.

(c) For 330 mm (13 in.) section, 45 m/s (8850 sfm); for 360 mm (14 in.), 49 m/s (9550 sfm).

(d) Two machines, run by one operator.

(e) Buff made up of 360 mm (14 in.), 381 mm (15 in.), and 410 mm (16 in.) sections.

(f) 42 m/s (8250 sfm) for 360 mm (14 in.) sections, 45 m/s (8800 sfm) for 380 mm (15 in.) sections, and 48 m/s (9400 sfm) for 410 mm (16 in.) sections.

(g) Eight-spindle machine

Table 7 gives the conditions and sequence of operations for automatic buffing of wrought aluminum frying-pan covers. A specular finish was required. In another case, the sides of die-cast aluminum frying pans made from alloy 360 were buffed to a bright finish by an automatic machine with four buffing heads. The buffing wheel of each head consisted of a 14-ply, 16-spoke sewed bias buff with a 430 mm (17 in.) outside diameter, a 230 mm (9 in.) inside diameter, and a 44 mm ($13\frac{3}{4}$ in.) diameter arbor hole. Wheel speed was 1745 rev/min, equal to 39 m/s (7700 sfm). Each buff was made up of four sections. A liquid buffing compound was applied by one gun per wheel at the rate of 3 g per shot (0.1 oz per shot) for the first wheel, 2.5 g per shot (0.09 oz per shot) for the second and third wheels, and 1 g per shot (0.04 oz per shot) for the fourth wheel. The gun was on for 0.1 s and off for 5 s. The service life of each buffing wheel was 1600 to 2100 pieces.

**Table 7 Sequence and conditions of automatic buffing operations for obtaining specular finish on aluminum frying-pan covers**

| Operation | Area buffed | Buffing head No. | Buffing wheel | | | | | | | | | | | | | | Application of compound(a) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Type | Diameter | | | | | | Ply | Thread count | Density | No. of sections | Speed | | Life, pieces | | | | | |
| | | | | Overall | | Center | | Arbor hole | | | | | | | | | No. of guns | Cycle,s | | g per shot | oz per shot |
| | | | | mm | in. | mm | in. | mm | in. | | | | | m/s | sfm | | | On | Off | | |
| 1 | Sides (4) | 1,2,3,4 | Bias, air cooled | 430 | 17 | 180 | 7 | 45 | 1 $\frac{3}{4}$ | . . . | 86/93 | 2.4 | 20 | 40 | 7750 | 40,000 | 3 | 0.1 | 7 | 0.5 | 0.02 |
| 2 | Corners (2) | 5,6,7,8 | Bias, 20-spoke sewed | 430 | 17 | 180 | 7 | 45 | 1 $\frac{3}{4}$ | 16 | 86/93 | 4 | 4 | 40 | 7750 | 35,000 | 1 | 0.1 | 7 | 0.5 | 0.02 |
| 3 | Sides (2) | 9,10,11,12 | Bias, 20-spoke sewed | 430 | 17 | 180 | 7 | 45 | 1 $\frac{3}{4}$ | 16 | 86/93 | 4 | 4 | 40 | 7750 | 50,000 | 1 | 0.1 | 7 | 0.5 | 0.02 |
| 4 | Sides (2) | 13,14,15,16 | Bias, 20-spoke sewed | 430 | 17 | 180 | 7 | 45 | 1 $\frac{3}{4}$ | 16 | 86/93 | 4 | 4 | 40 | 7750 | 35,000 | 1 | 0.1 | 8 | 0.5 | 0.02 |
| 5 | Top | 17 | Bias, 45° spoke sewed | 430 | 17 | 180 | 7 | 45 | 1 $\frac{3}{4}$ | 16 | 86/93 | 4 | 15 | 40 | 7750 | 65,000 | 3 | 0.1 | 8 | 0.2 | 0.01 |
| 6 | Top | 18 | Bias | 430 | 17 | 180 | 7 | 45 | 1 | 12 | 86/93 | 8 | 18 | 40 | 7750 | 70,000 | 3 | 0.1 | 8 | 0.2 | 0.01 |

| | | | | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | 3/4 | | | | | | | | | | | | |
| 7 | Top bias | 19 | Bias | 430 | 17 | 180 | 7 | 45 | 1 3/4 | 12 | 86/93 | 8 | 18 | 40 | 7750 | 70,000 | 3 | 0.1 | 8 | 0.2 | 0.01 |
| 8 | Top bias | 20 | Bias | 410 | 16 | 125 | 5 | 45 | 1 3/4 | 14 | 64/68 | 2 | 19 | 37 | 7300 | 45,000 | 3 | 0.1 | 8 | 0.2 | 0.01 |
| 9 | Corners (4) | 21,22,23,24 | Bias | 430 | 17 | 180 | 7 | 45 | 1 3/4 | 12 | 86/93 | 8 | 4 | 40 | 7750 | 65,000 | 1 | 0.1 | 10 | 0.5 | 0.02 |
| 10 | Sides (4) | 25,26,27,28 | Bias | 430 | 17 | 180 | 7 | 45 | 1 3/4 | 12 | 86/93 | 8 | 4 | 40 | 7750 | 80,000 | 1 | 0.1 | 10 | 0.5 | 0.02 |
| 11 | Top bias | 29 | Bias | 410 | 16 | 125 | 5 | 45 | 1 3/4 | 14 | 64/68 | 2 | 15 | 23 | 4600 | 80,000 | 3 | 0.1 | 10 | 0.5 | 0.02 |
| 12 | Sides (4) | 30,31(b) | Domet flannel | 430 | 17 | 180 | 7 | 70 | 2 3/4 | 20 | (d) | (d) | 40 | 20 | 4000 | 80,000 | 6 | 0.1 | 11 | 0.2 | 0.01 |
| 13 | Top | 32 | Domet flannel(c) | 430 | 17 | 180 | 7 | 40 | 1 5/8 | 32 | (d) | (d) | 24 | 25 | 4900 | 30,000 | 3 | 0.1 | 11 | 0.2 | 0.01 |
| 14 | Top | 33 | Domet flannel(c) | 430 | 17 | 180 | 7 | 40 | 1 | 32 | (d) | (d) | 24 | 18 | 3550 | 30,000 | 3 | 0.1 | 11 | 0.2 | 0.01 |

| | | | | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | $\frac{5}{8}$ | | | | | | | | | | | | |

(a) Liquid tripoli compound applied to buffing heads No. 1 through 29; stainless steel buffing compound applied to heads No. 30 through 33.

(b) Each head buffs two sides.

(c) Domet flannel sections interleaved with 180 mm (7 in.) diam disks of Kraft paper.

(d) Inapplicable to flannel buff

Die-cast aluminum soleplates for steam irons (Table 8) were buffed to a bright finish on an automatic machine with eight buffing heads. The soleplates were made of alloy 380.0 and were prepolished with 320-mesh grit. A liquid buffing compound was applied by one gun per wheel for the first four heads and by two guns per wheel for the last four heads. The guns were on for 0.12 s and off for 13 s. The service life was 72,000 pieces for each buff of the first four heads, and 24,000 pieces for each buff of the last four heads.

**Table 8 Automatic bright-finish buffing of aluminum soleplates**

| **Operation** | **Area buffed** | **Buffing head No.** | **Buffing wheel** | | | | | | | | | | **Application of compound[b]** | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | **Type** | **Size** | **Diameter[a]** | | | | **No. of sections** | **Speed** | | **Life, pieces** | | | |
| | | | | | **Overall** | | **Arbor hole** | | | | | | | | |
| | | | | | **mm** | **in.** | **mm** | **in.** | | **m/s** | **sfm** | | **No. of guns** | **g per shot** | **oz per shot** |
| 1 | Side | 1,2 | Sisal | 10 mm($\frac{3}{8}$ in.) spiral sewed | 410 | 16 | 40 | $1\frac{1}{4}$ | 2 | 37 | 7350 | 72,000 | 1 | 0.5 | 0.02 |
| 2 | Side | 3 | Bias | 16-ply, 20-spoke sewed | 430 | 17 | 45 | $1\frac{3}{4}$ | 2 | 40 | 7800 | 72,000 | 1 | 0.5 | 0.02 |
| 3 | Side | 4 | Bias | 16-ply, 20-spoke sewed | 430 | 17 | 45 | $1\frac{3}{4}$ | 2 | 40 | 7800 | 72,000 | 1 | 0.5 | 0.02 |
| 4 | Top | 5 | Sisal | 10 mm ($\frac{3}{8}$ in.) spiral sewed | 410 | 16 | 45 | $1\frac{3}{4}$ | 15 | 37 | 7350 | 24,000 | 2 | 3.0 | 0.1 |
| 5 | Top | 6 | Sisal | 10 mm ($\frac{3}{8}$ in.) spiral sewed | 410 | 16 | 45 | $1\frac{3}{4}$ | 15 | 37 | 7350 | 24,000 | 2 | 3.0 | 0.1 |
| 6 | Top | 7, 8 | Bias | 16-ply, 20-spoke sewed | 430 | 17 | 45 | 1 | 10 | 40 | 7800 | 24,000 | 2 | 3.0 | 0.1 |

(a) All wheels had 180 mm (7 in.) diam centers.

(b) Proprietary liquid compound was used. Cycle time: 0.12 s on, 13.0 s off

## Satin Finishing

Mechanical satin finishing is an established method for obtaining an attractive surface texture on aluminum hardware items such as knobs, hinges, rosettes, and drawer pulls. Satin finishes are also used for architectural, appliance, and automotive trim. The satin finish results from small, nearly parallel scratches in the metal surface, which give the surface a soft, smooth sheen of lower reflectivity than that of polished or buffed surfaces.

Satin finishes can be applied by fine wire brushing. Other methods use a greaseless abrasive compound in conjunction with a conventional buffing head, tampico brush, cord brush, string buff, or brush-backed sander head. Abrasive-impregnated nylon disks mounted like buffs are also used, as are abrasive cloth sections mounted on a rotating hub. All of these methods produce about the same type of finish; the use of any particular one depends on the surface contour of the workpiece.

Surfaces of workpieces to be satin-finished should be free of grease and oil, and low contact pressures should be used. Wire brushes must be kept free of oxide and accumulations of aluminum metal. This is accomplished by frequently bringing a pumice stone or soft brick in contact with the rotating brush. A common wire brushing setup consists of a 250 mm (10 in.) diameter wheel having a surface speed of about 8.0 m/s (1600 sfm) and wires 0.4 mm (0.015 in.) in diameter. Undue pressure on a rotating wire wheel will bend the wires and cause excessive tearing of the aluminum surface.

Stainless steel wires are recommended, because other metals such as brass or steel may become embedded in the aluminum surface, producing discoloration or corrosion. If brass or steel wire wheels are used, the embedded particles can be removed by immersing the work in a nitric acid solution (1 part water to 1 part acid by volume) at room temperature.

The satin finish processes in which a greaseless abrasive compound is used are essentially dry. Water is required to soften the binder in the abrasive compound so that it will adhere to the surface of the buff. After the binder dries, the buff is ready for operation. At this stage a lubricant, such as a buffing compound or tallow, may be used to produce a higher reflection.

Table 9 describes the equipment and techniques employed in mechanical satin finishing processes. If the satin-finished parts are to be anodized, etching or bright dipping should not precede anodizing, because the satin appearance will be lost. Cleaning treatments that do not etch or that only slightly etch the metal should be used before anodizing.

### Table 9 Methods, equipment, and conditions for mechanical satin finishing of aluminum

| **Method** | **Suitable equipment** | | | **Speed** | | **Lubricant** |
|---|---|---|---|---|---|---|
| | **Buffing lathe** | **Portable power head** | **Power required** | **m/s** | **sfm** | |
| Wire brushing[a] | Yes | Yes | [b] | 6-11 | 1200-2250 | None |
| Sanding with brush-backed head[c] | Yes | No | [d] | 900-1800 rev/min | 900-1800 rev/min | Optional |
| Tampico or string brushing[e] | Yes | No | [b] | 15-31 | 3000-6000 | Pumice[f] |
| Finishing with abrasive-coated cloth[g] | Yes | Yes | [d] | 31-36 | 6000-7000 | Optional |
| Finishing with nylon disks[h] | Yes | Yes | [i] | 23-33 | 4500-6500 | Optional |

| | | | | | | |
|---|---|---|---|---|---|---|
| Buffing with compounds[j] | Yes | Yes | [b] | 15-26 | 3000-5000 | [k] |

(a) 305 mm (12 in.) diam brush of stainless steel wire 0.125 mm (0.005 in.) in diameter.

(b) 1 hp per 25 mm (1 in.) of brush width.

(c) Using 60- to 600-mesh abrasive cloth loadings.

(d) 1 hp per head.

(e) 300 mm. (12 in.) diam brush.

(f) With oil or water; emery cake also may be used.

(g) Cloth is mounted radially on rotating hubs; coated with 50- to 320-mesh emery abrasive.

(h) Disks impregnated with silicon carbide abrasive, coarse to ultrafine.

(i) $\frac{1}{4}$ hp per 25 mm (1 in.) of disk width.

(j) Greaseless satin-finishing compounds containing aluminum oxide abrasive (200 or 240 mesh) used with unstitched or loosely stitched buffs (360 mm or 14 in.) or with string brush.

(k) Dry, or with buffing compound or grease stick

## Chemical Cleaning

The cleanliness requirements for an aluminum surface are governed by the subsequent finishing operations. For example, plating or the application of chromate or another mild-reaction conversion coating requires cleaning procedures that are somewhat more stringent than for anodizing.

When establishing a cleaning cycle or when testing different cleaners or cleaning conditions, it is desirable to test the cleanliness of the processed surface. Wetting an aluminum surface with water, known as the water break test, does not always provide an indication of cleanliness if oxides are of concern, because oxide-coated surfaces free of oil or grease can be wetted uniformly. Also, a surface that has been processed with a detergent containing a wetting agent can be wetted even though not thoroughly clean, because the film of wetting agent remains on the unclean surface. Two other methods of testing aluminum for cleanliness are to:

- Spray or coat the work surface with, or dip a test panel into, an unheated aqueous solution containing 30 g/L (4 oz/gal) of cupric chloride and 29 mL/L (3.8 fluid oz/gal) of concentrated hydrochloric acid. Uniform gassing or a deposit of copper indicates that the surface is chemically clean.
- Spray or coat the work surface with, or dip a test panel into, an unheated chromate conversion coating bath of the acid type until an orange-colored film is formed. A uniform orange film indicates a

chemically clean surface.

**Solvent Cleaning.** The primary function of solvent cleaners is to remove oil and grease compounds. Organic solvents alone rarely provide sufficient cleaning to permit final finishing operations; solvents usually are used to remove large amounts of organic contaminants to minimize overloading of subsequently used alkaline cleaners.

Greases and oils vary as to solubility in specific solvents. Fish oils are more difficult to remove than other types of oils. In the dried condition, some oxidizing oils, such as linseed oil, form a leathery film that is difficult to remove with any solvent.

Polishing and buffing compounds are readily removed by most solvents when cleaning is performed immediately after buffing. If the compounds are permitted to harden, they may be difficult to remove. Heated solutions, agitation, or mechanical action (ultrasonics or physical force) may be required for satisfactory cleaning. To remove compounds burned in the surface, the parts must be soaked in a liquid using an organic degreaser. such as trichlorethylene or methylene dichloride (rather than vapor degreasing), or in an inhibited alkaline cleaner.

If polishing and buffing compounds cannot be removed immediately after buffing, the application of a neutral mineral oil over the buffed surface will maintain the compounds in a more soluble condition for subsequent removal by a solvent. The sequence of operations usually required for buffed aluminum surfaces is: solvent cleaning, rinsing, removal of surface oxides, rinsing, and finally the application of the desired finish. Some of these steps may be omitted, depending on the type and quality of the buffing compound, the quality of workmanship in buffing, and the quality of solvents and cleaners used.

**Emulsifiable solvents** also are used to clean aluminum. These are organic solvents, such as kerosene, Stoddard solvent, and mineral spirits, to which small amounts of emulsifiers and surfactants are added. In use, this type of cleaner emulsifies the oil or grease on the surface. The soil and cleaner are removed with water, preferably applied by spraying.

This type of degreasing is satisfactory prior to anodizing, etching, removal of surface oxides, chemical conversion coating, plating, or painting. In some instances, intermediate treatments are required, such as the removal of surface oxides before etching.

The emulsifiable solvent should have a pH of 8 or less; otherwise, it will stain or corrode the aluminum if permitted to remain on the surface prior to rinsing or additional cleaning. However, emulsifiable solvents with higher pH are more efficient cleaners, and they can be used if the surfaces are rinsed or are cleaned by additional methods within 2 or 3 min after degreasing.

A lower-cost cleaning solution can be obtained by adding water to the emulsifiable solvent. This less-efficient type of solution is limited to the removal of light oil and grease. It is now common practice to use alkaline cleaners to remove oil and grease instead of solvents, the use of which is under increasing scrutiny by the Environmental Protection Agency (EPA).

**Alkaline cleaning** is the most widely used method for cleaning aluminum and aluminum alloys. This method is easy to apply in production operations, and equipment costs are low. Aluminum is readily attacked by alkaline solutions. Most solutions are maintained at a pH between 9 and 11, and they are often inhibited to some degree to minimize or prevent attack on the metal. The most frequently used alkaline cleaner is the mildly inhibited type.

Cleaners of either the etching or nonetching type have some ability to emulsify vegetable and animal oils or greases, but not mineral oils or greases. Therefore, they can sometimes remove fresh buffing compounds and the lard oils used in spinning operations.

Nonetching cleaners can be classified as either silicated or nonsilicated. The silicated cleaners are based on aqueous solutions of sodium carbonate, trisodium phosphate, or other alkalis, to which small amounts of sodium silicate are added to inhibit etching. The main disadvantage of the silicated types, aside from their inability to emulsify and remove mineral oils, is that the silicate may react with the aluminum to form an insoluble aluminum silicate, especially when the temperature of the bath exceeds 80 °C (180 °F). However, lower operating temperatures decrease the efficiency of the solution for the removal of certain soils. Silicated alkaline cleaners are available that are used at 50 to 60 °C (120 to 140 °F) to reduce energy consumption.

Nonsilicated cleaners are often based on the use of relatively large concentrations of surfactants. High operating temperatures are required, but some cleaners used above 70 °C (160 °F) etch the aluminum surface. Cleaners containing a large quantity of surfactants, particularly those types that resist complete rinsing, must not be carried into baths used for bright dipping, anodizing, or chemical conversion coating.

Neither silicated nor nonsilicated cleaners remove aluminum oxide uniformly. Because oxide removal is essential for the application of decorative or functional finishes, the best procedure is to clean, remove oxide with an acid solution, and then proceed with finishing.

Nonetching cleaners may be used after solvent cleaning to produce water-wettable surfaces, or they may be used alone when soils are light and easily removed. The surfaces should be treated to remove oxides afterward. When sodium orthosilicate or sodium metasilicate is used, the concentration of carbonates must be kept at a minimum to minimize the formation of floc, which may redeposit on the work. Unlike sodium hydroxide, the alkali silicates have good wetting, emulsifying, and rinsing properties. The ratio of silicon dioxide to sodium oxide in the compound determines the effectiveness of the alkali silicates. Sodium orthosilicate has good detergency and is effective in the cleaner at a ratio of 1 to 2, whereas the ratio of sodium metasilicate should be 1 to 1.

Agitation of the cleaner increases the cleaning action and is best created by pumps, propellers, or movement of the work. Air agitation, although easier to install and convenient to operate, has the following disadvantages:

- Air can reduce the solution temperature.
- The additional oxygen may cause staining and tarnishing on some alloys.
- Air agitation introduces carbon dioxide, which may increase the carbonate content.

The work should be rinsed immediately after removal from the alkaline bath to prevent dry-on. Warm water is preferred; if low-temperature cleaners are used, then rinsing with cold water is satisfactory.

Aluminum surfaces sometimes contain areas of localized corrosion, referred to as atmospheric etch, caused by contaminants in the air during storage. The corroded areas are more visible after alkaline cleaning or etching than before. When corrosion spots are present, the work may be dipped in a sodium bisulfate solution of 45 g/L (6 oz/gal), or in a cold 70% nitric acid solution, to minimize the effect of the subsequent alkaline cleaning.

During alkaline cleaning, especially if etching occurs, some alloys containing copper, iron, manganese, or silicon develop a black smut on the surface. Compositions and operating conditions of common alkaline cleaners are given in Table 10.

**Table 10 Alkaline cleaners used to clean aluminum surfaces**

| Constituent or condition | Amount or value |
|---|---|
| **Etching cleaners** | |
| Sodium hydroxide | 22-75 g (3-10 oz) |
| Sodium phosphate | 0.8-4 g (0.1-0.5 oz) |
| Water, to make | 4 L (1 gal) |
| Temperature of bath | 60-80 °C (140-180 °F) |

| | |
|---|---|
| Immersion time | 30 s-10 min |
| Sodium hydroxide | 2-6 g (0.25-0.75 oz) |
| Sodium phosphate | 8-60 g (1-8 oz) |
| Sodium carbonate | 8-60 g (1-8 oz) |
| Water, to make | 4 L (1 gal) |
| Temperature of bath | 60-80 °C (140-180 °F) |
| Immersion time | 2-5 min |
| **Nonetching cleaners** | |
| Sodium pyrophosphate and sodium metasilicate | Total of 15-75 g (2-10 oz) |
| Water, to make | 4 L (1 gal) |
| Temperature of bath | 60-70 °C (140-160 °F) |
| Immersion time | 2-5 min |
| Trisodium phosphate and sodium metasilicate | Total of 15-75 g (2-10 oz) |
| Water, to make | 4 L (1 gal) |
| Temperature of bath | 60-70 °C (140-160 °F) |
| Immersion time | 2-5 min |
| Sodium carbonate | 4-8 g (0.5-1 oz) |
| Sodium metasilicate | 4-8 g (0.5-1 oz) |
| Water, to make | 4 L (1 gal) |
| Temperature of bath | 6-70 °C (140-160 °F) |
| Immersion time | 2-5 min |

| | |
|---|---|
| Borax | 22-38 g (3-5 oz) |
| Sodium pyrophosphate | 4-8 g (0.5-1 oz) |
| Water, to make | 4 L (1 gal) |
| Temperature of bath | 60-70 °C (140-160 °F) |
| Immersion time | 2-5 min |

**Electrocleaning** is seldom used for cleaning aluminum and aluminum alloys, because it offers no advantage over an etching cleaner. However, a few processes are used in production operations. These use low voltage, usually in the range of 6 to 12 V. Cathodic cleaning, in which the work is the cathode, is more common than anodic cleaning. Common practice is to reverse the current during the last 5 to 10 s of the cleaning operation.

After removal from the cleaner, the work is rinsed in warm or hot water, dipped in acid to neutralize any residual alkali, and finally rinsed in cold water. The work can then be finished as desired. The composition of two solutions that are recommended for electrocleaning are:

| **Constituents** | **Composition, %** |
|---|---|
| **Solution A** | |
| Sodium orthosilicate | 85 |
| Sodium carbonate (anhydrous) | 10 |
| Sodium resinate | 5 |
| **Solution B** | |
| Sodium carbonate (anhydrous) | 46 |
| Trisodium phosphate | 32 |
| Sodium hydroxide | 16 |
| Rosin | 6 |

Note: For typical operating conditions, see text.

**Acid Cleaning.** Acid cleaners may be used alone or in conjunction with other acid, alkaline, or solvent cleaning systems. Vapor degreasing and alkaline cleaning may be required for the removal of heavy oils and grease from workpieces before they are immersed in an acid bath. One of the main functions of an acid cleaner is to remove surface oxides prior to resistance welding, painting, conversion coating, bright dipping, etching, or anodizing.

A mixture of chromic and sulfuric acids is commonly used to remove surface oxides, burnt-in oil, water stains, or other films, such as the iridescent or colored films formed during heat treating. This acid mixture cleans and imparts a slightly etched appearance to the surface, preparing it for painting, caustic etching, conversion coating, or anodizing. Nonpolluting, proprietary products free of chromic acid are available for acid cleaning and deoxidizing.

Oxide films must be thoroughly removed before spot welding. A mixture of phosphoric and chromic acids is another solution that can be used for this purpose. Because of the corrosive nature of the chlorides and fluorides in welding fluxes, the fluxes should be removed as soon as possible after welding. Mixtures of nitric and hydrofluoric acids are best for removing fluxes. Most fluxes can also be satisfactorily removed by a dilute (5 to 20 vol%) nitric acid solution.

Proprietary nonetching acid cleaners are available for cleaning aluminum and aluminum alloys. Operating temperatures of these solutions range from 55 to 80 °C (130 to 180 °F), and pH usually ranges from 4.0 to 5.7. Compositions and operating conditions for typical acid cleaning solutions are given in Table 11.

**Table 11 Acid cleaners used to clean aluminum surfaces**

| Constituent or condition | Amount or value |
|---|---|
| **Solution 1** | |
| Chromic acid | 45-90 g (6-12 oz) |
| Sulfuric acid (66° Bé) | 150-190 mL (19-24 fluid oz) |
| Water, to make | 4 L (1 gal) |
| Temperature of bath | 45-80 °C (110-180 °F) |
| Immersion time | up to 20 min |
| **Solution 2** | |
| Nitric acid (42° Bé) | 500-750 mL (64-96 fluid oz) |
| Hydrofluoric acid (48%) | 25-190 mL (3-24 oz) |
| Water, to make | 4 L (1 gal) |
| Temperature of bath | Room temperature |
| Immersion time | 1-5 min |

| | |
|---|---|
| **Solution 3** | |
| Sulfuric acid (66° Bé) | 100 mL (13 fluid oz) |
| Hydrofluoric acid (48%) | 25 mL (3 fluid oz) |
| Chromic acid | 40 g (5 oz) |
| Water, to make | 4 L (1 gal) |
| Temperature of bath | 65-70 °C (150-160 °F) |
| Immersion time | 2-5 min |
| **Solution 4** | |
| Nitric acid (42° Bé) | 38-125 mL (5-16 fluid oz) |
| Sodium sulfate (hydrate) | 60-120 g (8-16 oz) |
| Water, to make | 4 L (1 gal) |
| Temperature of bath | 75-80 °C (170-175 °F) |
| Immersion time | 4-8 min |
| **Solution 5** | |
| Phosphoric acid | 70 mL (9 fluid oz) |
| Chromic acid | 20 g (2.75 oz) |
| Water, to make | 4 L (1 gal) |
| Temperature of bath | 45-65 °C (110-150 °F) |
| Immersion time | 1-5 min |

Aluminum parts should be insulated from ferrous metal baskets or supports when immersed in acid cleaning solutions, because contact of these two metals can produce a galvanic action that causes corrosion. Materials such as vinyl plastisols, epoxy, polyethylene, and polypropylene may be used for insulation. When practical, baskets or rods should be of the same or similar material as the workpieces.

## Chemical Brightening (Polishing)

Chemical brightening, also known as bright dipping and chemical polishing, smoothens and brightens aluminum products by making use of the solution potential of the aluminum surface in the various baths employed and of the local differences in potential on the aluminum surface.

In general, chemical brightening baths can be concentrated or dilute acid solutions that contain oxidizing agents. The acids commonly used are sulfuric, nitric, phosphoric, acetic, and, to a lesser extent, chromic and hydrofluoric. Ammonium bifluoride is used when it is desirable to avoid the hazards that attend the use of hydrofluoric acid. Fluoboric and fluosilicic acids may also be used as alternates to hydrofluoric acid. An alkaline bath, such as Alupol, can also be used for chemical etching. This bath consists of 20 kg (44 lb) sodium nitrate, 15 kg (33 lb) sodium nitrite, 25 kg (55 lb) sodium hydroxide, and 20 kg (44 lb) water. An aluminum part is immersed for 1 to 5 min at a bath temperature of 90 to 140 °C (195 to 285 °F). Protrusions, valleys, and scratches are eliminated, and reflectance is increased.

**Phosphoric-Nitric Acid Baths.** Among the various types of concentrated baths, the phosphoric-nitric acid baths are the most widely used in the United States. Compositions and operating conditions for two commercial baths of this type are given below:

| Constituent or condition | Range |
|---|---|
| **Phosphoric-nitric**(a) | |
| Phosphoric acid (85%) | 45-98 wt%(b) |
| Nitric acid (60%) | 0.5-50 wt%(b) |
| Water | 2 to 35 wt% |
| Temperature | 85-110 °C (190-230 °F) |
| Immersion time | 30 s to 5 min |
| **Phosphoric-acetic-nitric**(c) | |
| Phosphoric acid (85%) | 80 vol% |
| Acetic acid (glacial, 99.5%) | 15 vol% |
| Nitric acid (60%) | 5 vol% |
| Temperature | 85-110 °C (190-230 °F) |
| Immersion time | 30 s to 5 min |

(a) U.S. Patent 2,729,551 (1956).

(b) Recommended volumetric make-up consists of 93.5 parts of 85% phosphoric acid and 6.5 parts of 60% nitric acid.

(c) U.S. Patent 2,650,157 (1953)

Additionally, certain proprietary chemical bright dips can be operated at 75 to 80 °C (170 to 180 °F), which is significantly lower than the normal 85 to 110 °C (190 to 230 °F) for conventional baths. The low-temperature baths, however, are limited in allowable water drag-in from prior rinse operations. Excessive water drag-in results in poor brightening.

Alkali nitrates may be used as substitutes for nitric acid. Acetic acid, copper salts, and other additives are used in some phosphoric-nitric acid baths. As additive content increases, solution control becomes more complex.

For economy, some phosphoric-nitric acid baths are operated with an aluminum phosphate content near the tolerable maximum of 10 to 12%, with a dissolved aluminum content of about 40 g/L (5 oz/gal). This is close to the saturation point, at which precipitation of this compound on the work produces etch patterns.

The addition of surfactants increases the amount of metal removed under a given set of operating conditions. Surfactants help to enhance the chemical polishing as well as to suppress the evolution of fumes. Acetic and sulfuric acids alter the physical property/composition relationship in the concentrated acid baths and also complicate control problems. Acetic acid volatilizes rapidly from the bath.

Small concentrations of heavy metals in the bath enhance the brightening effect, particularly on alloys with negligible copper content. Copper can be introduced into the bath by one of three methods: the direct dissolution of a small amount of copper; the addition of a small amount of a copper compound, such as 0.01 to 0.02% cupric nitrate; or the use of racks made of aluminum-copper alloys. Copper is added to the bath when brightening aluminum alloys such as 2024 and 7075, which contain high percentages of copper. Excess copper can plate out of the bath. In some baths, however, excess copper causes etching, and sometimes nickel or zinc is used instead.

Phosphoric-nitric acid baths are not recommended for brightening alloys that contain silicon. Excessive dissolution causes dispersion of undissolved silicon, which deposits on the work surfaces and is difficult to remove by rinsing. When high-silicon alloys are used, the addition of 1 to 2% hydrofluoric acid to the bath is recommended. The gradual buildup of other metals in the bath from the aluminum alloys processed usually causes no difficulty unless the amount of aluminum dissolved exceeds the solubility limit. When this occurs, excess aluminum precipitates and causes coprecipitation of trace elements, which may be difficult to remove from the work.

Contamination of the bath by more than trace amounts of buffing or polishing compounds and other soils should be avoided. These compounds may cause the bath to foam excessively and may interfere with its polishing action. Food-grade or National Formulary phosphoric acid should be used. Lower grades contain fluorides, arsenic, and other impurities that are harmful to the process.

Close control of the nitric acid and water contents, necessary for optimum chemical brightening, is difficult because of the rapid volatilization of these liquids and because of the time required for chemical analysis of the bath. A control method based on an electronic device that monitors the nitric acid content and on the physical measurement of specific gravity and viscosity has been developed.

Drag-out is a major factor in the cost of chemical brightening. The amount of solution and the weight of chemicals lost by drag-out are related to the specific gravity and viscosity of the solution. Drag-out can be minimized by operating the bath at higher temperatures, but this condition may increase the amount of transfer etch while moving to the rinse tank, as well as the rate of aluminum dissolution and the rate of evaporation of nitric acid and water. However, transfer etch can be avoided by rapid transfer into the rinse, and the rate of aluminum dissolution can be minimized by a shorter period of immersion. In general, an operating temperature in the range of 85 to 100 °C (190 to 212 °F) is satisfactory, provided an optimum bath composition, including additives, is maintained. Also, evaporation of nitric acid and water is not excessive at this temperature. Acetic acid also reduces transfer etch, but this acid volatilizes rapidly from the bath.

Surfactants are employed in some baths to suppress the evolution of fumes; however, they may cause foaming and increase the amount of drag-out. Surfactants also increase the rate of workpiece dissolution. The generation of heat accompanying high dissolution rates must be considered when providing for the control of bath temperatures within the specified range.

Agitation is useful for maintaining a uniform temperature and composition throughout the bath, and for fast removal of reaction products and replenishment of reactants at the surfaces of the work. The most satisfactory method is mechanical agitation and movement of the work in an elliptical pattern. Air agitation is commonly used, but it must be properly controlled. Small air bubbles cause excessive loss of volatile acids by evaporation and an excess of nitrous oxide fumes. Large air bubbles sufficient to create uniform bath temperature provide satisfactory agitation. Excessive solution agitation can cause pitting and streaking on work, so the agitation should always be moderate.

The bath must be well vented to remove the noxious fumes; an exhaust of about 90 $m^3$/min per square meter (300 $ft^3$/min per square foot) of bath surface is recommended. Fumes evolved during transfer of the parts to the first rinse tank should likewise be vented, and it is good practice also to vent the first rinse tank, for which an exhaust of about 60 $m^3$/min per square meter (200 $ft^3$/min per square foot) of water surface is satisfactory. Water should be warm and air-agitated.

The fumes can be exhausted by fan or steam jet. Fume separators are required when the fumes cannot be exhausted into the atmosphere. Dilute caustic soda solutions are used to scrub the fumes and neutralize the acid.

**Phosphoric and Phosphoric-Sulfuric Acid Baths.** Concentrated solutions of phosphoric acid at operating temperatures above 80 °C (175 °F) were the first baths used for brightening aluminum. A more effective bath, which combines some smoothening or polishing with brightening action, is one containing 75 vol% phosphoric acid and 25 vol% sulfuric acid. This bath, which is operated at 90 to 110 °C (195 to 230 °F) for 30 s to 2 min, produces a diffuse but bright finish.

Under some conditions of composition and bath temperature, a white film of phosphate salts remains on the metal after treatment in either of these baths. The film must be removed by using a hot (60 to 70 °C, or 140 to 160 °F) aqueous solution of chromic and sulfuric acids. The composition of this acid solution is not critical and may range from 2 to 4% $CrO_3$ and 10 to 15% $H_2SO_4$ by weight.

## Electrolytic Brightening (Electropolishing)

Electrolytic brightening, also known as electrobrightening and electropolishing, produces smooth and bright surfaces similar to those that result from chemical brightening. After pretreatment (which consists of buffing, cleaning in an inhibited alkaline soak cleaner, and thorough rinsing) the work is immersed in the electrobrightening bath, through which direct current is passed. The work is the anode.

Solution compositions and operating conditions for three commercial electrolytic brightening processes, as well as for suitable post-treatments, are given in Table 12. Operating conditions for electrolytes used in electrobrightening are selected to produce the desired selective dissolution and may vary for optimum results on different aluminum alloys.

**Table 12 Electrolytic brightening and polishing solutions and processes for use on aluminum and aluminum alloys**

| Bath | Percentage | Temperature | | Duration, min | Voltage, V | Current density | | Film thickness | | Appearance properties | Remarks |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | °C | °F | | | $A/dm^2$ | $A/ft^2$ | μm | mils | | |
| **Seignette salt brightener (alkaline process)** | | | | | | | | | | | |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Sodium potassium tartrate | 15 wt% | 38-42 | 100-108 | 2-15 | 10 | 3-5 | 30-50 | . . . | . . . | High luster, mirror-like reflectivity | For pure aluminum, Raffinal, Reflektal, and for jewelry and reflectors |
| Sodium hydroxide | 1.2 wt% | | | | | | | | | | |
| Aluminum powder | 0.2 wt% | | | | | | | | | | |
| Water | 83.6 wt% | | | | | | | | | | |
| **Acid brightening** | | | | | | | | | | | |
| Sulfuric acid | 70 vol% | 75-85 | 167-185 | 2-10 | 10-20 | 10-15 | 100-150 | . . . | . . . | High luster, mirror-like reflectivity | For pure aluminum, and its alloys and for reflectors, architectural and structural shapes, and appliance parts |
| Phosphoric acid | 15 vol% | | | | | | | | | | |
| Nitric acid | 1 vol% | | | | | | | | | | |
| Water | 14 vol% | | | | | | | | | | |
| **VAW brightener** | | | | | | | | | | | |
| Sodium bisulfate | 20 wt% | 87-93 | 188-199 | 8-10 | 8-10 | 10-15 | 100-150 | . . . | . . . | Colorless, transparent oxide film with effect on reflectivity | Used as a post-treatment after conventional anodizing is accomplished |
| Sodium sulfate | 10 wt% | | | | | | | | | | |
| Sodium hydroxide | 1 wt% | | | | | | | | | | |
| Water | 69 wt% | | | | | | | | | | |
| **Smudge remover** | | | | | | | | | | | |
| Sodium carbonate | 2 wt% | 92-97 | 198-207 | . . . | . . . | . . . | . . . | . . . | . . . | Preserve reflectivity | For removing the thin film produced on the aluminum |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Water | 96.5 wt% | | | | | | | | | | reflectivity |
| **Anodic post-treatments** | | | | | | | | | | | |
| Sulfuric acid | 71 wt% | 23-27 | 74-81 | 10 | 12 | 1 | 10 | 4 | 0.1 | Colorless, transparent film | Without anodizing good results; best results with anodizing |
| Water | 93 wt% | | | | | | | | | | |
| Sulfuric acid | 10-20 wt% | 18-22 | 64-72 | 10 | 12 | 1 | 10 | 4 | 0.1 | Colorless, transparent film | Without anodizing good results; best results with anodizing |
| Water | 90-80 wt% | | | | | | | | | | |
| Sodium bisulfate | 20 wt% | 33-37 | 91-98 | 10 | 10 | 0.5 | 5 | 2 | 0.08 | Colorless, transparent film | Without anodizing good results; best results with anodizing |
| Water | 80 wt% | | | | | | | | | | |

Fluoboric acid electrobrightening operating conditions and suitable post-treatments are given in Table 13. This process can be used for specular and diffuse reflectors, products made of super-purity aluminum (99.99%) in combination with up to 2% Mg, and products made of high-purity aluminum (99.7 to 99.9%).

### Table 13 Fluoboric acid electrobrightening of aluminum and aluminum alloys

| **Constituent or condition** | **Amount or value** |
|---|---|
| **Electrobrightening**[(a)] | |
| Fluoboric acid | 2.5 wt% |
| Temperature of bath | 30 °C (85 °F) |
| Current density | 1-2 A/dm$^2$ (10-20 A/ft$^2$) |
| Voltage | 15-30 V |
| Immersion time | 5-10 min |
| Agitation | None |
| **Smut removal** | |

| | |
|---|---|
| Phosphoric acid | 1.0 wt% |
| Chromic acid | 0.5 wt% |
| Temperature of bath | 90-95 °C (190-200 °F) |
| Immersion time | 30 s |
| **Anodizing** | |
| Sulfuric acid | 7-15 wt% |
| Current density | 1.3 A/dm$^2$ (12 A/ft$^2$) |
| Temperature of bath | 20 °C (70 °F) |
| Immersion time | 10 min |
| **Sealing** | |
| Distilled water | 100% |
| Temperature of bath | 95-100 °C (200-212 °F) |
| Immersion time | 10 min |

(a) U.S. Patent 2,108,603 (1938)

Sodium carbonate electrobrightening can be used for specular reflectors, automotive trim, decorative ware, and jewelry. It can also be used for products made of super-purity aluminum in combination with up to 2% Mg, products made of high-purity aluminum, and products made of the following commercial alloys (in approximate order of decreasing quality of finish): 5457, 5357, 6463, 6063, 5052, 1100, 5005, 3003, and 6061. Sodium carbonate electrobrightening operating conditions and suitable post-treatments are given in Table 14.

### Table 14 Sodium carbonate electrobrightening of aluminum and aluminum alloys

| Constituent or condition | Amount or value |
|---|---|
| **Electrobrightening** | |
| Sodium carbonate (anhydrous) | 15 wt% |

| | |
|---|---|
| Trisodium phosphate | 5 wt% |
| pH | 10.5 |
| Temperature of bath | 80-82 °C (175-180 °F) |
| Current density | 2-3 A/dm$^2$ (20-30 A/ft$^2$) |
| Voltage | 9-12 V |
| Initial immersion without current | 20 s |
| Immersion time with current | 5 min |
| Agitation | Work rod only |
| **Anodizing**[(b)] | |
| Sodium bisulfate | 20 wt% |
| Temperature of bath | 35 °C (95 °F) |
| Current density | 0.5 A/dm$^2$ (5 A/ft$^2$) |
| Voltage | 10 V |
| Immersion time | 15 min |
| **Smut removal**[(a)] | |
| Sulfuric acid | 10 vol% |
| Temperature of bath | 20-25 °C (70-80 °F) |
| Immersion time | 15-30 s |
| **Sealing** | |
| Distilled water | 100% |
| Temperature of bath | 85 °C (185 °F) |

| | |
|---|---|
| Immersion time | 20 min |

(a) Smut may also be removed mechanically.

(b) The anodizing treatment in the preceding list may be used as an alternative.

Sulfuric-phosphoric-chromic acid electrobrightening operating conditions and suitable post-treatments are given in Table 15. This process is used primarily for macrosmoothening to replace mechanical polishing wholly or in part. Other applications include architectural trim, decorative ware, jewelry, and products made of commercial alloys.

**Table 15 Sulfuric-phosphoric-chromic acid electrobrightening of aluminum and aluminum alloys**

| **Constituent or condition** | **Amount or value** |
|---|---|
| **Electrobrightening**(a) | |
| Sulfuric acid | 4-45 wt% |
| Phosphoric acid | 40-80 wt% |
| Chromic acid | 0.2-9.0 wt% |
| Trivalent metals | 6 wt% max |
| Temperature of bath | 70-95 °C (160-200 °F) |
| Viscosity of bath at 82 °C (180 °F) | 9-13 cP |
| Current density | 2.5-95 A/dm$^2$ (25-950 A/ft$^2$) |
| Voltage | 7-15 V |
| Agitation | Mechanical |
| **Smut removal** | |
| Phosphoric acid | 3.5 wt% |
| Chromic acid | 2.0 wt% |
| Temperature of bath | 90-95 °C (190-200 °F) |

| | |
|---|---|
| **Anodizing** | |
| Sulfuric acid | 7-15 wt% |
| Current density | 1.2 A/dm$^2$ (12 A/ft$^2$) |
| Temperature of bath | 20 °C (70 °F) |
| Immersion time | 10-20 min |
| **Sealing** | |
| Distilled water | 100% |
| Temperature of bath | 95-100 °C (200-212 °F) |
| Immersion time | 10 min |

(a) U.S. Patent 2,550,544 (1951)

## Selection of Chemical and Electrolytic Brightening Processes

Chemical and electrolytic brightening are essentially selective-dissolution processes, in which the high points of a rough surface are attacked more rapidly than the depressions. An important feature of these processes is their ability to remove a surface skin of metal that is contaminated with oxides and with traces of residual polishing and buffing compounds, or other inclusions, while at the same time brightening the surface.

**Metallurgical Factors.** The composition, orientation, and size of the individual grains within a workpiece have a direct effect on the uniformity of dissolution during brightening. Fine-grain material is the most desirable for chemical or electrolytic brightening. Best results are obtained with alloys that are of uniform chemical composition and that do not precipitate constituents of different potential from the matrix during any necessary heating or heat treatment. Also, the alloys should be such that forming operations cause only relatively minor detrimental effects.

Mill operations must be controlled to produce material that can be brightened satisfactorily. It is important that the material be fine-grain and that surfaces be free of imperfections, such as segregation, oxide inclusions, laps, die marks, and stains.

**Optical Factors.** In general, the highest total and specular reflectance of a brightened surface is obtained on pure aluminum having a fine grain structure. Reflectance, both total and specular, decreases as alloy content increases; however, at a given alloy content the decrease will vary with the process. Magnesium has a very small effect on reflectance. The effect of alloying elements varies greatly with different brightening processes.

In a few applications, chemically or electrolytically brightened surfaces are protected by a clear organic coating. However, most surfaces brightened by these methods are anodized to produce a clear, colorless, protective oxide coating. For many decorative uses, the anodic coating is subsequently dyed.

**Applications** of chemical and electrolytic brightening processes are functional and decorative. They include jewelry, razor parts, automotive trim, fountain pens, searchlight reflectors, natural-finish or brightly colored giftware, architectural trim, household appliances, and thermal reflectors for components of space vehicles.

Chemical and electrolytic brightening may be used before or after buffing, as an intermediate operation, or to replace buffing either completely or partly. In processes where brightening is used to replace buffing completely, aluminum is dissolved at relatively rapid rates, and 25 μm (1 mil) or more of metal is removed. In processes where brightening is used as the final operation of the finishing sequence, metal is dissolved more slowly, and total metal removal usually ranges from about 3 to 13 $\mu$m (0.1 to 0.5 mil). Such procedures are used primarily on super-purity aluminum with up to 2% Mg and on high-purity aluminum.

**Chemical versus Electrolytic Brightening.** Because of improvements in chemical brightening processes, brightening results are equivalent to those obtained by the electrolytic processes, with the exception of reflector-type finishes on super-purity and high-purity aluminum.

Initial and operating costs for equipment are lower for chemical brightening than for electrolytic brightening, because electrical power and associated equipment are not required. Chemical brightening can be used on a variety of alloys.

Electrobrightening processes can have low chemical costs, because the chemicals used are less expensive and because baths operate well at high levels of dissolved aluminum. Other advantages of some baths used in electrobrightening are chemical stability of the solution and the ability of the bath to operate continuously for long periods at optimum efficiency with relatively simple control.

**Advantages over Buffing.** In performance and economy, chemical and electrolytic polishing processes offer the following advantages over buffing:

### Performance

- Contaminants are not introduced into the metal surface. Chemical or electrolytic processes remove trace amounts of contaminants initially present in the surface skin or embedded in the metal during prior operations. Surfaces brightened by these processes have better total and specular reflectance.
- Anodized and dyed surfaces that have been chemically or electrolytically brightened have a brilliance, clarity, and depth not attainable with buffed surfaces. Anodizing reduces the reflectance values of chemically or electrolytically brightened surfaces less than it reduces the reflectance of buffed surfaces.
- Chemical or electrolytic brightening of aluminum prior to electroplating provides better adhesion and continuity of the plated deposits. This improves corrosion resistance and serviceability.

### Economy

- Labor costs are lower than for buffing.
- Processes are readily adaptable to high-production parts that, because of their shape, cannot be finished on automatic buffing machines, and to parts that require buffing of a large percentage of the total surface area. Modification of automatic buffing machines to accommodate parts of different shapes may be more expensive than changes in racking for chemical or electrolytic brightening of these parts.
- Incorporation of processes into an automatic anodizing or electroplating line can result in economies in terms of space, equipment, and operations, and it may eliminate one or more cleaning or pickling operations in the pretreatment cycle. Deburring can sometimes be completely eliminated because of the high rate of metal removal on edges and corners.

## Chemical Etching

Chemical etching, using either alkaline or acid solutions, produces a matte finish on aluminum products. The process may be used for final finishing, but it is more often used as an intermediate step prior to lacquering, conversion coating, anodizing, or other finishing treatments. Chemical etching also is used extensively in conjunction with buffing or chemical brightening.

The advantages of etching with alkaline or acid solution prior to anodizing are that it removes oxide films and embedded surface contaminants that otherwise would discolor the anodic coating; roughens the surface slightly, to produce a less glossy anodized surface and to minimize slight differences in the mill finish of different production lots; and minimizes color-matching differences, which are more apparent with glossy or specular surfaces. Matte finishes are readily produced by chemical etching on the following wrought and cast aluminum alloys:

### Wrought alloys

- *Sheet and plate:* 1100, 2014, 2024, 3003, 5005, 5052, 5457, 6061, 7075
- *Extrusions:* 2014, 2024, 6061, 6063, 6463, 7075

### Casting alloys

- 242, 295, 514, A514, B514, F514, 518, 510

**Cleaning** prior to etching is recommended for attainment of the highest-quality finish. The need for prior cleaning, however, is determined by the amount and type of soil present on the surface of work being processed. In many instances, the etching solution serves as both a cleaner and a finishing medium.

**Post-Treatments.** Subsequent treatments, such as anodizing or chromate conversion coating, are required for protection against corrosion and against mechanical damage to the soft, easily marred surface. Clear lacquer may be applied to protect the matte finish produced by the etching process. Before being lacquered, the work must be cleaned of etching smut, thoroughly rinsed in clean cold water, and dried in warm air. Lacquering or painting should be done as soon as possible in a clean atmosphere.

## Alkaline Etching

Alkaline etching reduces or eliminates surface scratches, nicks, extrusion die lines, and other imperfections. However, some surface contaminants, if not removed before the work enters the etching solution, may accentuate these imperfections during etching. Oxides, rolled-in dirt, and many other surface contaminants can sometimes be eliminated by deoxidizing the work with a 2 to 4 wt% chromic acid/10 to 15 wt% sulfuric acid etchant at 60 to 70 °C (140 to 160 °F) prior to alkaline etching. This treatment removes stains resulting from heat treatment and other causes without removing much metal.

**Solution Makeup and Control.** A hot (50 to 80 °C, or 120 to 180 °F) solution of sodium hydroxide, potassium hydroxide, trisodium phosphate, or sodium carbonate is used for alkaline etching. The solution may contain more than one alkali. The use of uninhibited alkaline solutions (such as sodium hydroxide solutions) is not recommended for high-strength 7*xxx* and 2*xxx* aluminum alloys in certain artificially aged tempers because of the danger of intergranular attack.

Sequestrants, such as gluconic acid, sodium gluconate, the glucamines, and sorbitol, are added to alkaline solutions to prevent the formation of hydrated alumina. If permitted to form, this compound coats tank walls and heating coils with a difficult-to-remove scale. Sequestrants increase the life of the bath by preventing the formation of scale and by reducing the accumulation of sludge in the tank. They are added in concentrations of 1 to 5%.

Sodium hydroxide is the alkali most commonly used. Its reaction with aluminum is exothermic, produces hydrogen gas and sodium aluminate, and may increase the temperature of the bath, depending on the relationship between rate of metal removal and tank volume. Uniform finishes may thus be more difficult to obtain with large loads or rapid dissolution rates in small tanks, because the increase in temperature causes faster etching and more rapid depletion of the chemical constituents in the bath.

The concentration of sodium hydroxide in the etching solution usually ranges from 15 to 60 g/L (2 to 8 oz/gal). For most applications, a concentration of 30 to 45 g/L (4 to 6 oz/gal) is adequate. The choice of concentration is influenced by the finish desired, the operating temperature of the bath, the quality of water, the transfer time between the etchant and rinse, and the amount of drag-out.

Solution control is guided by regular titration of samples to determine free sodium hydroxide and sodium aluminate (aluminum). In a common method of operation, the concentration of free sodium hydroxide is not permitted to fall below

26 or 30 g/L (3.5 or 4 oz/gal) when a uniform, medium-deep etch is required. The normal working concentration of aluminum is about 30 g/L (4 oz/gal), or about 2.5 wt%. When the aluminum content of the solution approaches 55 to 75 g/L (7 to 10 oz/gal) and the free sodium hydroxide content about 40 g/L (5 oz/gal), the finish may become brighter and more reflective, indicating that the solution is nearly exhausted and should be partly or completely replaced.

Determination of specific gravity also is useful in solution control. A solution that has a specific gravity of 1.15 to 1.18 while maintaining a free sodium hydroxide content of 30 to 38 g/L (4 to 5 oz/gal) is considered to be approaching exhaustion. When this condition is reached, the finish being produced should be carefully observed for nonuniform etching and shiny appearance. As the aluminum content of the solution increases, the solution becomes more viscous, which may result in poor rinsing and greater drag-out. Special proprietary rinse additives are available that help to reduce the drag-out and streaking problems caused by high viscosity of the etchant.

Environmental regulations have led to the development of waste recovery technology for used caustic etching solutions. These baths can be operated without any chelating agents, such as sodium gluconate. Recovery processes depend on a controlled precipitation of dissolved aluminum with an accompanying regeneration of free sodium hydroxide. Closed-loop recovery systems of this type also reduce chemical costs and provide more uniform etching. Because of the high capital investment required, these recovery processes are most feasible for large installations.

**Equipment and Operating Procedures.** Tanks and heating coils for alkaline etching may be made of low-carbon steel. Ventilation is required for the etching tanks, because the mistlike fumes generated are a health hazard to personnel, and because alkali-contaminated air can corrode or etch unprotected aluminum in the work area, especially during periods of high humidity. Efficient venting should be provided to exhaust the fumes and spray generated during the transfer of the parts to the first rinse tank.

Sometimes a blanket of foam on the solution is used to reduce the amount of mist. Foam is usually created by the addition of surface-active, or wetting, agents to the bath. A layer of 25 or 50 mm (1 or 2 in.) of foam on the surface of the bath is usually adequate.

Work to be processed may be placed on appropriate racks or loaded in baskets for immersion in the etching solution. Dipping is the method most often used for etching, although in some instances spray etching has been used. Workpieces to be bulk-processed in baskets must be positioned to prevent the formation of air or gas pockets. For best results, it is desirable to agitate the solution by air or by movement of the work.

Racks and baskets are usually used when etching is followed by subsequent treatments, such as chemical brightening or conversion coating. Stainless steel is a suitable material for bulk-etching baskets, because it withstands the corrosive conditions of the various solutions used in the cleaning and finishing processes. Baskets for bulk etching cannot be used for anodizing because an electrical contact cannot be made. Bulk parts must be transferred to specially designed containers with a pressure contact prior to anodizing.

In general, bath temperatures range from 50 to 80 °C (120 to 180 °F). Specific operating temperature is determined by the final finish desired, the time cycle, available equipment, and the concentration of the bath constituents.

After etching, the work should be rinsed immediately. A high etching temperature and a long transfer time from the etching tank may cause dry-on of the etchant. This condition produces a nonuniform finish characterized by cloudy, pitted, or stained areas.

An air-agitated rinse is beneficial, as is a double rinse in cold water flowing in a countercurrent. The latter method uses smaller tanks, uses less water, and produces better rinsing than the use of warm water or only one rinse tank. Warm water may cause staining as a result of postetching, especially when only one rinse tank is used. The work should not remain too long in the first rinse tank following etching, because the tank usually contains sufficient residual sodium hydroxide to cause staining or a cloudy finish.

Spot welds, riveted areas, and folded edges may contain small cracks or crevices that entrap the alkaline solution. Rinsing may not remove the entrapped solution; the alkaline solution will subsequently bleed out and leave a residue of white powder after the finishing process is completed. Bleed-out also can occur after anodizing. Bleed-out is unattractive and can cause failure of organic films, such as lacquers and paints, applied for added protection.

**Dimensional Changes.** Etching in alkaline solutions can remove a considerable amount of metal. Figure 1 shows the dimensional changes that occurred when sheet materials of various aluminum-base alloys were etched for 1, 2, or 3 min in air-agitated sodium hydroxide solution (5 wt% NaOH) operated at 70 ± 5 °C (160 ± 5 °F). When clad materials are being treated, the etching cycle must be carefully controlled to prevent loss of the cladding.

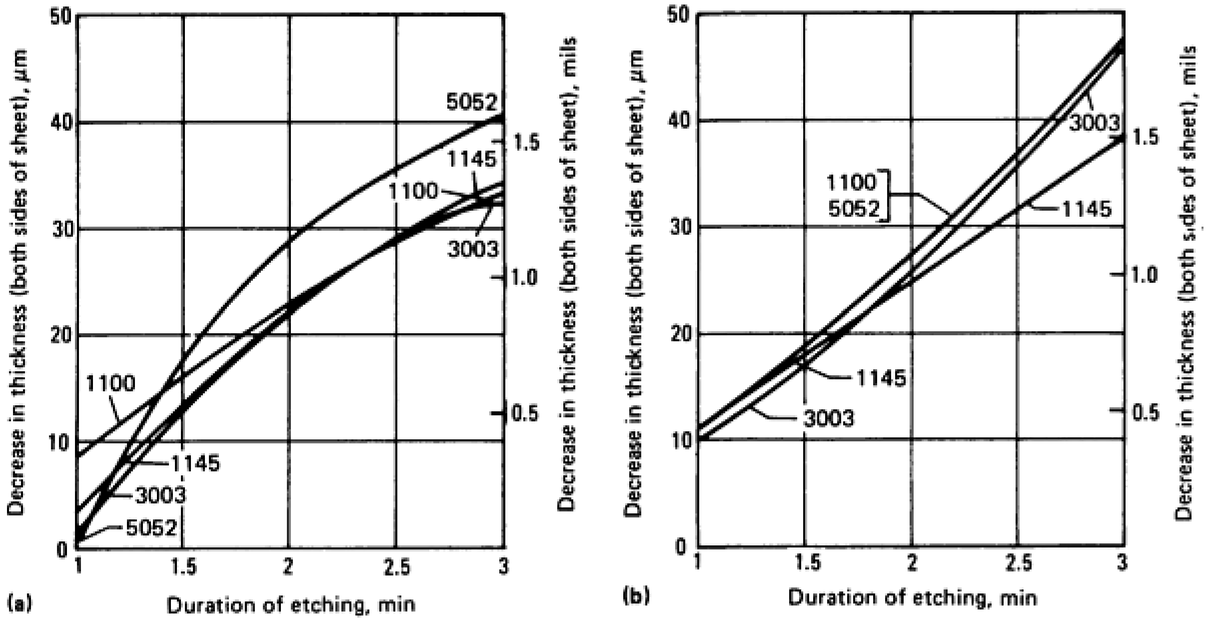


**Fig. 1 Effect of time on the amount of metal removed from aluminum alloys during alkaline etching. (a) By micrometer measurement. (b) Calculated from loss in weight. Both solutions contain 5 wt% NaOH at 70 ± 5 °C (160 ± 5 °F).**

**Desmutting.** During the cleaning and etching operation, smut (a gray-to-black residual film) is deposited on the surface of the work. This deposit usually consists of iron, silicon, copper, or other alloying constituents (in an aluminum-base material) that are insoluble in sodium hydroxide. When etching is to be followed by anodizing, the smut can sometimes be removed by the anodizing solution (current flowing); however, this practice generally cannot be controlled to produce a finish of uniform appearance. Copper and iron smuts dissolved in the anodizing electrolyte can accumulate until they make necessary premature disposal of the electrolyte. The recommended procedure is to remove the smut in a solution prepared specifically for this purpose.

A nitric acid solution (10 to 15 vol% $HNO_3$ or more) will remove smut. A solution containing 0.5 to 1 wt% chromic acid plus 4 to 6 wt% sodium bisulfate is similarly effective. Solutions of proprietary compounds that are nonchromated and hence nonpolluting are also used. Fluorides are usually added to solutions to aid the removal of smut from high-silicon aluminum alloys and aluminum die castings. Good results have been obtained with a room-temperature solution of 3 parts nitric acid and 1 part hydrofluoric acid.

The following example describes the solution to a problem encountered in the desmutting of die castings of a high-silicon alloy that was etched in a sodium hydroxide solution.

Because of the high silicon content of alloy 380.0 (7.5 to 9.5% Si), desmutting to obtain an attractive, uniform finish on the die castings was difficult. A chromate-type desmutting solution had been used after etching in sodium hydroxide, but it had not been entirely effective. The addition of an acid fluoride etch provided the desired finish. The sequence of operations used was as follows:

1. Soak in nonetching aluminum cleaner at 60 to 65 °C (140 to 150 °F) for 5 to 10 min.
2. Rinse in cold water.
3. Etch for 60 to 90 s in a sodium hydroxide etching solution at 60 to 65 °C (140 to 150 °F).
4. Rinse in cold water.

5. Remove part of the smut by immersing in an air-agitated, chromate-type desmutting solution at room temperature.
6. Rinse in cold water.
7. Immerse in a room-temperature acid etching solution containing fluoride and nitric acid for 30 to 60 s to remove the remaining smut.
8. Rinse in cold water.

After being prepared in this manner, the castings were chromate-conversion coated and dipped in lacquer.

Proprietary chromic-sulfuric acid desmutting solutions generally require a tank made of type 302 or 304 stainless steel, although some solutions may require type 316 or 347. They are usually operated at room temperature and normally do not require ventilation. This is an advantage over nitric acid solutions. A disadvantage of some proprietary solutions is the need for treatment of the wastes to remove the harmful effects of chromium salts before the wastes are discharged from the plant. EPA regulations and local ordinances regulate the disposition of waste solutions.

Hexavalent chromium compounds and nitric acid are especially undesirable from an EPA environmental viewpoint. As a result, these traditionally effective oxidizing agents are frequently replaced with such compounds as ferric salts, persulfates, and peroxides. (Additional information is available in the article "Chromium Elimination" in this Volume.)

## Acid Etching

Acid solutions are commonly used for finished castings, especially those made of high-silicon alloys. Acid etching can be done without heavy smut problems, particularly on aluminum die castings. Hydrochloric, hydrofluoric, nitric, phosphoric, chromic, and sulfuric acids are used in acid etching.

Combinations of these acids and mixtures of acids and salts are often used for specific applications. Sulfuric-chromic acid solutions remove heat-treating stains with little etching of the metal; dilute hydrofluoric-nitric acid solutions produce bright, slightly matte-textured surfaces; and hydrochloric acid containing sodium chloride and ferric chloride is used for deep etching of designs. Additions of cobalt and nickel salts to the hydrochloric acid solution accelerate etching, but they do not affect the ability of the solution to produce a sufficiently smooth surface. Alloys containing silicon, such as sand castings, should be acid-etched with a 2 to 5% aqueous solution of hydrofluoric acid prior to anodizing.

Compositions and operating conditions for three acid etching solutions are:

| | |
|---|---|
| **Solution 1** | |
| Nitric acid | 3 parts by vol |
| Hydrofluoric acid | 1 part by vol |
| Temperature of bath | 20 °C (70 °F) max |
| Immersion time | 15 s to 1 min |
| **Solution 2** | |

| | |
|---|---|
| Chromic acid | 80 g (10.5 oz) |
| Sulfuric acid | 675 mL (22.4 fluid oz) |
| Water, to make | 4 L (1 gal) |
| Temperature of bath | 60-70 °C (140-160 °F) |
| Immersion time | 30 s to 2 min |
| **Solution 3** | |
| Chromic acid | 175 g (23.5 oz) |
| Sulfuric acid | 75 mL (2.5 fluid oz) |
| Water, to make | 4 L (1 gal) |
| Temperature of bath | 60-70 °C (140-160 °F) |
| Immersion time | 30 s to 2 min |

Figure 2 is a flow chart of the operations used in acid etching.

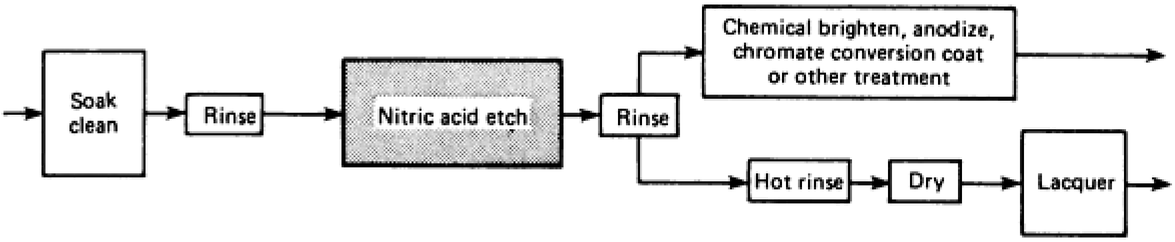


**Fig. 2 Operations used in etching of aluminum and aluminum alloys**

Fumes from most acid etching solutions are corrosive, and the mist or spray carried up by the gases generated constitutes a health hazard. Ventilation is required, even for solutions operated at room temperature. Tanks are made of stainless steel or plastic, or are plastic lined; plastic or plastic-lined tanks are used with solutions containing hydrochloric or hydrofluoric acid. Cooling coils may be required, because etching generates heat. Heating coils are required for solutions operated at elevated temperatures.

Acid etching is often used alone, but sometimes it may either precede or follow alkaline etching. It is usually used before alkaline etching when oxides are to be removed and after alkaline etching when smut removal is a problem. Acid etching solutions, especially those containing fluorides, are excellent smut and scale removers. After acid etching and thorough rinsing, the work is ready for further processing (Fig. 2).

## Anodizing

The basic reaction in all anodizing processes is the conversion of the aluminum surface to aluminum oxide while the part is the anode in an electrolytic cell. Aluminum surfaces are anodized for a number of reasons, including to:

- Increase corrosion resistance
- Increase paint adhesion
- Prepare the surface for subsequent plating
- Improve adhesive bonding
- Improve decorative appearance
- Provide electrical insulation
- Permit application of photographic and lithographic emulsions
- Increase emissivity
- Increase abrasion resistance
- Permit detection of surface flaws

The three principal types of anodizing processes are:

- *Chromic anodizing,* in which the agent is chromic acid
- *Sulfuric anodizing,* in which the active agent is sulfuric acid
- *Hard anodizing,* in which the agent is sulfuric acid, alone or in combination with additives

Other processes, used less frequently or for special purposes, employ sulfuric-oxalic, phosphoric, oxalic, boric, sulfosalicylic, or sulfophthalic acid solutions. Except for those produced by hard anodizing processes, most anodic coatings range in thickness from 5 to 18 $\mu$m (0.2 to 0.7 mil). The succession of operations typically employed in anodizing is illustrated in Fig. 3.

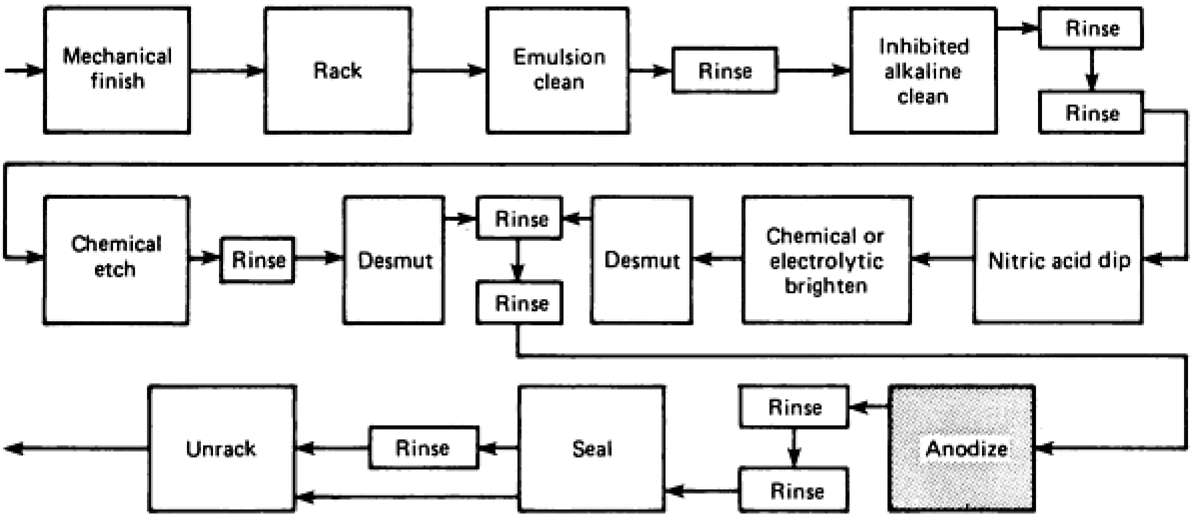


**Fig. 3 Typical sequence of operations for anodizing aluminum alloys**

The three major anodizing processes, as well as anodizing equipment, applications, troubleshooting, and coating evaluation, are described in detail in the article "Anodizing" in this Volume.

## Chemical Conversion Coating

Chemical conversion coatings are adherent surface layers of low-solubility oxide, phosphate, or chromate compounds produced by the reaction of suitable reagents with the metallic surface. These coatings affect the appearance, electrochemical potential, electrical resistivity, surface hardness, absorption, and other surface properties of the material. They differ from anodic coatings in that conversion coatings are formed by a chemical oxidation-reduction reaction at the surface of the aluminum, whereas anodic coatings are formed by an electrochemical reaction. The reaction that takes place in chemical conversion coating involves the removal of 0.3 to 2.5 μm (0.01 to 0.1 mil) of the material being treated.

Conversion coatings are excellent for:

- Corrosion retardation under supplementary organic finishes or films of oil or wax
- Improved adhesion for organic finishes
- Mild wear resistance
- Enhanced drawing or forming characteristics
- Corrosion retardation without materially changing electrical resistivity
- Decorative purposes, when colored or dyed

Conversion coatings are used interchangeably with anodic coatings in organic finishing schedules. One use of conversion coating is as a spot treatment for the repair of damaged areas in anodic coatings. Because of their low strength, conversion coatings should not be used on surfaces to which adhesives will be applied. Anodic coatings are stronger than conversion coatings for adhesive bonding applications.

The simplicity of the basic process, together with the fact that solutions may be applied by immersion, spraying, brushing, wiping, or any other wetting method, makes conversion coating convenient for production operations. Some applications using chemical conversion coatings on various aluminum alloys are given in Table 16. In most installations, conversion coating offers a cost advantage over electrolytic methods. Moreover, unlike some anodic coatings, chemical conversion coatings do not lower the fatigue resistance of the metal treated.

**Table 16 Applications of aluminum using chemical conversion coatings**

| **Application** | **Aluminum alloy** | **Subsequent coating** |
|---|---|---|
| **Oxide conversion coatings** | | |
| Baking pans[(a)] | 1100, 3003, 3004, 5005, 5052 | Silicone resin |
| **Phosphate conversion coatings** | | |
| Screen cloth | 5056 | Clear varnish |
| Storm doors | 6063 | Acrylic paint[(b)] |
| Cans | 3004 | Sanitary lacquer |
| Fencing | 6061 | None applied |
| **Chromate conversion coatings** | | |

| | | |
|---|---|---|
| Aircraft fuselage skins | 7075 clad with 7072 | Zinc chromate primer |
| Electronic chassis | 6061-T4 | None applied |
| Cast missile bulkhead | 356-T6 | None applied |
| Screen | 5056 clad with 6253 | Clear varnish |
| Extruded doubler | 6061-T6 | Clear lacquer |

(a) Baking pans of these alloys may alternatively be chromate conversion coated prior to the application of silicone resin.

(b) Thermosetting

**Procedure.** The sequence of operations for applying a satisfactory conversion coating to aluminum-base materials is as follows:

- Removal of organic contaminants
- Removal of oxide or corrosion products
- Conditioning of the clean surface to make it susceptible to coating
- Conversion coating
- Rinsing
- Acidulated rinsing (recommended if supplementary coating is to be applied)
- Drying
- Application of a supplementary coating when required

Surface preparation entails the same procedures as are used in preparation for anodizing. However, the cleaning procedure for preparing aluminum for conversion coating is much more critical than for anodizing. After cleaning, removal of the natural oxide film is accomplished in any of the standard aqueous solutions, such as chromate-sulfate, chromate, or phosphate.

Pretreatment immediately prior to the coating operation is required for the development of extremely uniform conversion coatings. Either acid or alkaline solutions are used. Subsequent to the above operations, the work is subjected to the conversion coating solution. The addition of a wetting agent, such as sodium alkyl aryl sulfonate, to the solution helps to produce a uniform and continuous coating. After coating, the work is thoroughly rinsed and dried. The final rinse is usually hot (60 to 80 °C, or 140 to 180 °F) to aid drying. Drying is important in order to prevent staining. Drying at temperatures higher than 65 °C (150 °F) usually dehydrates the coatings and thus increases hardness and abrasion resistance.

Supplementary coatings of oil, wax, paint, or other hard organic coatings frequently are applied. If the conversion coating is intended to improve subsequent forming or drawing, the final supplementary coating may be soap or a similar dry-film lubricant.

**Oxide Coating Processes.** The modified Bauer-Vogel (MBV), Erftwerk (EW), and Alrok processes are the principal methods for applying oxide-type conversion coatings. Nominal compositions of the solutions used and typical operating conditions are given in Table 17. The MBV process is used on pure aluminum as well as on aluminum-magnesium, aluminum-manganese, and aluminum-silicon alloys. The coating produced varies from a lustrous light gray to a dark gray-black color. The EW process is used for alloys containing copper. The film produced is usually very light gray. The

Alrok process is for general-purpose use with all alloys, and it is often the final treatment for aluminum products. Coatings vary in color from gray to green and are sealed in a hot dichromate solution.

**Table 17 Process conditions for oxide conversion coating of aluminum**

| **Process** | **Bath composition** | **Amount** | | **Temperature** | | **Duration, min** | **Uses** |
|---|---|---|---|---|---|---|---|
| | | **g/L** | **oz/gal** | **°C** | **°F** | | |
| I MBV | Sodium chromate | 15 | 1.7 | 96 | 205 | 5-10 or 20-30 | Corrosion protection or foundation for varnishes or lacquers |
| | Sodium carbonate | 50 | 5.7 | | | | |
| II MBV | Sodium chromate | 15 | 1.7 | 65 | 150 | 15-30 | In situ treatment of large objects with paint brush or spray. When 8 g/L (0.9 oz/gal) sodium hydroxide is added, MBV oxidation may be carried out at 35 °C (95 °F) for 30 min |
| | Sodium chromate | 50 | 5.7 | | | | |
| | Sodium hydroxide | 4 | 0.5 | | | | |
| EW | Sodium carbonate | 56 | 6.4 | 88-100 | 190-212 | 8-10 | For copper-containing alloys |
| | Sodium chromate | 19 | 2.2 | | | | |
| | Sodium silicate | 0.75-4.5 | 0.09-0.5 | | | | |
| Alrok | Sodium carbonate | 20 | 2.3 | 88-100 | 190-212 | 20 | Final treatment for aluminum products |
| | Potassium dichromate | 5 | 0.6 | | | | |

**Phosphate Coating Process.** The range of operating conditions and a formula for a standard solution for phosphate coating are given below:

| **Specific formulations** |
|---|

| | |
|---|---|
| Ammonium dihydrogen phosphate ($NH_4H_2PO_4$) | 61.7% |
| Ammonium bifluoride ($NH_4HF_2$) | 22.9% |
| Potassium dichromate ($Kr_2Cr_2O_7$) | 15.4% |
| Operating temperature | 45-50 °C (110-120 °F) |
| Treatment time | 1-5 min |
| **Desired operating range** | |
| Phosphate ion | 20-100 g/L (2.6-13.2 oz/gal) |
| Fluoride ion | 2-6 g/L (0.26-0.80 oz/gal) |
| Dichromate ion | 6-20 g/L (0.80-2.6 oz/gal) |
| Operating temperature | 18-50 °C (65-120 °F) |
| Treatment time | 1.5-5 min |

Each liter (gallon) of solution contains 75 to 150 g (10 to 20 oz) of a mixture consisting of the above formulations (U.S. Patent 2,494,910, 1950).

Phosphate coatings vary in color from light bluish-green to olive green, depending on the composition of the aluminum-base material and the operating conditions of the bath. The phosphate-chromate conversion coatings are used extensively on aluminum parts or assemblies to provide galvanic protection from components of different kinds of materials, such as bushings or inserts made of steel.

**Chromate Coating Process.** Solution compositions and operating conditions for two chromate conversion coating processes are given in Table 18. Chromate coatings vary from clear and iridescent to light yellow or brown, depending on the composition of the aluminum-base material and the thickness of the film. Chromate coatings are used when maximum resistance to corrosion is desired.

**Table 18 Process conditions for chromate conversion coating of aluminum**

| Process | Solution composition | Amount | | pH | Temperature | | Treatment time |
|---|---|---|---|---|---|---|---|
| | | g/L | oz/gal | | °C | °F | |
| Process A(a) | $CrO_3$ | 6(b) | 0.80(b) | 1.2-2.2 | 16-55 | 60-130 | 5 s-8 min |
| | $NH_4HF_2$ | 3 | 0.40 | | | | |

|  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|
|  | $SnCl_4$ | 4 | 0.6 |  |  |  |  |
| Process B(c) | $Na_2Cr_2O_7 \cdot 2H_2O$ | 7(b) | 1(b) | 1.2-2.2 | 16-55 | 60-130 | 5 s-8 min |
|  | NaF | 1 | 0.1 |  |  |  |  |
|  | $K_3Fe(CN)_6$ | 5 | 0.7 |  |  |  |  |
|  | $HNO_3$ (48° Bé) | (d) | (d) |  |  |  |  |
| Process C(e) | $H_3PO_4$ | 64 | 8.5 | 1.2-2.2 | 40-80 | 105-175 | 1-10 min |
|  | NaF | 5 | 0.6 |  |  |  |  |
|  | $CrO_3$ | 10 | 1.3 |  |  |  |  |

(a) U.S. Patents 2,507,959 (1950) and 2,851,385 (1958).

(b) Desired range of hexavalent chromium ion, 1 to 7 g/L (0.13 to 0.90 oz/gal).

(c) U.S. Patent 2,796,370 (1957).

(d) 3 mL (0.1 fluid oz).

(e) Process for Alodine, Alochrome, and Bonderite

Chromate coatings exhibit low electrical resistivity. At a contact pressure of 1380 kPa (200 psi), in a direct-current circuit, the resistivity of a normal chromate film varies from 0.30 to 3.0 $\mu\Omega/mm^2$ (200 to 2000 $\mu\Omega/in.^2$). This resistivity is low enough so that a chromate-coated article can be used as an electrical ground. The conductivity of the films at radio frequencies is extremely high. This permits the use of a chromate film on electrical shields and wave guides. Thus, chromate conversion coating is widely used for treatment of aluminum articles for the electronics industry.

**Processing equipment** for conversion coating solutions must be made from acid-resistant materials. Tanks may be made of type 316 stainless steel or of low-carbon steel if lined with polyvinyl chloride or another suitably protective material. Tanks for solutions that do not contain fluorides can be constructed of acid-resistant brick or chemical stoneware. Racks can be made of low-carbon steel but must be coated with an acid-resistant compound. Heating coils or electrical immersion heaters should be made of stainless steel or stainless-clad material.

Some conversion coating solutions cause a sludge to form in the bottom of the tank. To prevent contact between the sludge and the workpieces, the tank may be equipped with a false bottom through which sludge can fall.

Adequate ventilation must be provided to remove vapors. The inhalation of fluoride vapors is dangerous. Solutions should not contact the skin; if they do, the affected area should be washed immediately with running water and then be treated by a physician. Respirators, goggles, and gloves should be worn when handling all chemicals used to make up solutions. Brushes used to apply solutions should have natural bristles; synthetic bristles are attacked by solutions.

**Control of Solution.** Most users of conversion coating solutions purchase prepared formulations for makeup and solution adjustment. In general, the solutions require control of both pH and the concentration of the critical elements. Direct measurement of pH is made with a glass-cell electric pH meter. The percentage concentration of active ion is obtained by direct titration with a suitable base.

Solution control becomes more critical as the size of the bath decreases with respect to the amount of work treated. Experienced operators of a conversion coating process can detect changes in the composition of the solution by observing the color and appearance of the treated work. A skilled operator often can control the bath by this method alone.

During use, coating solutions are depleted by drag-in, drag-out, and consumption of the basic chemicals. In one plant, drag-in of alkaline cleaner into the conversion coating bath adversely affected the appearance of the conversion coating. Details of this problem and the method adopted for correcting it are given in the following example.

Aluminum screen cloth made from wires of alloy 5056 clad with alloy 6253 had a rejection rate as high as 3% because of the presence of sparklers on the product after chemical conversion coating. Sparklers, also known as shiners, are areas that have higher metallic reflectance than the rest of the conversion-coated surface; they are merely an appearance defect and do not affect the adherence of organic coatings. The following processing cycle was being used:

1. Alkaline cleaning for 1 min in an inhibited solution at 70 °C (160 °F)
2. Rinsing for 30 s in overflowing cold water
3. Conversion coating for $2\frac{1}{2}$ min in a phosphate-chromate solution at 40 to 45 °C (100 to 115 °F)
4. Rinsing for 30 s in overflowing cold water
5. Second rinsing for 30 s in overflowing cold water
6. Drying
7. Application of a clear varnish (baked at 135 °C, or 275 °F for $1\frac{1}{2}$ to 2 min) or of a gray pigmented paint. (For material to be painted, conversion coating required only $1\frac{1}{2}$ min.)

The coating defects were found to be caused by contamination (and neutralization) of the acid conversion coating solution by drag-in from the alkaline cleaner. The use of a rotating beater to shake droplets of cleaning solution out of the screen openings had reduced drag-out from that bath, but it had not eliminated it.

To prevent neutralization of the acid conversion coating solution by contamination with alkali from step 1, the slightly acid overflow from the rinse in step 4 was piped back into the rinse tank in step 2, thus keeping it slightly acid. Rejects were eliminated. This procedure also reduced the amount of overflow rinse water needed to operate the line.

**Control of Coating Quality.** A properly applied coating should be uniform in color and luster and should show no evidence of a loose or powdery surface. Poor luster or powder surfaces are caused by low pH, improper cleaning and rinsing, excessive treatment temperature or treatment time, a contaminated bath, or insufficient agitation. Light and barely visible coatings are caused by high pH, low operating temperatures, insufficient treatment times, or high ion concentrations. Usually, the quality of a conversion coating is established on the basis of its appearance, corrosion resistance, hardness, and adherence. These qualities may be determined by the ASTM test methods described in the standards listed below:

### Corrosion resistance

- Salt spray: B 117
- Copper-accelerated acetic acid salt spray (fog): B 368
- Evaluation of painted or coated specimens subjected to corrosive exposure: D 1654

### Resistance to blistering

- Evaluation of blistering of paints: D 714

### Adherence

- Elongation of attached organic coatings with conical mandrel apparatus: D 522

Hexavalent chromium compounds are especially effective components of solutions that form conversion coatings on aluminum. However, environmental regulations often make the handling of chromate-containing rinses a high-cost operation. Two types of technology address this problem. One is a dried-in-place chromate coating system, which eliminates the need for subsequent rinsing. The second involves the use of chromium-free treatments that form oxide films containing selected metal ions. The use of either of these processes, when possible, eliminates the need for expensive chrome destruction.

## Electroplating

Aluminum-base materials are more difficult to electroplate than the common heavier metals because aluminum has a high affinity for oxygen, which results in a rapidly formed, impervious oxide film, and because most metals used in electroplating are cathodic to aluminum, so that voids in the coating lead to localized galvanic corrosion. Following are comparisons between the electrolytic potentials of several common metals and those of pure aluminum:

| **Metal** | **Potential, mV[(a)]** |
|---|---|
| Magnesium | -850 |
| Zinc | -350 |
| Cadmium | -20 to 0 |
| Aluminum (pure) | 0 |
| Aluminum-magnesium alloys | +100 |
| Aluminum-copper alloys | +150 |
| Iron, low-carbon steel | +50 to 150 |
| Tin | +300 |
| Brass | +500 |
| Nickel | +500 |

| | |
|---|---|
| Copper | +550 |
| Silver | +700 |
| Stainless steel | +400 to 700 |
| Gold | +950 |

Note: Metals above aluminum in this list will protect it; those below cause aluminum to corrode preferentially. Cathode and anode polarization, however, can cause a reversal of these relationships.

Source: *Metal Finishing,* Nov 1956

(a) In a 6% sodium chloride solution.

Electrodeposits of chromium, nickel, cadmium, copper, tin, zinc, gold, or silver are used for various decorative and functional applications. For example, automotive aluminum bumpers get a zincate treatment, copper strike, and a plating of copper, nickel, and chromium. A copper strike coated with cadmium and chromate or by flowed tin enables the soft soldering of electrical terminals to an aluminum chassis. Brass enhances the bonding of rubber to aluminum. Silver, gold, and rhodium provide specific electrical and electronic surface properties. Examples of applications of plated aluminum with typical finishing sequences are given in Table 19.

**Table 19 Applications using electroplated coatings on aluminum products**

| **Product** | **Form** | **Preplating treatment** | **Electroplating system** | **Thickness** | | **Reason for plating** |
|---|---|---|---|---|---|---|
| | | | | **µm** | **mils** | |
| **Automotive applications** | | | | | | |
| Bearings | Sheet | None | Pb-Sn-Cu alloy | 6-32 | 0.25-1.25 | Prevent seizing |
| Bumper guards | Castings | Buff and zincate | Cu + Ni + Cr | 2.5 + 51 + 0.8 | 0.1 + 2 + 0.03 | Appearance; corrosion resistance |
| Lamp brackets; steering-column caps | Die castings | Buff and zincate | Cu + Ni + Cr | 0.8 + 20 + 1.3 | 0.03 + 0.8 + 0.05 | Appearance; corrosion resistance |
| Tire molds | Castings | None | Hard Cr | 51 | 2 | Appearance; corrosion resistance |
| **Aircraft applications** | | | | | | |
| Hydraulic parts; landing gears; small engine pistons | Forgings | Machine and zincate | Cu flash + Cu + hard Cr | 2.5 + 25 + 76 | 0.1 + 1 + 3 | Wear resistance |

| | | | | | | |
|---|---|---|---|---|---|---|
| Propellers | Forgings | Conductive rubber coating | Ni | 203 | 8 | Resistance to corrosion and erosion |
| Shell | Extrusion | Double zincate | Cu flash + Cd(a) | 8-13(a) | 0.3-0.5(a) | Dissimilar-metal protection |
| **Electrical and electronics applications** | | | | | | |
| Busbars; switchgears | Extrusions | Zincate | Cu flash + Cu + Ag(b) | 8 + 5(b) | 0.3 + 0.2(b) | Nonoxidized surface; solderability; corrosion resistance |
| Intermediate-frequency housings | Die castings | Zincate | Cu flash + Cu + Ag + Au(c) | 13 + 13 + 0.6(c) | 0.5 + 0.5 + 0.025(c) | Surface conductivity; solderability; corrosion resistance |
| Microwave fittings | Die castings | Zincate | Cu flash + Cu + Ag + Rh | 0.25 + 13 + 0.5 | 0.01 + 0.5 + 0.02 | Smooth, nonoxidized interior; corrosion resistance of exterior |
| Terminal plates | Sheet | Zincate | Cu flash | . . . | . . . | Nonoxidized surface; solderability; corrosion resistance |
| **General hardware** | | | | | | |
| Screws; nuts; bolts | Castings | Buff and zincate | Cd (on threads) | 13; 0.5 on threads | 0.5; 0.2 on threads | Corrosion resistance |
| Die cast spray guns and compressors | . . . | Buff and zincate | Hard Cr | 51 | 2 | Appearance |
| Die cast window and door hardware | . . . | Barrel burnish and zincate | Brass(d) | 8(d) | 0.3(d) | Appearance; low cost |
| **Household appliances** | | | | | | |
| Coffee maker | Sheet | Buff and zincate | Cr | 5 | 0.2 | Appearance; cleanness; resistance to food contamination |
| Refrigerator handles; salad makers; cream dispensers | Die castings | Buff and zincate | Cu + Ni + Cr | 2.5 + 13 + 0.8 | 0.1 + 0.5 + 0.03 | Appearance; cleanness; resistance to food contamination |
| **Personal products** | | | | | | |
| Compacts; fountain pens | Sheet | Buff and | Cu flash + brass | 5 | 0.2 | Appearance; low cost |

| | | | | | | |
|---|---|---|---|---|---|---|
| | | zincate | | | | |
| Hearing aids | Sheet | Zincate | Cu flash + Ni + Rh | 19 + 0.25 | 0.75 + 0.01 | Nonoxidizing surface; low cost |
| Jewelry | Sheet | Buff and zincate | Brass + Au | 8 + 0.25 | 0.3 + 0.01 | Appearance; low cost |

(a) Chromate coating applied after cadmium plating.

(b) Soldering operation follows silver plating.

(c) Baked at 200 °C (400 °F) after copper plating and after silver plating. Soldering operation follows gold plating.

(d) Brass plated in barrel or automatic equipment

**Effect of Substrate Characteristics on Plating Results.** Each aluminum alloy, according to its metallurgical structure, behaves differently from others during electroplating. Alloying elements may be in solid solution in the aluminum, or they may be present in discrete particles or as intermetallic compounds. These microconstituents have different chemical or electrochemical reactivities, and their surfaces do not respond uniformly to treatment. Variations in response also occur between different lots or product forms of the same alloy.

**Surface Preparation Methods.** The three established methods for surface preparation prior to electroplating are surface roughening, anodizing, and immersion coating in zinc or tin solutions.

Surface roughening, which is accomplished either by mechanical abrasion or by chemical etching, assists in mechanically bonding the electrodeposits to the aluminum surface. Surface roughening is sometimes used in preparation for the application of hard chromium to aluminum engine parts, such as pistons. A water blast of fine quartz flour may be used to remove surface oxides and to abrade the surface. The adherent wet film protects the aluminum surface from further oxidation before plating. The quartz film is dislodged by the evolution of hydrogen that occurs during plating. Chemical etching produces undercut pits that provide keying action for the electrodeposited metal. In general, mechanical bonding of electrodeposits is not reliable, particularly for applications involving temperature variations. Therefore, preparation by surface roughening is not recommended.

Anodizing is sometimes used as a method of surface preparation prior to electroplating. However, the adherence of the subsequent electrodeposit is limited; plated deposits over anodic films are highly sensitive to surface discontinuities, making the time, temperature, and current density of the anodizing process critical. Phosphoric acid anodizing has been used for the aluminum alloys listed in Table 20; the sequence of operations is:

1. Vapor degreasing or solvent cleaning
2. Mild alkaline cleaning
3. Rinsing
4. Etching for 1 to 3 min in a solution containing sodium carbonate (23 g/L, or 3 oz/gal) and sodium phosphate (23 g/L, or 3 oz/gal), at 65 °C (150 °F)
5. Rinsing
6. Dipping in nitric acid solution (50% $HNO_3$ by volume) at room temperature
7. Rinsing
8. Phosphoric acid anodize according to the conditions given in Table 20; the anodic coating should not be sealed.
9. Rinsing

10. Electroplating in a copper pyrophosphate or nickel sulfamate bath

### Table 20 Conditions for anodizing aluminum alloys prior to electroplating

Electrolyte solution of aqueous $H_3PO_4$

| **Alloy**[(a)] | **Specific gravity** | **Temperature** | | **Voltage** | **Time, min** |
|---|---|---|---|---|---|
| | | **°C** | **°F** | | |
| 1100 | 1.300 | 30 | 87 | 22 | 5 |
| 3003 | 1.300 | 29 | 85 | 22 | 5 |
| 5052 | 1.300 | 29 | 85 | 22 | 10 |
| 6061 | 1.300 | 29 | 85 | 22 | 7 |

(a) With special care, phosphoric acid anodizing may be used also for aluminum-copper or aluminum-silicon alloys.

Immersion coating in a zincate solution is a traditional method of preparing aluminum surfaces for electroplating. It is simple and low in cost, but it is also critical with respect to surface pretreatment, rinsing, and the strike sequence used. The principle of zincating is one of chemical replacement, whereby aluminum ions replace zinc ions in an aqueous solution of zinc salts. Thus, a thin, adherent film of metallic zinc is deposited on the aluminum surface. Adhesion of the zinc film depends almost entirely on the metallurgical bond between the zinc and the aluminum. The quality and adhesion of subsequent electrodeposits depend on obtaining a thin, adherent, and continuous zinc film. The electrolytic Alstan strike is coming into general use as a more dependable method than the zincate process for obtaining good adhesion. It is followed by a bronze strike.

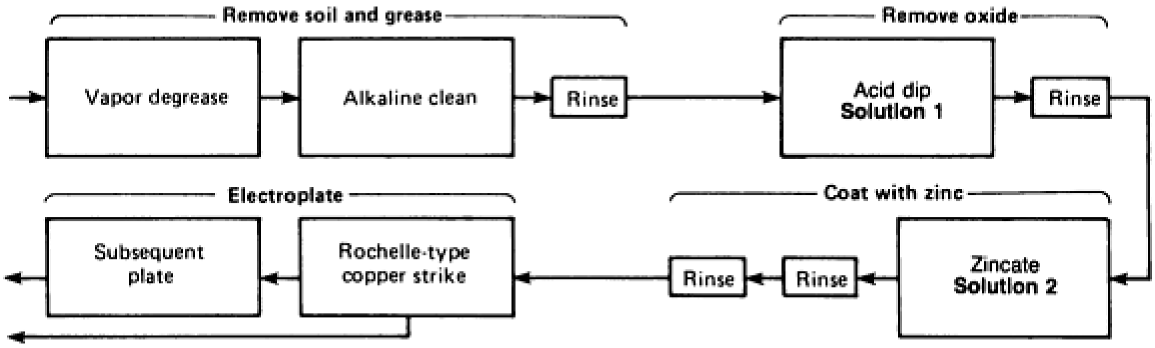
Another immersion process is based on the deposition of tin from a stannate solution. This offers improved corrosion resistance because of the more favorable electrolytic potential of tin versus zinc in chloride solutions.

**Immersion Procedures.** To obtain consistently good results with zinc or tin immersion procedures, it is essential that cleaning and conditioning treatments produce a surface of uniform activity for deposition. Vapor degreasing or solvent cleaning followed by alkaline cleaning is used for removing oil, grease, and other soils. The alkaline cleaner may be a mild etching solution of water containing 23 g/L (3 oz/gal) each of sodium carbonate and sodium phosphate. The solution temperature should range from 60 to 80 °C (140 to 180 °F), and the material should be immersed for 1 to 3 min and then be thoroughly rinsed. After cleaning, the material is further treated to remove the original oxide film as well as any microconstituents that may interfere with the formation of a continuous film or that may react with the subsequent plating solutions.

Castings present special problems, because their surfaces are more porous than those of wrought products. Solutions entrapped in pores are released during subsequent processing, resulting in unplated areas, staining, or poor adhesion of the electrodeposit. Sometimes the trapped solutions become evident much later, during storage or further processing (such as heating for soldering). Furthermore, even if pores are free of solution, the deposit may not bridge them, thus creating a point of attack for corrosion of the base metal. This is of particular significance in the electroplating of aluminum castings: The electrodeposited metal is electrolytically dissimilar to aluminum, and thus every opening in a casting surface will be a source of corrosion. To circumvent these problems, it is essential when preparing cast aluminum surfaces for electroplating that all processing steps be carefully controlled to avoid surfaces with excessive porosity.

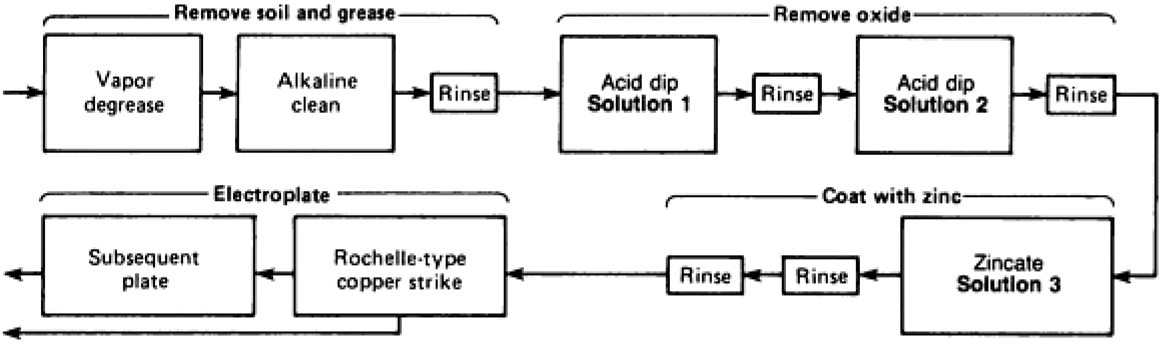
In zincating, the procedures used for removal of the original oxide film and for application of a zinc film depend to a considerable degree on the aluminum alloy. Several methods are available for accomplishing this surface conditioning, and some alloys can be conditioned by more than one procedure. In such instances, the order of preference follows the order of discussion of these procedures in the following paragraph.

Wrought alloys without interfering microconstituents and casting alloys containing high silicon are prepared for electroplating according to the procedure shown by the flow chart in Fig. 4. The flow chart in Fig. 5 represents the procedure for alloys that contain interfering microconstituents; this procedure is suitable for all wrought alloys, most casting alloys, and especially aluminum-magnesium alloys. Figure 6 indicates the procedure for treating most casting alloys, wrought alloys that contain less than approximately 3% Mg, and alloys of unknown composition.



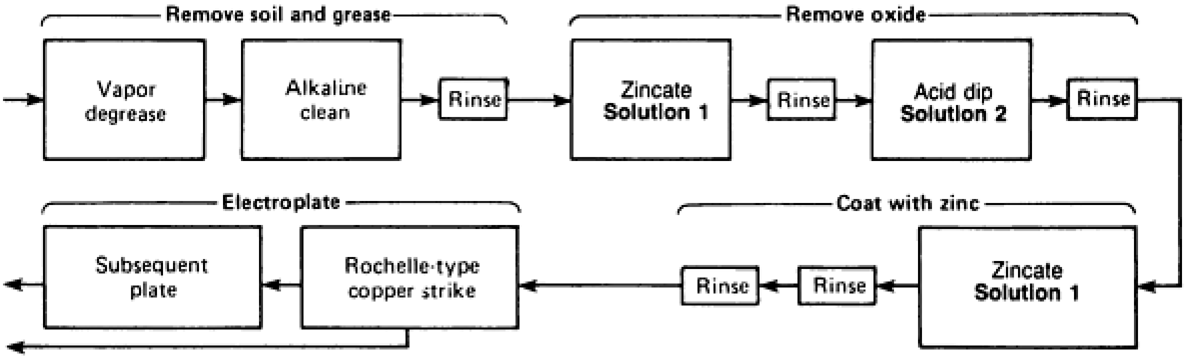
| Solution No. | Type of solution | Composition | Amount | Operating temperature | | Cycle time, s |
|---|---|---|---|---|---|---|
| | | | | °C | °F | |
| **Alloys 1100 and 3003** | | | | | | |
| 1 | Acid dip | $HNO_3$ | 50 vol% | Room | Room | 15 |
| 2 | Zincating | NaOH | 525 g/L (70 oz/gal) | 16-27 | 60-80 | 30-60 |
| | | ZnO | 98 g/L (13 oz/gal) | | | |
| **Alloys 413, 319, 356 and 380** | | | | | | |
| 1 | Acid dip | $HNO_3$ | 75 vol% | Room | Room | 3-5 |
| | | HF | 25 vol% | | | |
| 2 | Zincating | NaOH | 525 g/L (70 oz/gal) | 16-27 | 60-80 | 30 max |
| | | ZnO | 98 g/L (13 oz/gal) | | | |

**Fig. 4 Preplating surface preparation procedures suitable for wrought aluminum alloys that contain high amounts of silicon or do not contain interfering microconstituents (e.g., 1100 and 3003) and for aluminum casting alloys 413, 319, 356, and 380**



| Solution No. | Type of solution | Composition | Amount | Operating temperature | | Cycle time, s |
|---|---|---|---|---|---|---|
| | | | | °C | °F | |
| 1 | Acid dip | $H_2SO_4$ | 15 vol% | 85 min | 185 min | 120-300 |
| 2 | Acid dip | $HNO_3$ | 50 vol% | Room | Room | 15 |
| 3 | Zincating | NaOH | 525 g/L (70 oz/gal) | 16-27 | 60-80 | 30-60 |
| | | ZnO | 100 g/L (13 oz/gal) | | | |

**Fig. 5 Preplating surface preparation procedures suitable for all wrought aluminum alloys, for most aluminum casting alloys, and for magnesium-containing aluminum alloys with interfering microconstituents. Applicable alloys include 1100, 3003, 3004, 2011, 2017, 2024, 5052, 6061, 208, 295, 319, and 355.**



| Solution No. | Type of solution | Composition | Amount | Operating temperature | Cycle time, s |
|---|---|---|---|---|---|

|  |  |  |  | °C | °F | s |
|---|---|---|---|---|---|---|
| 1 | Zincating | NaOH | 525 g/L (70 oz/gal) | 16-27 | 60-80 | 30-60 |
|  |  | ZnO | 100 g/L (13 oz/gal) |  |  |  |
| 2 | Acid dip | $HNO_3$ | 50 vol% | Room | Room | 15 |

**Fig. 6 Preplating surface preparation procedures suitable for most aluminum casting alloys, for wrought aluminum alloys containing less than approximately 3% Mg (e.g., 1100, 3003, 3004, 2011, 2017, 2024, 5052, and 6061), and for aluminum alloys whose identities are not known**

Table 21 gives details of three zincating solutions that may be used alternatively to the solution indicated in the tables that accompany Fig. 4, 5, and 6. The modified solution in Table 21 is recommended when double-immersion zincating (Fig. 6) is required; it is not essential for alloys 2024 and 7075. This solution produces more uniform coverage than the unmodified solution and also imparts greater corrosion resistance to the treated work. Dilute solution No. 1 in Table 21 is recommended when there are problems in rinsing and drag-out. Dilute solution No. 2 provides a greater reserve of zinc for high-production operations, but at a slight sacrifice in effectiveness of rinsing. In some special operations, triple zincate treatment is used. This involves essentially stripping the second zinc film formed in double zincate and adding a zincate from a third solution. Triple zincate provides an even more uniform and fine-grain zinc coating than double zincate.

**Table 21 Zincating solutions for use with aluminum alloys**

| Solution type | Sodium hydroxide |  | Zinc oxide |  | Ferric chloride crystals |  | Rochelle salt |  | Sodium nitrate |  | Operating temperature |  | Processing time,s |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  | g/L | oz/gal | g/L | oz/gal | g/L | oz/gal | g/L | oz/gal | g/L | oz/gal | °C | °F |  |
| Modified[(a)] | 525 | 70 | 100 | 13 | 1.00 | 0.13 | 9.8 | 1.3 | . . . | . . . | 15-27 | 60-80 | 30-60 |
| Dilute 1[(b)] | 50.3 | 6.7 | 5 | 0.7 | 2.03 | 0.30 | 50 | 6.7 | 0.98 | 0.13 | 21-24 | 70-75 | 30 max |

(a) U.S. Patent 2,676,916 (1954).

(b) U.S. Patents 2,676,916 (1954) and 2,650,886 (1953)

If correct procedures are followed, the resulting zinc deposit is uniform and firmly adherent to the aluminum surface. The appearance of the surface will vary with the alloy being coated, as well as with the rate at which the coating forms. The weight of zinc deposit should be from 1.5 to 5.0 mg/dm$^2$ (0.1 to 0.3 mg/in.$^2$). Generally, it is desirable to limit the deposit to 3 mg/dm$^2$ (0.2 mg/in.$^2$).

The thinner and more uniform zinc deposits are the most suitable for plating preparation and for the service performance of plated coatings. Heavy zinc deposits usually are spongy, less adherent, and undesirable from the standpoint of corrosion resistance.

**Plating Procedures.** Copper is one of the easiest metals to electrodeposit on zincated aluminum surfaces. For this reason, it is used extensively as an initial strike over which other metals may be subsequently deposited. An advantage of the copper strike is that it protects the thin zinc film from attack by the plating solutions. Penetration of the zinc film and attack of the underlying aluminum surface by the plating solutions result in a poorly bonded electrodeposit.

The copper strike bath should be a Rochelle-type copper cyanide solution. The composition and operating conditions recommended for this bath are:

| | |
|---|---|
| Copper cyanide | 4 g/L (5.5 oz/gal) |
| Total sodium cyanide | 50 g/L (6.5 oz/gal) |
| Free sodium cyanide | 4 g/L (0.5 oz/gal) max |
| Sodium carbonate | 30 g/L (4.0 oz/gal) |
| Rochelle salt | 60 g/L (8.0 oz/gal) |
| Operating temperature | 40-55 °C (100-130 °F) |
| pH | Varies with alloy; see Table 22 |

**Table 22 Conditions for electroplating various metals on zincated aluminum surfaces**

| **Electroplate** | **Minimum deposit** | | **Plating time, min** | **Bath temperature** | | **Current density** | | **Type of electrolyte** |
|---|---|---|---|---|---|---|---|---|
| | **µm** | **mils** | | **°C** | **°F** | **A/dm$^2$** | **A/ft$^2$** | |
| Copper: | | | | | | | | |
| 1 Copper strike[(a)] | 7.5 | 0.3 | 2[(b)] | 34-54 | 100-130 | 2.4[(b)] | 24[(b)] | Rochelle cyanide[(c)] |
| 2 Brass strike[(a)] | 7.5 | 0.3 | 2-3 | 27-32 | 80-90 | 0.5 | 5 | Cyanide |
| 3 Copper plate[(d)] | 12.5 | 0.5 | 40 s-2 min | 76-83 | 170-180 | 3-6 | 30-60 | High-speed NaCN or KCN |
| Brass | 12.5 | 0.5 | 3-5 | 27-32 | 80-90 | 1 | 10 | Cyanide |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Cadmium: | | | | | | | | |
| 1 Copper strike(a) | 12.5 | 0.5 | 2(b) | 34-54 | 100-130 | 2.4(b) | 24(b) | Rochelle cyanide(c) |
| 2 Cadmium plate | 12.5 | 0.5 | 8-20 | 21-35 | 70-95 | 1.4-4.5 | 14-45 | Cyanide |
| Chromium, decorative: | | | | | | | | |
| 1 Copper strike(a) | 7.5 | 0.3 | 2(b) | 34-54 | 100-130 | 2.4 | 24(b) | Rochelle cyanide(c) |
| 2 Brass strike(a) | 7.5 | 0.3 | 2-3 | 27-32 | 80-90 | 0.5 | 5 | Cyanide |
| 3 Nickel undercoat | 2.5-5 | 0.1-0.2 | (e) | (e) | (e) | (e) | (e) | (e) |
| 4 Chromium plate | 25-50 | 0.01-0.02 | 10-12 | 43-46 | 110-115 | 0.07-0.15 | 0.7-1.5 | Conventional |
| Chromium, decorative (direct on zincate) | 0.75 | 0.03 | 5-10 | 18-21 | 65-70 | 0.07-0.15 | 0.7-1.5 | Conventional |
| Chromium, hard: | | | | | | | | |
| 1 Copper strike | 7.5 | 0.3 | 2(b) | 34-54 | 100-130 | 2.4(b) | 24(b) | Rochelle cyanide(c) |
| 2 Chromium plate | 1.25 | 0.05 | 5 | 54 | 130 | 0.07-0.15 | 0.7-1.5 | Conventional |
| Chromium, hard (direct on zincate) | 1.25 | 0.05 | 10-20; then 54(f) | 18-21; then 130(f) | 65-70 | 0.07-0.15; then 0.3(f) | 0.7-1.5; then 3 A in.$^2$ | Conventional |
| Chromium, hard (for corrosion protection): | | | | | | | | |
| 1 Copper strike | 7.5 | 0.3 | 2(b) | 34-54 | 100-130 | 2.4(b) | 24 | Rochelle cyanide(c) |
| 2 Brass strike | 7.5 | 0.3 | 2-3 | 27-32 | 80-90 | 0.5 | 5 | Cyanide |
| 3 Nickel undercoat | 25-50 | 1-2 | (e) | (e) | (e) | (e) | (e) | (e) |
| 4 Chromium plate | 2.5-5 | 0.1-0.2 | 10-12 | 43-46 | 110- | 0.07-0.15 | 0.7-1.5 | Conventional |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | 115 | | | |
| Gold: | | | | | | | | |
| 1 Copper strike | 7.5 | 0.3 | 2(b) | 34-54 | 100-130 | 2.4(b) | 24(b) | Rochelle cyanide(c) |
| 2 Brass strike | 7.5 | 0.3 | 2-3 | 27-32 | 80-90 | 0.5 | 5 | Cyanide |
| 3 Nickel undercoat | 17.5 | 0.7 | (e) | (e) | (e) | (e) | (e) | (e) |
| 4 Gold plate | 0.625 | 0.025 | 10 s-1 min | 49-71 | 120-160 | 0.5-1.5 | 5-15 | Potassium cyanide |
| Nickel (for minimum corrosion protection): | | | | | | | | |
| 1 Copper strike | 7.5 | 0.3 | 2(b) | 34-54 | 100-130 | 2.4(b) | 24(b) | Rochelle cyanide(c) |
| 2 Brass strike | 7.5 | 0.3 | 2-3 | 27-32 | 80-90 | 0.5 | 5 | Cyanide |
| 3 Nickel plate | 7.5-12.5 | 0.3-0.5 | (e) | (e) | (e) | (e) | (e) | (e) |
| Nickel (for maximum corrosion protection): | | | | | | | | |
| 1 Copper strike | 7.5 | 0.3 | 2(b) | 34-54 | 100-130 | 2.4(b) | 24(b) | Rochelle cyanide(c) |
| 2 Brass strike | 7.5 | 0.3 | 2-3 | 27-32 | 80-90 | 0.5 | 5 | Cyanide |
| 3 Nickel plate | 25-50 | 0.3-0.5 | (e) | (e) | (e) | (e) | (e) | (e) |
| Silver: | | | | | | | | |
| 1 Double silver strike | 0.625 | 0.025 | 10 s(g) | 30(g) | 80(g) | 1.5-2.5(g) | 15-25(g) | Cyanide(h) |
| 2 Silver plate | 1.25-2.5 | 0.05-0.1 | 18-35 | 27-32 | 80 | 0.5 | 5 | Cyanide |
| Silver (alternative method): | | | | | | | | |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 1 Copper strike | 7.5 | 0.3 | 2(b) | 34-54 | 100-130 | 2.4(b) | 24(b) | Rochelle cyanide(c) |
| 2 Silver strike | 0.50 | 0.02 | 10 s | 27-32 | 80 | 1.5-2.5 | 15-25 | Cyanide(i) |
| 3 Silver plate | 1.25-2.5 | 0.05-0.1 | 18-35 | 27-32 | 80 | 0.5 | 5 | Cyanide |
| Tin: | | | | | | | | |
| 1 Copper strike | 7.5 | 0.3 | 2(b) | 34-54 | 100-130 | 2.4(b) | 24(b) | Rochelle cyanide(c) |
| 2 Tin plate(j) | 17.5 | 0.7 | 15-30 | 93-99 | 200-210 | 4.5-6.5 | 45-65 | Sodium stannate |
| Zinc: | | | | | | | | |
| 1 Copper strike | 7.5 | 0.3 | 2(b) | 34-54 | 100-130 | 2.4(b) | 24(b) | Rochelle cyanide(c) |
| 2 Zinc plate | 12.5 | 0.5 | 18-45 | 24-30 | 75-86 | 1-3 | 10-30 | Pyrophosphate |
| Zinc (direct on zincate) | 12.5 | 0.5 | 10 | 24-35 | 75-95 | 0.5-5(k) | 5-50(k) | Pyrophosphate |

(a) An initial cyanide copper strike is generally used to achieve complete metal coverage of zincated aluminum parts prior to plating, because of the excellent throwing power of the copper electrolyte. A copper strike is not, however, recommended as the initial coating for alloys 5056, 214, 218, and others that contain substantial amounts of magnesium; these will achieve a better initial coverage in a brass strike. Neither copper strike nor brass strike should be used as a final finish; both should always have an electroplated top coat.

(b) The copper strike is achieved during the first 2 min while the current density of the electrolyte is maintained at 2.4 A/dm$^2$ (24 A/ft$^2$). Instead of being transferred from the strike bath to a high-speed sodium or potassium electrolyte for subsequent copper plating, the work may be allowed to remain (3 to 5 min) in the Rochelle-type electrolyte to be copper plated, provided the current density is lowered to 1.2 A/dm$^2$ (12 A/ft$^2$).

(c) Colorimetric pH of electrolyte is 12.0 for all treatable alloys except 5052, 6061, and 6063, for which pH is 10.2 to 10.5

(d) Work for which copper strike plating may be used may be left in the copper strike for copper plating, instead of being transferred to the high-speed sodium or potassium cyanide electrolyte (see footnote c).

(e) As discussed in the article on nickel plating, various electrolytes are used, depending on the specific purpose of the plated deposit. If the nickel is to be deposited directly on the zincated surface, a bath must be selected that is suitable for application over zinc (examples of such baths are fluoborate and sulfamate nickel electrolytes).

(f) The transition from low-temperature to high-temperature plating may be accomplished either by heating the electrolyte to 54 °C (130 °F) after deposition has started at 18 to 21 °C (65 to 70 °F) or by transferring the work (without rinsing) from an electrolyte at 18 to 21 °C (65 to 70 °F) to one at 54 °C (130 °F) and holding the work in the high-temperature electrolyte without current until the work reaches bath temperature. Current density is 0.07 to 0.15 A/dm$^2$ (0.7 to 1.5 A/in.$^2$) in the electrolyte at 18 to 21 °C (65 to 70 °F). 1935 AS/mm$^2$ (3 A/in.$^2$) at 54 °C (130

°F).

(g) Each bath.

(h) First strike bath contains 1 g (0.11 oz) of AgCN and 90 g (10.2 oz) of NaCN per litre (gallon); second bath, 5.3 g (0.60 oz) of AgCN and 67.5 g (7.7 oz) of NaCN per litre (gallon).

(i) Contains 5.3 g (0.60 oz) of AgCN and 67.5 g (7.7 oz) of NaCN per litre (gallon).

(j) After the aluminum material has been copper strike plated, tin may be applied also by immersion for 45 min to 1 h in a sodium stannate solution at 49 to 74 °C (120 to 165 °F). Time and temperature depend on solution used.

(k) Current is applied as work is being immersed in electrolyte.

A brass strike is sometimes used in place of copper; however, a bronze strike is frequently used on a tin immersion coating. Table 22 gives operating conditions for the electrodeposition of different metals on zincated aluminum surfaces. Environmental considerations sometimes necessitate substitution for cyanide-containing solutions. Nickel strikes, which are successful as a result of careful control of composition and operation conditions, permit this.

## Immersion Plating

Immersion plating refers to processes in which another metal is deposited from solution on an aluminum surface under the influence of the potential that exists between the solution and the immersed aluminum material. An external potential is not required. Deposits produced by immersion plating are thin and of little protective value.

Zincating, the procedure used for coating aluminum surfaces with zinc prior to electroplating (see the preceding section), is an example of immersion plating. Brass deposits can be produced by adding copper compounds to the sodium zincate solutions used in zincating.

Tin can be deposited from solutions containing potassium stannate, stannous chloride, or stannous sulfate-fluoride. The lubricating qualities of these tin deposits are desirable for aluminum alloy piston and engine components. Immersion tin coatings also are used to facilitate soft soldering and as a base coating for building up electrodeposits. The composition and operating conditions of a successful immersion tin bath are given below:

| | |
|---|---|
| Potassium stannate | 100 g/L (13.40 oz/gal) |
| Zinc acetate | 2 g/L (0.27 oz/gal) |
| *m*-Cresol sulfonic acid | 35 g/L (4.40 oz/gal) |
| Temperature of solution | 60 °C (140 °F) |
| Immersion time | 2 min |

Degreasing is the only pretreatment required. The thickness of the tin coating is about 1.3 μm (0.05 mil); solution life is about 0.75 $m^2$/L (30 $ft^2$/gal).

## Electroless Plating

Electroless plating, often called chemical plating, refers to nonelectrolytic processes that involve chemical reduction, in which the metal is deposited in the presence of a reducing agent. Deposition may take place on almost any type of material, even the container of the solution. For a variety of applications in the aircraft industry, nickel is chemically plated on aluminum parts of shapes for which electroplating is not practical. However, electroless plating is too expensive to be used when conventional electroplating is feasible. The composition and operating conditions of a bath for the successful deposition of nickel are given below:

| | |
|---|---|
| Nickel chloride | 30 g/L (4 oz/gal) |
| Sodium hypophosphite | 7.5 g/L (1 oz/gal) |
| Sodium citrate | 72 g/L (9.60 oz/gal) |
| Ammonium chloride | 48 g/L (6.40 oz/gal) |
| Ammonium hydroxide (0.880 sp gr) | 13 g/L (1.75 oz/gal) |
| pH | 10 |
| Temperature of solution | 80-90 °C (180-190 °F) |
| Immersion time | 1 h |

Deposits produced contain about 6 wt% P and usually are not considered suitable as a base for chromium plate. The immersion time given is for deposits 50 μm (2 mil) or more thick.

Silver can be plated using the electroless process on anodized aluminum-base materials. The procedure consists of degreasing the anodized surface, dipping in dilute hydrochloric acid, water rinsing, and then immersing the object in a silvering solution. A mixture of two solutions is required for silvering. The first consists of 3.33 mL (0.113 fluid oz) of a 10% solution of silver nitrate to which a 7.5 vol% solution of ammonium hydroxide is added until the precipitate first formed just redissolves, after which an excess of 40 mL (1.3 fluid oz) of ammonium hydroxide solution is added. The second solution is made by adding 80 g (3 oz) of Rochelle salt or 40 g (1.4 oz) of potassium citrate to water, to a total volume of 330 mL (11 fluid oz). Solutions are filtered and mixed immediately before use.

Additional information on electroless plating processes is available in the Section "Plating and Electroplating" in this Volume.

## Painting

The difference between painting of aluminum and painting of iron or steel lies primarily in the method of surface preparation. Aluminum is an excellent substrate for organic coatings if the surface is properly cleaned and prepared. For many applications, such as indoor decorative parts, the coating may be applied directly to a clean surface. However, a suitable prime coat, such as a wash primer or a zinc chromate primer, usually improves the performance of the finish coat.

For applications involving outdoor exposure, or for indoor applications that expose the part to impact or abrasive forces, a surface treatment such as anodizing or chemical conversion coating is required prior to the application of a primer and a finish coat. These processes were discussed above.

Anodizing in sulfuric or chromic acid electrolytes provides an excellent surface for organic coatings. Usually, only thin anodic coatings are required as a prepaint treatment. Decorative parts for home appliances generally are anodized before painting to ensure good paint adhesion over an extended period. Sulfuric acid anodic coatings are used when painting of only part of the surface is required for decorative effects; the anodic coating protects the unpainted portions of the surface.

Conversion coatings usually are less expensive than anodic coatings, provide a good base for paint, and improve the life of the paint by retarding corrosion of the aluminum substrate material. Adequate coverage of the entire surface by the conversion coating is important for good paint bonding.

The article "Painting" in this Volume contains additional information on surface preparation, paint formulations, and application procedures.

## Porcelain Enameling

Porcelain enamels are glass coatings applied to products to improve appearance and protect the metal surface. Porcelain enamels are distinguished from other ceramic coatings by their predominantly vitreous nature and the types of applications for which they are used. They are distinguished from paint by their inorganic composition and the fusion of the coating matrix to the substrate metal.

Aluminum products, including tanks and vessels, architectural panels, cookware, and signs, may be finished by porcelain enameling to enhance appearance, chemical resistance, or weather resistance. The common porcelain enameling alloys for the various forms of aluminum are:

- *Sheet:* 1100, 3003, and 6061
- *Extrusions:* 6061
- *Casting alloys:* 443 and 356

Of the wrought alloys, only 6061 alloy is heat-treatable. Because of its higher strength, 6061 alloy has better handling characteristics before and during porcelain enameling, and it is stronger after porcelain enameling. The non-heat-treatable alloys are easier to form before porcelain enameling and are used for small parts for which the amount of distortion and low strength encountered after firing are acceptable. However, non-heat-treatable alloys are unsuitable for more than one coat of porcelain because of the crazing that occurs after a second firing.

**Frits.** The basic material of the porcelain enamel coating is frit, a special glass of small friable particles produced by quenching a molten glassy mixture. Because porcelain enamels are usually designed for specific applications, the compositions of the frits from which they are made vary widely.

Enamel frits for aluminum are usually based on lead silicate and on cadmium silicate, but they may be based on phosphate or barium. Table 23 gives the compositions of several frits used for aluminum.

**Table 23 Melted-oxide compositions of frits for porcelain enameling of aluminum**

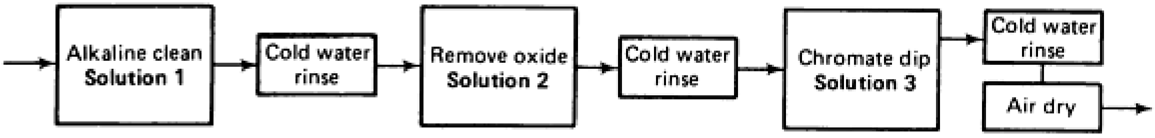
| Constituent | Composition, wt% | | |
|---|---|---|---|
| | Lead-base enamel | Barium enamel | Phosphate enamel |

|  |  |  |  |
|---|---|---|---|
| PbO | 14-45 | . . . | . . . |
| $SiO_2$ | 30-40 | 25 | . . . |
| $Na_2O$ | 14-20 | 20 | 20 |
| $K_2O$ | 7-12 | 25 | . . . |
| $Li_2O$ | 2-4 | . . . | 4 |
| $B_2O_3$ | 1-2 | 15 | 8 |
| $Al_2O_3$ | . . . | 3 | 23 |
| BaO | 2-6 | 12 | . . . |
| $P_2O_5$ | 2-4 | . . . | 40 |
| $F_2$ | . . . | . . . | 5 |
| $TiO_2$ | 15-20 | (a) | (a) |

(a) $TiO_2$, 7 to 9 wt%, added to frit during mill preparation of the enamel slip

The high-lead enamels for aluminum have a high gloss, good acid and weather resistance, and good mechanical properties. The phosphate enamels generally are not alkali-resistant or water-resistant, but they may have good acid resistance. They melt at relatively low temperatures and are useful in many applications. The barium enamels are not as low-melting as the lead or phosphate glasses, but they do have good chemical durability.

**Surface Preparation.** The preparation of heat-treatable aluminum alloy parts for porcelain enameling involves the removal of soil and surface oxides and the application of a chromate coating. Figure 7 shows the sequence of these surface preparation treatments and gives operating conditions. Final drying removes all surface moisture; drying must be accomplished without contaminating the cleaned surface. Parts made of non-heat-treatable aluminum alloys require only the removal of soil, which can be done by alkaline cleaning or vapor degreasing.



| No. | Type | Composition of solution | | Operating temperature | | Cycle time, min |
|---|---|---|---|---|---|---|
| | | Constituent | wt% | °C | °F | |
| 1 | Alkaline cleaner(a) | (b) | (b) | 60-82 | 140-180 | 2-5 |
| 2 | Oxide removal | Chromic acid | 3.5 | 82 | 180 | 3-10 |
| | | Sulfuric acid | 18.0 | | | |
| 3 | Chromate dip | Chromic sulfate | 0.2 | Ambient | | 1-6 |
| | | Potassium dichromate | 14.4 | | | |
| | | Sodium hydroxide | 7.75 | | | |

(a) Vapor degreasing may be used instead of alkaline cleaning.

(b) Either inhibited or mildly etching (uninhibited) cleaners can be used

**Fig. 7 Process for preparing heat-treatable aluminum alloys for porcelain enameling**

Because enamel ordinarily is applied to aluminum to only about half the thickness to which it is applied to steel, freedom from surface scratches, burrs, and irregularities is doubly important for aluminum. Most shaping of aluminum is done before enameling, but the thin coating permits some bending, shearing, punching, and sawing of the enameled part.

Surfaces to be enameled should have generous inside radii of not less than 4.8 mm ($\frac{3}{16}$ in.) and outside radii of not less than 1.6 mm ($\frac{1}{16}$ in.). Attachments should be welded to the unenameled back side of enameled heavy-gage aluminum sheet or extrusions. The visible metal surfaces must not be overheated; overheating causes the aluminum to blister and alters the color and gloss of the enamel. Welding can be done before enameling, provided that the weld area is cleaned properly before coating.

**Additives and Application.** Porcelain enamel is usually applied to aluminum as a suspension of finely milled frit in water. Mill additions for wet process enamel frits for aluminum consist of boric acid, potassium silicate, sodium silicate, and other additives. These materials are used to control the wet suspension of the frits, and they contribute to the characteristics of the fired enamel. Titanium dioxide and ceramic pigments can also be added to produce opacity and the desired color, respectively.

Porcelain enamel slips for aluminum usually are applied by spraying, using either manual or automatic equipment with agitated pressure tanks. Slips for aluminum are not self-leveling and thus must be deposited smoothly in an even thickness and without runs or ripples.

Many aluminum parts are coated satisfactorily by the one-coat/one-fire method. Although the heat-treatable alloys can be recoated one or more times, the opacity and color of the coating will change with the thickness of the porcelain and with repeated firing. The desirable minimum fired enamel thickness is 65 μm (2.5 mil), and the desirable maximum is 90 μm (3.5 mil).

**Furnaces.** Forced convection is the preferred method of heating furnaces for firing porcelain enamel on aluminum. The heat is provided by electric package heaters, quartz-tube electric heaters, or metal-sheath heaters, all specially designed for operation at high ambient air temperature. Quartz-tube and metal-sheath heaters are adapted to the furnace so that radiant heat is available in the firing zone along with forced circulation. Package heaters are placed remote from the firing zone; this is the most effective method of eliminating direct radiation and hot spots. Heat imparted to the work from the package heater is derived completely from adequate air circulation to maintain a uniform temperature throughout the furnace of ±1% of the nominal operating temperature.

Forced-convection heating is also accomplished with gas-fired radiant tubes as the heat source. The tubes are baffled from the work or firing zone so that air circulation provides the same advantages as in electric-package forced-convection heating.

Furnace construction for aluminum enameling generally requires the use of stainless steel inner liner sheets, low-density wall insulation, and plain-carbon steel exterior shell. This type of fabrication eliminates long heat-up and cool-down periods.

Firing of enamel on aluminum is accomplished between 525 and 550 °C (980 and 1020 °F); cycles are shown in Table 24. To control color and gloss of the enamel within acceptable limits, the temperature throughout the work must be held to 1.5 °C (2.5 °F).

**Table 24 Cycles for firing procelain enamel on aluminum**

| **Type of part** | **Section thickness, 0.025 mm (0.001 in.)** | **Firing time, min** | **Firing temperature** | |
|---|---|---|---|---|
| | | | **°C** | **°F** |
| Any configuration | 26-40 | 5-6 $\frac{1}{2}$ | 540 | 1000 |
| Any configuration | 51-64 | 7-8 | 540 | 1000 |
| Extrusions | 125 | 10 | 550 | 1020 |

Detailed information about porcelain enamel coatings is available in the article "Porcelain Enameling" in this Volume.

## Shot Peening

Shot peening is a method of cold working in which compressive stresses are induced in the exposed surface layers of metallic parts by the impingement of a stream of shot, which is directed at the metal surface at high velocity under controlled conditions. It differs from blast cleaning in primary purpose and in the extent to which it is controlled to yield accurate and reproducible results. Cast steel shot is the most widely used peening medium, but glass beads often are used for peening aluminum and other metals that might be contaminated by steel shot.

Although shot peening cleans the surface being peened, this function is incidental. The major purpose of shot peening is to increase fatigue strength. For example, the fatigue strength of several aluminum alloys peened with cast steel shot can be improved by 23 to 34%. The process has other useful applications, such as relieving tensile stresses that contribute to stress-corrosion cracking (SCC), and forming and straightening metal parts.

Peening action improves the distribution of stresses in surfaces that have been disturbed by grinding, machining, or heat treating. Shot peening is especially effective in reducing the harmful stress concentration effects of notches, fillets, forging pits, surface defects, and the heat-affected zones of weldments.

The surface tensile stresses that cause SCC can be effectively overcome by the compressive stresses induced by shot peening with either steel shot or glass beads. In one application, test bars were cut in the short transverse direction from a 7075-T6 aluminum alloy hand forging and stressed to 75% of the yield strength. During alternate immersion tests in 3.5% sodium chloride solution, unpeened specimens failed in 1, 5, 17, and 28 days. Specimens peened in the unstressed condition with cast steel shot lasted 365 and 730 days, when failure occurred in the unpeened grip outside the test area. During exposure to an industrial atmosphere, similar unpeened test bars failed in 20, 37, 120, and 161 days, whereas a peened specimen under the same conditions was uncracked when it was removed from testing after an exposure of $8\frac{1}{2}$ years.

Additional information is provided in the article "Shot Peening" in this Volume.

## Designation System for Aluminum Finishes

Finishes used on aluminum are categorized as mechanical or chemical finishes or as coatings. Types of coatings that can be applied include anodic coatings, resinous and other organic coatings, and vitreous coatings. In addition, laminated, electroplated, or other metallic coatings can be used on aluminum.

In the designation system developed by the Aluminum Association, each of these categories is assigned a letter, and the various finishes in each category are designated by two-digit numerals. Specific finishes of the various types thus are designated by a letter followed by two numbers, as shown in Table 25. Two or more designations can be combined into a single designation to identify a sequence of operations covering all the important steps leading to a final complex finish.

**Table 25 Designations for aluminum finishes**

| **Designation**[(a)] | **Finish** |
|---|---|
| **Mechanical finishes--M** | |
| As fabricated: | |
| M10 | Unspecified |
| M11 | Specular finish as fabricated |
| M12 | Nonspecular finish as fabricated |
| M1X | Other (to be specified) |
| Buffed: | |
| M20 | Unspecified |

| | |
|---|---|
| M21 | Smooth specular |
| M22 | Specular |
| M2X | Other (to be specified) |
| Directional textured: | |
| M30 | Unspecified |
| M31 | Fine satin |
| M32 | Medium satin |
| M33 | Coarse satin |
| M34 | Hand rubbed |
| M35 | Brushed |
| M3X | Other (to be specified) |
| Nondirectional textured: | |
| M40 | Unspecified |
| M41 | Extra fine matte |
| M42 | Fine matte |
| M43 | Medium matte |
| M44 | Coarse matte |
| M45 | Fine shot blast |
| M46 | Medium shot blast |
| M47 | Coarse shot blast |

| | |
|---|---|
| M4X | Other (to be specified) |
| **Chemical finishes[(b)]--C** | |
| Nonetched cleaned: | |
| C10 | Unspecified |
| C11 | Degreased |
| C12 | Inhibited chemical cleaned |
| C1X | Other (to be specified) |
| Etched: | |
| C20 | Unspecified |
| C21 | Fine matte |
| C22 | Medium matte |
| C23 | Coarse matte |
| C2X | Other (to be specified) |
| Brightened: | |
| C30 | Unspecified |
| C31 | Highly specular |
| C32 | Diffuse bright |
| C3X | Other (to be specified) |
| Chemical coatings: | |
| C40 | Unspecified |

| | |
|---|---|
| C41 | Acid chromate-fluoride |
| C42 | Acid chromate-fluoride-phosphate |
| C43 | Alkaline chromate |
| C44 | Nonchromate |
| C45 | Nonrinsed chromate |
| C4X | Other (to be specified) |
| **Anodic coatings--A** | |
| General: | |
| A10 | Unspecified |
| A11 | Preparation for other applied coatings |
| A12 | Chromic acid coatings |
| A13 | Hard, wear- and abrasion-resistant coatings |
| A1X | Other (to be specified) |
| Protective and decorative: | |
| (Less than 10 $\mu$m, or 0.4 mil) | |
| A21 | Clear (natural) |
| A22 | Integral color |
| A23 | Impregnated color |
| A24 | Electrolytically deposited color |
| A2X | Other (to be specified) |

| | |
|---|---|
| Architectural Class II(c): | |
| (10 to 18 $\mu$m, or 0.4 to 0.7 mil) | |
| A31 | Clear |
| A32 | Integral color |
| A33 | Impregnated color |
| A34 | Electrolytically deposited color |
| A3X | Other (to be specified) |
| Architectural Class I(c): | |
| (18 $\mu$m, or 0.7 mil) | |
| A41 | Clear (natural) |
| A42 | Integral color |
| A43 | Impregnated color |
| A44 | Electrolytically deposited color |
| A4X | Other (to be specified) |
| **Resinous and other organic coatings(d)--R** | |
| R10 | Unspecified |
| R1X | Other (to be specified) |
| **Vitreous (porcelain and ceramic) coatings(d)--V** | |
| V10 | Unspecified |
| V1X | Other (to be specified) |

| **Electroplated and other metal coatings[d]--E** | |
|---|---|
| E10 | Unspecified |
| E1X | Other (to be specified) |
| **Laminated coatings[d]--L** | |
| L10 | Unspecified |
| L1X | Other (to be specified) |

(a) All designations are preceded by the letters "AA," to identify them as Aluminum Association designations. Examples of methods of finishing are given in the Aluminum Association publication from which the presentation here is derived.

(b) Includes chemical conversion coatings, chemical or electrochemical brightening and cleaning treatments.

(c) Classification established in Aluminum Association Standards for Anodically Coated Aluminum Alloys for Architectural Applications, October 1978.

(d) These designations may be used until more complete series of designations are developed for these coatings.

When designations for chemical coatings are used alone, other processing steps normally used ahead of these finishes are at the option of the processor. Where a finish requires two or more treatments of the same class, the class letter is repeated, each time being followed by the appropriate two-digit numeral.

Designations for specific coatings have been developed only for the anodic coatings. Coatings of the four other classes may be tentatively designated by the letters respectively assigned for them; detailed designations for these four categories may be developed and added to the system later.

The examples that follow show how the designation system for aluminum finishes is used. Each designation is preceded by the letters "AA" to identify it as an Aluminum Association appellation. More detailed information can be found in the Association document titled "Designation Systems for Aluminum Finishes, 1980."

**Smooth Specular Finish.** A finish can be obtained by polishing aluminum with an aluminum oxide compound according to the following schedule. Begin with grits coarser than 320; follow with 320-grit and a wheel speed of 30 m/s (6000 ft/min); complete polishing by buffing with tripoli-based buffing compound at 35 to 41 m/s (7000 to 8000 ft/min). The designation for this finish is AA-M21 (Table 25).

**Architectural Building Panel.** A matte-anodized finish for a building, such as that produced by giving aluminum a matte finish, then chemical cleaning followed by architectural class II natural anodizing, would be designated as AA-M32C12A31:

| | |
|---|---|
| AA | Aluminum Association |
| M32 | Mechanical finish, directional textured, medium satin appearance |
| C12 | Chemical treatment, inhibited alkaline cleaning |
| A31 | Anodic coating, architectural class II (10 to 18 µm, or 0.4 to 0.7 mil thick), clear (natural) |

**Architectural Aluminum with Anodized Integral Color.** An anodized panel with an integral color for architectural application would be designated as AA-M10C22A42:

| | |
|---|---|
| AA | Aluminum Association |
| M10 | Unspecified as-fabricated finish |
| C22 | Chemically etched medium matte finish |
| A42 | Anodic coating, architectural class I (18 µm, or 0.7 mil or thicker), integral color |

**Chromium-Plated Aluminum Panel.** The finish for a chromium-plated aluminum panel that is first given a highly specular mechanical finish, then a nonetch chemical cleaning, followed by a thin anodic coating produced in phosphoric acid, and finally direct chromium plating, would be designated as AA-M21C12A1XE1X:

| | |
|---|---|
| AA | Aluminum Association |
| M21 | Mechanical finish, polished, smooth specular (see smooth specular finish, (above) |
| C12 | Inhibited alkaline cleaned |
| A1X | Specify exact anodizing process |
| E1X | Specify exact chromium plating method |

# Introduction

COPPER and copper alloys constitute one of the major groups of commercial metals. They are widely used because of their excellent electrical and thermal conductivities, outstanding resistance to corrosion, ease of fabrication, and good strength and fatigue resistance. They are generally nonmagnetic. They can be readily soldered and brazed, and many coppers and copper alloys can be welded by various gas, arc, and resistance methods. For decorative parts, standard alloys having specific colors are readily available. Copper alloys can be polished and buffed to almost any desired texture and luster. They can be plated, coated with organic substances, or chemically colored to further extend the variety of available finishes.

Pure copper is used extensively for cables and wires, electrical contacts, and a wide variety of other parts that are required to pass electrical current. Coppers and certain brasses, bronzes, and cupronickels are used extensively for automobile radiators, heat exchangers, home heating systems, panels for absorbing solar energy, and various other applications requiring rapid conduction of heat across or along a metal section. Because of their outstanding ability to resist corrosion, coppers, brasses, some bronzes, and cupronickels are used for pipes, valves, and fittings in systems carrying potable water, process water, or other aqueous fluids.

The elements most commonly alloyed with copper are aluminum, nickel, silicon, tin, and zinc. Other elements and metals are alloyed in small quantities to improve certain material characteristics, such as corrosion resistance or machinability. Copper and its alloys are divided into nine major groups. These major groups are:

- *Coppers,* which contain a minimum of 99.3% Cu
- *High-copper alloys,* which contain up to 5% alloying elements
- *Copper-zinc alloys (brasses),* which contain up to 40% Zn
- *Copper-tin alloys (phosphor bronzes),* which contain up to 10% Sn and 0.2% P
- *Copper-aluminum alloys (aluminum bronzes),* which contain up to 10% Al
- *Copper-silicon alloys (silicon bronzes),* which contain up to 3% Si
- *Copper-nickel alloys,* which contain up to 30% Ni
- *Copper-zinc-nickel alloys (nickel silvers),* which contain up to 27% Zn and 18% Ni
- *Special alloys,* which contain alloying elements to enhance a specific property or characteristic, for example, machinability

Many copper alloys have common names, such as oxygen-free copper (99.95% Cu min), beryllium copper (0.2 to 2.0% Be), Muntz metal (Cu-40Zn), Naval brass (Cu-39.25Zn-0.75Sn), and commercial bronze (Cu-10Zn).

A more standardized system of identification is the unified Numbering System (UNS). In this system, wrought alloys of copper are designated by numbers 1*xxxx* to 7*xxxx*, and cast alloys are designated 8*xxxx* to 9*xxxx*; thus, the same alloy can be produced as a wrought and cast product.

Additional information about the classification, metallurgy, properties, and applications of copper and copper alloys is available in *Properties and Selection: Nonferrous Alloys and Special-Purpose Materials,* Vol 2 of *ASM Handbook.*

The selection of surface treatments for copper and copper alloys is generally based on application requirements for appearance and corrosion resistance. These treatments range from simple low-cost chemical processes that provide a uniform surface appearance, to expensive electroplates that provide maximum corrosion resistance. This article describes the cleaning, finishing, and coating processes used with copper and copper alloys.

## Acknowledgements

This article was adapted from Robert M. Paine and Bob Srinivasan, Cleaning and Finishing of Copper and Copper Alloys, *Surface Cleaning, Finishing, and Coating,* Volume 5, 9th Edition, *Metals Handbook,* American Society for Metals, 1982, p 611-627. It was revised for this edition by Andrew J. Brock, Olin Corporation.

## Cleaning and Finishing

Prior to subsequent processing or the application of a protective or decorative coating, the copper or copper alloy surface must be prepared by suitable cleaning procedures. The severity of these cleaning procedures will depend on the past processing history of the metal. Copper and copper alloys obtained from major materials suppliers should be received reasonably clean (free from heat treat scale or tarnish) and should only require minimal cleaning prior to further processing.

Heat treating of copper and copper alloys in air results in the formation of copper oxides; further cleaning will be necessary to remove these oxides, as discussed below. The need for such cleaning can be prevented by heat treating in reducing atmospheres, such as nitrogen with 1 to 4% H, in which the formation of copper oxides will be completely suppressed. Such atmospheres will not, however, prevent the oxidation of reactive alloying constituents such as aluminum, silicon, or zinc.

### *Pickling and Bright Dipping*

Pickling in solutions containing 4 to 15 vol% sulfuric acid or 40 to 90 vol% hydrochloric acid is used for the removal of oxides formed on the surface of copper-base materials during mill processing and fabricating operations. The sulfuric acid solution is used to remove black copper oxide scale on brass extrusions, forgings, and machined parts; oxide on copper tubing, forgings, and machined parts; and light annealing scale or tarnish. The hydrochloric acid solution is primarily used for finishing, but is also used to remove scale and tarnish from brass forgings and machined parts, and oxide on copper forgings and machined parts. Conditions for pickling copper-base metals with sulfuric acid and hydrochloric acid are shown in Table 1. Sometimes no additional surface preparation is necessary to produce the uniformity of appearance required for further finishing of copper; however, heavily scaled material may need a bright dip or color dip after pickling.

**Table 1 Pickling conditions for copper-base materials**

| **Constituent or condition** | **Amount or value** |
|---|---|
| **Sulfuric acid bath** | |
| Sulfuric acid[(a)] | 15-20 vol% |
| 35% hydrogen peroxide | 3-5 vol% |
| Water | bal |
| Temperature of solution | Room temperature to 60 °C (140 °F) |
| Immersion time | 15 s to 5 min |
| **Hydrochloric acid bath** | |
| Hydrochloric acid[(b)] | 40-90 vol% |
| Water | bal |
| Temperature of solution | Room temperature |

| | |
|---|---|
| Immersion time | 1-3 min |

(a) 1.83 sp gr. The bath needs additives to stabilize peroxide and accelerators to maintain etch rate. Proprietary products are available from metal finishing suppliers.

(b) 1.16 sp gr

Except for bright annealed material, copper alloys must be pickled after each annealing treatment, completely descaled, and bright dipped to produce a natural surface color and luster suitable for other finishing treatments such as electroplating or painting. Scale dip and bright dip solutions are given in Table 2. Bright dips for copper-base materials consist of sulfuric and nitric acids in varying proportions with a small amount of water and hydrochloric acid. Proprietary pickle and bright dips, using sulfuric acid and stabilized hydrogen peroxide, are also available. Whereas the conventional bright dips use highly concentrated acids, this sulfuric acid-hydrogen peroxide bath is dilute and reduces worker safety hazards.

### Table 2 Scale dip and bright dip conditions for copper-base metals

These solutions remove scale that is not removed by sulfuric or hydrochloric acid solutions; lower concentrations of nitric acid and higher concentrations of sulfuric acid produce a bright lustrous finish; these solutions can remove 0.0255 mm (0.001 in.) of metal and should not be used when close dimensional tolerances must be maintained. Solutions are used at room temperature.

| **Solution** | **Sulfuric acid, vol%**[(a)] | **Nitric acid, vol%**[(b)] | **Hydrochloric acid**[(c)] | | **Water, vol%** | **Immersion time,s** |
|---|---|---|---|---|---|---|
| | | | **g/L** | **oz/gal** | | |
| Scale dip | | | | | | |
| Solution A | 0 | 50 | 4 | $\frac{1}{2}$ | 50 | 15-60 |
| Solution B | 25-35 | 35-50 | 4 | $\frac{1}{2}$ | 35-40 | 15-60 |

(a) 1.83 sp gr.

(b) 1.41 sp gr.

(c) 1.16 sp gr. Excess hydrochloric acid spots brass. Wood soot and activated charcoal are added to the solution to prevent this condition.

After bright dipping and thorough rinsing in cold running water, stain or tarnish may be removed by dipping in a cyanide solution. Some proprietary bright dips, incorporated with corrosion inhibitors, eliminate the use of toxic cyanides and chromates and are easy to waste treat.

When a semibright finish is satisfactory, a dichromate color dip is less expensive and more convenient to use than the conventional acid dip. Color dip should not be used if parts are to be plated or soldered. The following conditions for color dipping include a solution that removes red copper oxide and imparts a film that resists discoloration during storage and work:

| | |
|---|---|
| Sodium dichromate | 30 to 90 g/L (4 to 12 oz/gal) |
| Sulfuric acid, 1.83 sp gr | 5 to 10 vol% |
| Water | bal |
| Immersion time | 30 s |
| Temperature of solution | Room temperature |

Extruded yellow brass rod may be pickled, usually in dilute sulfuric acid, to remove light oxide prior to drawing, forging, or machining. Yellow brass forgings are similarly treated for the removal of oxide scale and forging lubricant. Hydrochloric acid solutions may be used instead of sulfuric acid in some applications. Bright dipping follows pickling to complete the removal of all oxide. The yellow brass is then given a color dip to produce a uniform cartridge-brass color. Although brass sand castings are seldom pickled, a solution similar to that used for forgings may be used when pickling is indicated.

A typical acid treatment cycle for copper-base materials is given in the following list. The cycle may be terminated after any water rinse if the desired finish and color have been obtained:

- Pickling
- Cold water rinse
- Scale dip or bright dip
- Cold water rinse (repeat once)
- Color dip
- Cold water rinse (repeat once)
- Hot water rinse
- Air-blast dry

**Aluminum bronzes** form a tough, adherent aluminum oxide film during hot fabrication. This film can be removed or loosened by the following strong alkaline solution:

| | |
|---|---|
| Sodium hydroxide | 10 wt% |
| Water | bal |

| | |
|---|---|
| Temperature of solution | 75 °C (170 °F) |
| Immersion time | 2 to 6 min |

After this treatment the material can be treated in acid solutions by some of the same cycles used for other copper-base materials.

**Alloys containing silicon** may form oxides of silicon that are removable only by hydrofluoric acid. Proprietary fluorine-bearing compounds are also available for this purpose. If a dull brown-to-gray appearance is not objectionable, the material may be pickled in the conventional sulfuric acid solution to remove the copper oxides. If a brighter finish is required, one of the solutions in Table 3 may be used.

### Table 3 Pickling conditions for copper alloys containing silicon

Solutions are used at room temperature.

| Constituent or condition | Solution A | Solution B |
|---|---|---|
| Sulfuric acid[(a)] | 5-15 vol% | 40-50 vol% |
| Hydrofluoric acid[(b)] | $\frac{1}{2}$-15 vol% | $\frac{1}{2}$-5 vol% |
| Nitric acid[(c)] | . . . | 15-20 vol% |
| Water | bal | bal |
| Immersion time | $\frac{1}{2}$-10 min | 5-45 s |

(a) 1.83 sp gr.

(b) 52%.

(c) 1.41 sp gr

**Alloys containing beryllium** that have been heat treated at relatively low temperatures (below 400 °C, or 750 °F) can be pickled or bright dipped as any other copper alloy; however, alloys containing beryllium that have been heat treated at temperatures above 400 °C (750 °F) in operations such as solution annealing and those that have been bright annealed will generally possess a surface oxide that contains beryllium oxide as a major constituent. This oxide can be difficult to remove if present in a thickness greater than 0.04 to 0.05 μm (1.6 to 2.0 μin.). A 1 or 2 min soak in a solution of 50% sodium hydroxide at 130 °C (265 °F) before acid pickling facilitates removal of any beryllium oxide.

**Nickel silvers and copper-nickel alloys** do not respond readily to the pickling solution usually used for brasses, because nickel oxide has a limited solubility in sulfuric acid. Heavy scaling of these alloys should be avoided during annealing by using a reducing atmosphere. For example, the annealing of 18% nickel silver in a rich reducing atmosphere results in a slight tarnish that is easily removed in the sulfuric acid pickle and dichromate solutions ordinarily used for descaling brass. Controlling the atmosphere during annealing produces a bright metal finish.

Tubing made of 30% copper-nickel may be annealed in a reducing atmosphere, but not in a brightening atmosphere, to produce a clean surface that does not require acid treatment; 18% nickel silver wire is pretreated in a proprietary hot alkaline cleaning solution and then annealed in a controlled atmosphere furnace to produce a clean and bright surface. The wire is subsequently pickled in sulfuric acid and treated in a dichromate solution to remove zinc sweat. The wire is then finish pickled in 10 to 15% sulfuric acid solution at 60 °C (140 °F).

**Tarnish Removal.** Tarnish, the surface discoloration formed on copper-base materials during exposure to the atmosphere or to alkaline cleaning, usually consists of a thin film of oxide or sulfide. One of the most commonly used dips for removing tarnish is an aqueous solution of 8 to 60 g/L (1 to 8 oz/gal) of sodium cyanide. The metal to be cleaned is immersed for 1 to 2 min in the cyanide solution at room temperature. Steel tanks are used to contain the solution. Thorough rinsing is required after the dip treatment.

Extreme safety precautions must be followed when cyanide solutions are being used, because cyanide is highly poisonous. To prevent the formation of ammonia, metal previously cleaned in an alkaline solution must be thoroughly rinsed before it is brought into contact with the cyanide solution. Cyanide must not come in contact with acid because lethal hydrocyanic acid is produced. Despite the strict safety precautions that are necessary, cyanide solutions are commonly used.

A solution containing 5 to 10 vol% hydrochloric or sulfuric acid may also be used to remove tarnish from copper-base materials. Immersion time is a few seconds in either of these solutions at room temperature. Thorough rinsing in water is required after the treatment. The hydrochloric acid solution may be contained in a vitrified crock, or in a rubber-lined or glass-lined tank. A vitrified crock or lead-lined tank may be used as a container for the sulfuric acid solution. Plastics such as polypropylene or polyvinyl chloride are also suitable containers for hydrochloric and sulfuric acid solutions. These materials are resistant to 50% sulfuric acid and 37% hydrochloric acid up to 65 to 70 °C (150 to 160 °F).

Another noncyanide solution sometimes used for removing tarnish consists of 10% citric acid at 70 to 80 °C (160 to 175 °F). This solution removes most tarnish stains and poses no health or ecological hazards.

**Tarnish Prevention.** Tarnishing of copper alloys after pickling or degreasing operations is accelerated when the metal is inadequately dried following rinsing and can be particularly rapid if the final rinse solution is contaminated with the cleaning solutions. Significant resistance to tarnishing after cleaning can be rendered by incorporating benzotriazole (BTA) or tolyltriazole (TTA) into the final rinse. Typical concentrations are 0.1 to 0.5% with the rinse water being used at 40 to 60 °C (104 to 140 °F).

**Pickling Equipment.** Equipment requirements for the automatic pickling of brass forgings of various sizes are given in Table 4. The automatic pickling machine is similar to automatic plating equipment. Solution conditions for automatic pickling of brass forgings are as follows:

- Hydrochloric acid solution at room temperature
- Nitric-sulfuric acid solution, 38 °C (100 °F) maximum
- Sodium dichromate solution, room temperature
- Cold water rinse, 2300 L/h (600 gal/h)
- Hot water rinse, 66 to 82 °C (150 to 180 °F), 4 L/h (1 gal/h)

**Table 4 Production capacity of equipment for automatic pickling of brass forgings**

Immersion time, 40 s; total cycle time, 6 min

| Item or condition | Size of forgings | | |
|---|---|---|---|
| | Small | Medium | Large |

| | | | |
|---|---|---|---|
| Number of pieces per hour | 2500 | 500 | 250 |
| Pieces per basket | 250 | 50 | 25 |
| Pounds pickled per hour | 2500 | 2500 | 2500 |
| Configuration of forgings | Irregular | Irregular[(a)] | Irregular[(a)] |

(a) May contain cavities; require hand loading into baskets

Compositions of pickling tanks are determined by the type of solution used, such as:

| **Solution** | **Tank material** |
|---|---|
| Hydrochloric acid | Plastic-lined steel |
| Nitric-sulfuric acid | Type 316 stainless steel |
| Color dip (dichromate solution) | Plastic-lined steel |
| Cold water rinse (four tanks) | Steel |
| Hot water rinse | Steel or rubber-lined steel |

Work baskets require type 316 stainless steel or plastic composition with dimensions of 330 by 635 by 155 mm (13 by 25 by 6 in.) and 610 by 205 by 180 mm (24 by 8 by 7 in.). Equipment requirements for pickling brass tubes or rods and the equipment for pickling brass tubing are listed in Table 5.

### Table 5 Equipment requirements for pickling brass tubes or rods

Oxide scale is removed from 25 mm (1 in.) diam brass tubing and rods that are 1.9 to 21 m (6 to 70 ft) in length; immersion time varies from 5 to 30 min; the source of heat is steam, 105,000 kJ (100,000 Btu)

| **Tanks**[(a)] | **Material** | **Solution** | **Temperature** | | **Overflow**[(b)] |
|---|---|---|---|---|---|
| | | | **°C** | **°F** | |
| Acid tank | Stainless steel | 10% sulfuric acid | 38-60 | 100-140 | . . . |
| Cold water rinse tank | Wood | . . . | . . . | . . . | 380 L/h (100 gal/h) |

| | | | | | |
|---|---|---|---|---|---|
| Hot water rinse tank | Wood | . . . | 54-71 | 130-160 | 38 L/h (10 gal/h) |

(a) All tanks measure 1.1 by 0.9 by 21 m (3.5 by 3 by 70 ft) and hold 6738 L (1780 gal) for a 0.6 m (2 ft) depth of solution.

(b) Connected to bottom of tank

Tanks for sulfuric acid may be lined with natural rubber. Tanks intended to contain nitric and hydrofluoric acids may be lined with polyvinyl chloride or polypropylene. Additional information on materials and construction of acid tanks is given in the article "Acid Cleaning" in this Volume.

**Defects from Pickling.** By far the most common defect encountered in pickling brass is the presence of red stain on the metal. Caused by cuprous oxide, this defect may be removed by pickling in a solution of 10% sulfuric acid containing 98 g/L (13 oz/gal) of ferric sulfate at temperatures up to 60 °C (140 °F), or in a solution of 12% sulfuric acid containing 45 g/L (6 oz/gal) of sodium dichromate at room temperature. Alternatively, sulfuric acid-hydrogen peroxide solution can be used. Red stains may result from the presence of metallic iron in the pickling solution, causing copper to plate out on the parts when the parts come in contact with iron or steel. This is because iron is anodic to copper. Care must be taken to prevent any stray pieces of iron, such as nails or tools, from entering the pickling solution. Red stains can also result from the reaction of sulfuric acid on cuprous oxide ($Cu_2O$), forming cupric oxide (CuO) and copper. This can be removed in any of the above oxidizing acids.

Oil and lubricants remaining on formed metal must be removed before pickling and dipping. If formed material is to be bright dipped, it should first be degreased, or the lubricant remaining will prevent the bright dip from being effective. If the work is to be annealed and pickled, it should be degreased, usually in a hot water rinse, because the oil may cause excess cuprous oxide and unwanted red staining to form during annealing. In extreme instances, the more volatile constituents of the oil burn off readily, leaving a carbonaceous deposit that must be removed mechanically.

Acid stains will appear on the metal if it is not thoroughly rinsed and cleansed of all remaining acid after pickling or dipping. At least two separate washings in water or one thorough running water wash should be used before drying. Dipping in a soap solution or a buffered salt solution will neutralize traces of acid.

The metal is etched or pitted if it is immersed for too long in a pickling solution or dip, or if the solution is too strong or too hot. The proper time, temperature, and concentration of solution may be determined quickly during trial runs.

**Safety Practices.** Acids, even in dilute solution, can cause serious injuries to the eyes and other portions of the body. Operators should wear face shields, rubber boots, and rubber aprons for protection. Eye fountains and showers adjacent to acid tanks, for use in the event of an accident, should be provided. Adequate ventilation and suitable hoods for the tanks are recommended.

Extreme caution should be exercised when adding acid to a water solution, especially if sulfuric acid is used. Sulfuric acid should be added slowly and only while stirring the solution.

## *Abrasive Blast Cleaning*

Abrasive cleaning is used to remove molding, core sand, and investment material from the exterior and interior surfaces of copper-base castings. Selection of the proper kind and particle size of grit determines the type and color of the finish. The coarser grits clean faster but give a rougher finish.

**Dry abrasive cleaning** of beryllium copper is usually confined to castings. Steel shot is used for general cleaning to remove sand and slight surface imperfections from the casting after mold shakeout. Sands are used to blend in surface areas, to remove heat treat scale and to produce a uniform surface texture. Graded bronze chips, together with the regular commercial abrasives, are used in some applications to impart a better color and finish. Abrasive blast cleaning is seldom used to produce decorative finishes on copper alloys.

**Wet blasting** offers a means of cleaning previously blasted and machined surfaces without damaging the finished or threaded areas. Wet blasting produces various degrees of satin finish. The process is ideal for removing oxide film acquired during brazing, soldering, welding, or heat treating and for removing smudges, stains, and finger marks. For example, bronze castings that have been machined and brazed often are wet blasted with quartz (140-grit) for $\frac{1}{2}$ to 5 min to remove braze discoloration and shop dirt. The parts are normally degreased before wet blasting. After the castings are wet blasted, they are cleaned ultrasonically, inspected, and assembled.

Surfaces cleaned by wet blasting are uniform in appearance, although their color is not the same as original grit-blasted surfaces because of the abrasive used. Cleaning action is gentle but effective because water is the carrier.

### *Mass Finishing*

Mass finishing is best suited for stamped, formed, or machined parts. Castings with remnants of gates and parting lines; forgings with heavy scale, flash lines, or die marks; and heavily burred, pitted, or dented parts are not well suited for mass finishing. Light burrs can sometimes be removed by a prior bright dip, after which tumbling may be used for radius blending, polishing, and burnishing. High thin burrs of soft alloys are likely to peen over. Mass finishing of soft alloys at excessive speeds with insufficient amounts of solution can result in roughened and indented surfaces. Dry tumbling is generally restricted to small parts of simple shape and maximum dimension less than 50 mm (2 in.).

**Abrasives.** Aluminum oxide, silicon carbide, limestone, and flintstone are the abrasive materials most often used in mass finishing of copper and copper alloys. Combinations of these abrasives may be used for specific applications. For example, a blend of aluminum oxide and silicon carbide of mesh size 46 to 150 produces a reasonably fine matter surface on parts with heavy burrs. Aluminum oxide has a cutting action, and silicon carbide has a planing action.

Preshaped abrasives of various sizes and shapes also may be used. Although more expensive than material in its natural form, preshaped abrasives permit a more constant and uniform polishing action, are more effective in holes and recesses, and retain their effective cutting shape for a longer period of use.

**Compounds.** Parts heavily coated with grease or oil or contaminated with dirt or chips should be degreased before mass finishing, preferably in a separate barrel, dip tank, or degreaser. A better practice is to clean parts in the barrel when progressing from rough to finishing cycles and to bright dip before burnishing. A sulfuric-nitric acid or sulfuric acid-hydrogen peroxide bright dip should be used if plating follows burnishing.

Soft water and neutral compounds are preferred for mass finishing copper and copper alloys. The use of liquid soap-free alkaline compounds for mass finishing highly leaded, free-cutting brasses prevents the formation of lead soaps that impair the effectiveness of the operation.

Compounds for mass finishing are classified according to the following categories and are purchased as proprietary materials:

- *Cleaning compounds* possess high detergency and buffering action for removing oils, greases, and residues.
- *Descaling compounds* are used to remove tarnish from copper alloys; neutralizing cycles usually follow the use of these compounds.
- *Grinding compounds* are used with abrasive mediums for softening the water, saponifying oils, and keeping chips clean; these compounds inhibit tarnish and improve the color of parts.
- *Abrasive compounds* contain grits such as aluminum oxide, silicon carbide, emery, quartz sand, or pumice.

**Surface Finishes.** Although mass finishing produces the final finish for many parts, it is used more extensively for cleaning prior to plating and painting or for deburring and polishing before a final finish is applied. Examples of mass finishing applications are given in Table 6.

**Table 6 Operating conditions for mass finishing**

| **Material** | **Medium** | **Size of abrasive particles** | | **Tumbling time, h** | **Finish** |
|---|---|---|---|---|---|
| | | **mm** | **in.** | | |
| **Heavy cutting** | | | | | |
| Brass or bronze castings | Aluminum oxide | 6.4-19 | 0.25-0.75 | 6-16 | Matte |
| **Moderate cutting** | | | | | |
| Brass stampings | Aluminum oxide | 6.4-19 | 0.25-0.75 | 1-6 | Light matte |
| Brass screw-machine parts | Aluminum oxide or granite | 6.4-19 | 0.25-0.75 | $\frac{1}{2}$-6 | Light matte or bright |
| **Light cutting**(a) | | | | | |
| Brass stampings or screws(b) | Limestone | 3.2-13 | 0.13-0.50 | 2-6 | Bright |

(a) Submerged tumbling is used for fragile and precision parts.

(b) Screw-machine parts

Bright rolling or water rolling in a barrel is an economical bulk method of finishing small parts. The finishes may be dull, semibright, or of high luster. This operation consists of tumbling the parts in water containing a suitable additive. The water acts as the carrier for the fine burnishing materials. Selection of additive and cycle time controls the surface roughness, stock removal, color, and reflective luster. Examples of water rolling applications are given in Table 7.

### Table 7 Operating conditions for bright rolling or water rolling

Solutions are used at room temperature. Time, 20-60 min. Resulting surface has bright finish.

| **Parts** | **Weight of load** | | **Additive**(a) | **Water** | | **Speed, rev/min** |
|---|---|---|---|---|---|---|
| | **kg** | **lb** | | **L** | **gal** | |
| Blanks or buttons, copper(b) | 363-408 | 800-900 | Cream of tartar | 95 | 25 | 32 |
| Gripper post, nickel over brass | 136 | 300 | Proprietary(c) | 95 | 25 | 32 |
| Fragile tubular part, brass(d) | 18 | 40 | Proprietary | 20 | 5 | 7 |

(a) 9 g/L (1 oz/gal).

(b) Removal of burrs.

(c) Additive containing sodium bicarbonate, cream of tartar, sodium acid pyrophosphate, sodium sulfite, and a wetting agent.

(d) Wall thickness is 0.150 mm (0.006 in.).

A prime consideration for successful water rolling is the cleanness of the parts. Oil, grease, scale, and dirt should be removed before rolling for luster. Basic cleaning and pickling operating conditions used before water rolling are given in Table 8.

### Table 8 Operating conditions for cleaning and pickling in water rolling barrels

Barrel is made of Type 304 stainless steel. Speed of rotation, 7-32 rev/min; cycle time, 15-20 min. Parts are thoroughly rinsed in hot water after cycle is finished

| Solution | Concentration | Temperature | |
|---|---|---|---|
| | | °C | °F |
| Alkaline cleaner[a] | 15-20 g/L (2-3 oz/gal) | 71 | 160 |
| Pickling solution[b] | 1-2% | 54 | 130 |

(a) Sodium hydroxide or proprietary compound.

(b) $H_2SO_4$

For economy, cleaning and pickling should be done in the same barrel by the same operator. For example, oily gripper parts from eyelet machines are placed in an oblique stainless steel barrel and cleaned by a suitable alkaline cleaner. After rinsing, the parts are pickled in a 1 to 2% sulfuric acid solution and rinsed. Clear water and additives, burnishing compounds, are added, and the parts are rolled until the desired finish is obtained. If the work appears to darken during water rolling, the medium should be dumped, the barrel and parts rinsed and then charged with a fresh burnishing compound. Parts suitable for water rolling to a bright finish include posts, sockets, studs, tack buttons, and zipper parts.

**Vibratory finishing** is particularly effective for deburring, forming radii, descaling, and removing flash from castings and molded parts. It may also be used for burnishing. Vibratory finishers deburr parts 50 to 75% faster and are more versatile than rotary tumbling barrels. There is no cascading of parts, with the attendant possibility of damage by impact. The process is adaptable to both light castings and formed parts. Vibratory finishing is also effective on internal surfaces and recesses that are not usually worked by rotary tumbling.

The mediums for vibratory finishing of copper and copper alloys are similar to those used for rotary tumbling. Dry mediums are used occasionally, but usually a liquid is added to provide lubrication, suspension of worn-off particles, and a more gentle cleaning action. The selection of medium is frequently by trial and error. Conditions for vibratory finishing are given in Table 9.

**Table 9 Operating conditions for vibratory finishing**

| Machined part diam | | Material | Medium | Parts per load | Ratio of medium to parts[a] | Vibrations per min | Time, min | Purpose |
|---|---|---|---|---|---|---|---|---|
| mm | in. | | | | | | | |
| 25 | 1 | Nickel silver | Steel pins and quartz sand | 650 | 4 to 1 | 1500 | 40 | Deburr |
| 38 | $1\frac{1}{2}$ | Brass | Steel wire brads | 500 | 2 to 1 | 1300 | 60 | Deburr and form radii |
| 75 | 3 | Brass | Arkansas stone | 150 | 10 to 1 | 1500 | 35 | Deburr and finish |

(a) 0.03 $m^3$ (1 $ft^3$) bowl

Additional information is contained in the article "Mass Finishing" in this Volume.

## Polishing and Buffing

Copper alloy parts are polished after scale removal and dressing or rough cutting, but before final finishing operations, which include buffing, burnishing, or honing. Rough castings normally require two polishing operations before buffing. Forgings and stampings require one polishing operation before buffing. Pipe, tubing, and some stampings can be buffed without previous polishing. Buffing is not required when a brushed or satin finish is desired as the final finish.

Because copper-base materials are softer than steel, fewer stages of successively finer polishing are required to achieve a uniformly fine surface finish. For many parts, especially those having machined surfaces or those free of defects, a single-stage polishing operation using 180- to 200-grit abrasive on a lubricated belt or setup wheel may be all that is required before buffing. Poor-quality surfaces require preliminary rough polishing on a dry belt or wheel with 80- to 120-grit abrasive. Surfaces of intermediate quality may be given a first-stage polishing with 120- to 160-grit abrasive, either dry or lubricated. Belt polishing is generally advantageous for high-production finishing except when special shapes are processed. These are best handled by the contoured faces of setup polishing wheels.

Buffing of copper and copper alloys is usually accomplished with standard sectional cloth wheels operating at moderate speeds of 1200 to 1800 rev/min. Typical wheel speeds for various finishes are:

| Finish | Wheel speed | |
|---|---|---|
| | m/min | ft/min |
| Dull[a] | 915-1675 | 3000-5500 |
| Satin | 1220-1830 | 4000-6000 |

| | | |
|---|---|---|
| Cutting and coloring | 1675-2135 | 5500-7000 |
| High luster[(b)] | 2135-2440 | 7000-8000 |

(a) Using 120- to 200-grit aluminum oxide.

(b) Using tripoli, lime, and silica with no-free-grease binder

When it is necessary to mush a buff to the contour of a complicated part, buffing speeds may range between 200 and 1000 rev/min.

Neutral compounds that are free of sulfur must be used to avoid staining in the plating operation when polishing and buffing precede electroplating. Excessively high temperatures during polishing and buffing may cause difficulties in subsequent cleaning and plating operations. When flawless chromium-plated surfaces are required, it is necessary both to buff and color buff the polished copper alloy surfaces before plating. Chromium reproduces all imperfections in the underlying plating or base metal, and because chromium is hard and has a high melting point, it is more resistant to flow and is not readily buffed by normal methods. A good chromium-plated surface can be obtained without the color buff operation, by only polishing and cut-down buffing. An example of offhand belt polishing and wheel buffing operations is given in Table 10.

**Table 10 Offhand belt polishing and wheel buffing operations for sand cast red brass parts**

Sand cast lavatory fittings made of red brass are finished in a sequence of six operations in preparation for decorative chromium plating; sequential finishing of spout with flat surfaces

| **Operation** | **Type of contact wheel** | **Wheel speed, rev/min** | **Pieces per hour** | **Type of abrasive belt** | **Belt life, pieces** | **Polishing lubricant or buffing compound** |
|---|---|---|---|---|---|---|
| Rough polishing | Cloth[(a)] | 2100 | 23 | 80-grit silicon carbide | 29 | None or light application of grease stick |
| Final polishing | Cloth[(a)] | 2100 | 30 | 220-grit $Al_2O_3$ | 49 | Grease stick |
| Spot polishing | Cloth[(a)] | 2100 | 46 | 220-grit $Al_2O_3$ | 77 | Grease stick |
| General buffing | Spiral-sewn, treated cloth sections with intermediate airway[(b)] | 2400 | 32 | . . . | . . . | Tripoli |
| Spot buffing | Spiral-sewn, treated cloth sections with intermediate airway[(b)] | 2400 | 115 | . . . | . . . | Tripoli |
| Color buffing | Spiral-sewn, treated cloth sections with intermediate airway[(b)] | 1700 | 75 | . . . | . . . | Silica compound |

(a) 355 mm (14 in.) diam, 45 mm ($1\frac{3}{4}$ in.) width, 90 density.

(b) 355 mm (14 in.) diam, 60.3 mm ($2\frac{3}{8}$ in.) width, 18 ply, 86/93

**Scratch brushing** is used to produce a contrasting surface adjacent to a bright reflective surface; to produce an uneven surface for better paint adherence; to remove metal during final finishing of parts with intricate recesses that are inaccessible to polishing and buffing wheels; and to remove impacted soil and buffing compounds from previous finishing operations, prior to subsequent finishing in some applications.

Various types of scratching mediums are used to produce different finishes, such as butler, satin, directional, sunburst (or circular), and matte. These mediums are as follows:

- *Wire wheels* are used on copper or brass grill work to clean intricate recesses, holes, or ribbed areas and to produce a decorative noncontinuous scratch pattern on ornamental parts such as vases, lamps, and kitchenware.
- *Emery cloth or paper* is a common medium for producing a series of linear or circular parallel lines on flat objects with no sudden changes in contour. This type of decorative finish is applied to fireplace accessories, automotive hub caps, and kitchenware and appliances.
- *Polishing wheels headed with greaseless compounds* produce scratch-brush finishes with parallelism of the directional pattern. Decorative items such as jewelry, building paneling, and built-in refrigerator and stove parts can be finished in this manner.
- *Soft tampico and manila brushes* remove soil from scrollwork and embossed areas on ornate tableware serving sets and jewelry prior to final processing.

Table 11 gives the sequence of operations and mediums for scratch-brush finishing several copper alloy products.

**Table 11 Suggested sequence of operations for scratch brushing of copper alloy parts**

| Part | Finish desired | Abrasive | Type of wheel | Size of wheel | | Speed, rev/min |
|---|---|---|---|---|---|---|
| | | | | mm | in. | |
| Black fuse body, yellow brass[a] | Dull, smooth, black | None | Tampico | 80 diam by 75 thick, 5 rows wide | 7 diam by 3 thick, 5 rows wide | 1200 |
| Silver-plated red brass lipstick case[b] | Semibright | Solution of soap bark and cream of tartar | Nickel-silver wire, 0.100 mm (0.004 in.) diam | 150 diam by 75 thick, 6 rows wide | 6 diam by 3 thick, 6 rows wide | 850 |
| Black-on-bronze bookends, highlights relieved[b] | Black background with colored copper highlights | Pumice in water | Cloth, sewn sections | 180 diam by 13 wide | 7 diam by $\frac{1}{2}$ wide | 850 |
| Silver-plated lipstick | Satin | Greaseless rouge, | Loose cloth wheel | 150 diam by | 6 diam by 2 | 1800 |

|  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|
| cap[c] |  | proprietary |  | 51 wide | wide |  |
| Nickel-plated refrigerator panels or stove parts[d] | Satin | Greaseless compound | Loose cloth wheel | 305 diam by 50-510 wide | 12 diam by 2-20 wide | 1800 |

(a) Clean brush often by running pumice stone across face of wheel.

(b) Lacquer after scratch brushing.

(c) Lacquer after finishing.

(d) Chromium plate after finishing

Although scratch-brush finishing is useful for producing eye-appealing finishes and as a mechanical means for preparing surfaces for subsequent processing, certain hazards must be recognized. Extreme care and control are required when the part being worked contains patterns with sharp corners or embossments, because the sharpness of detail may be destroyed. In salvage or rework operations, it is difficult and sometimes impossible to blend the original brush pattern into a repaired area from which a defect has been removed by grinding.

### *Chemical and Electrochemical Cleaning*

During fabrication, copper alloys may become coated with lubricating oils, drawing compounds, greases, oxides, dirt, metallic particles, or abrasives. These must be removed by cleaning. The selection of the cleaning process depends on the type of lubricant and other materials to be removed, the equipment available, the environmental restrictions, and the degree of cleanness required. The nature and size of the pieces also influence the selection of equipment or process.

Where permissible, mechanical scrubbing, accomplished by turbulent boiling, pressure spraying, or agitating, aids in the removal of any substances that are not exceptionally adherent. Occasionally, hand brushing may be used for small production quantities.

Lubricants made from animal or vegetable oils or greases, such as tallow, lard oil, palm oil, and olive oil, can usually be removed by saponification. In this process, the parts are immersed in an alkaline solution where the oil reacts with the alkali to form water-soluble soap compounds. Mineral oils that are not saponifiable, such as kerosine, machine oil, cylinder oil, and general lubricating oils, are usually removed from the metal by emulsion cleaning.

Dirt particles, abrasives, metal dust, and inert materials are removed by one or both of these processes. To remove undesirable materials by saponification, emulsification, or similar means, it is necessary to use particular chemicals or combinations of chemicals.

**Solvent Cleaning and Vapor Degreasing.** Solvent cleaning of copper alloys involves immersion in special naphthas with flash points over 38 °C (100 °F) for the removal of light grease and light oil. An example of this type of naphtha is Stoddard solvent. These solvents are preferred to kerosine and to the naphthas used in paints, because less residue remains on the work after the special naphthas have evaporated.

The straight-chain naphthas are not effective for complete removal of heavy grease, burned-on hydrocarbons, pigmented drawing compounds, and oils containing solid contaminants. Buffing compounds containing tallow, stearic acid, and metallic soaps require cyclic hydrocarbons such as toluol and xylol for effective cleaning. Table 12 gives cycles for solvent cleaning of copper alloys.

**Table 12 Cycles for cleaning copper alloy parts with a solvent cleaner**

| **Part** | **Solvent cleaner** | **Temperature of solvent** | | **Immersion time, min** | **Soil removed** |
|---|---|---|---|---|---|
| | | **°C** | **°F** | | |
| Dose cap[(a)] | Stoddard solvent or mineral spirits | RT to 49 | RT to 120 | 2 | Heavy drawing compound |
| Brass retainer ring[(a)] | Stoddard solvent or mineral spirits | RT to 49 | RT to 120 | 2 | Eyelet machine lubricant |
| Brass rods | Sawdust, dampened with Stoddard solvent or mineral spirits | RT | RT | 5[(b)] | Mill lubricant |

RT, room temperature.

(a) Hand cleaning necessary with fragile parts.

(b) Tumbled in barrel

Chlorinated solvents such as methylene chloride (boiling point, 40 °C, or 104 °F), trichloroethylene (boiling point, 90 °C, or 189 °F), and perchloroethylene (boiling point, 120 °C, or 250 °F) have been used instead of naphtha. These compounds are less of a fire hazard than straight petroleum solvents but are much more toxic. Because of environmental constraints their use is gradually being curtailed.

Vapor degreasing effectively removes many soils from copper alloys. Stabilized trichloroethylene is used extensively in vapor degreasing because it does not attack copper alloys during degreasing and because it has high solvency for the oils, greases, waxes, tars, lubricants, and coolants in general use in the copper and brass industry. Perchloroethylene is used especially for removing high-melting pitches and waxes, for drying parts by vaporizing entrapped moisture, and for degreasing thin-gage materials.

Vapor degreasing or solvent cleaning is not effective for removing inert materials and inorganic soils such as metal salts, oxides, or compounds that are not generally soluble in chlorinated solvents. Similarly, vapor degreasing for removal of hard and dry buffing compounds could leave behind the insoluble and hard-to-clean abrasives. Solvent emulsion cleaners, although slow, are highly effective for complete removal of buffing compounds.

Solid particles of metal dust or chips that are held on the surface by organic soil can be removed mechanically by the washing action of the solvent. Removal of these particles is accelerated and accomplished better with solvent sprays or by immersion in boiling solvent than with the vapor phase of the degreaser.

**Emulsion and Alkaline Cleaning.** Parts with heavy soils such as machine oils, grease, and buffing compounds are treated first with emulsion cleaners to remove most of the soil. After the parts have been rinsed, the remaining soil is removed by alkaline soak or electrolytic cleaning. Precleaning reduces the contamination of the alkaline solution, extending the life of the solution. Thorough alkaline cleaning must follow the emulsion cleaning cycle before the subsequent acid cycles. Extreme caution must be exercised to avoid dragging emulsifiers through the rinses and into a plating solution, especially an acid solution.

Emulsion cleaning may be accomplished by soaking the work for 3 min or less in a mildly agitated solution. Spraying is helpful only when all surfaces being cleaned can be thoroughly contacted. The thin film of oil remaining after emulsion cleaning acts as a temporary tarnish preventive. Some parts may be stored after drying, depending on the composition of the solution and the metal being cleaned; however, brass may become pitted by prolonged exposure to certain emulsifier films. When emulsion-cleaned zinc-bearing brass parts are cleaned electrolytically by alkalines, sufficient time should be allowed for the dispersal of the emulsifier in the alkaline solution to avoid pitting.

The environmental restrictions placed on the use of chlorinated solvents have resulted in the industry turning more and more to alkaline cleaners for degreasing copper and its alloys. Table 13 lists typical compounds from which these are formulated. A great number of these cleaners, which usually contain proprietary additives, are available on the market. Selection of a cleaner is best achieved by a test program in which several cleaners are evaluated. However, the most critical factor in their effective use is to ensure vigorous flow of the cleaner across the parts being cleaned. Additional information is available in the article "Vapor Degreasing Alternatives" in this Volume.

### Table 13 Compounds used for formulating alkaline cleaners

| Component | Soak cleaners, % | Electrolytic cleaners, % |
|---|---|---|
| Sodium hydroxide | 10-20 | 10-15 |
| Sodium polyphosphates | 5-20 | 5-20 |
| Sodium orthosilicate, sesquisilicate, metasilicate | 30-50 | 30-50 |
| Sodium carbonate, bicarbonate | 0-25 | 0-25 |
| Resin-type soaps | 5-10 | None |
| Organic emulsifiers, wetting agents, chelating agents | 2-10 | 1-3 |

Solutions for soak cleaning usually contain 30 to 60 g/L (4 to 8 oz/gal) of cleaner and are operated at 60 to 88 °C (140 to 190 °F). For every 6 °C (10 °F) rise in temperature above 60 °C (140 °F), the cleaning time is reduced by about 25%. Regardless of the concentration of the cleaning solution, there is a practical limit to the amount of contamination a given volume can accommodate without redepositing soil on the metal. In this condition, the solution should be discarded even though analysis reveals unused cleaner.

Dissolved air in fresh cleaning solutions is frequently the cause of tarnishing of copper alloys. The air can be eliminated by heating the solution to the boiling point for about $\frac{1}{2}$h before use. This procedure may not be advisable with every proprietary cleaner because of constituents that break down at the boiling temperature. Some uninhibited alkaline cleaners may also cause a slight darkening or tarnishing of the work surface. The darkening may be removed by dipping in dilute hydrochloric acid or in cyanide solution.

**Electrolytic alkaline cleaning** is the most reliable method for cleaning parts for plating. The work is the cathode, and steel electrodes are the anodes. Reverse-current anodic cleaning cannot be used for more than a few seconds because copper dissolves in the solution. Copper alloys will tarnish readily during exposure to the oxygen that is released at the anode, but this can be minimized by the addition of inhibitors. In many electroplating operations, anodic cleaning for a few seconds is used to develop tarnish, because it indicates that all soil has been removed. The small amount of metal dissolved by anodic cleaning exposes a more active surface for electroplating, and the light tarnish formed is readily dissolved by a mild hydrochloric or sulfuric acid solution. Current density during anodic electrocleaning of brass should be about 3 A/dm$^2$ (30 A/ft$^2$) at 3 to 4 V. Use of high currents will etch the brass and cause dezincification.

Copper-base materials are electrolytically cleaned by cathodic cleaning followed by short-time anodic cleaning, or by soak cleaning followed by anodic cleaning. Positively charged particles plated onto the work during cathodic cleaning cause smut, which may lead to blistering and poor adhesion of the plated metal if not completely removed. To avoid this condition, a short period of anodic cleaning should follow the cathodic electrocleaning.

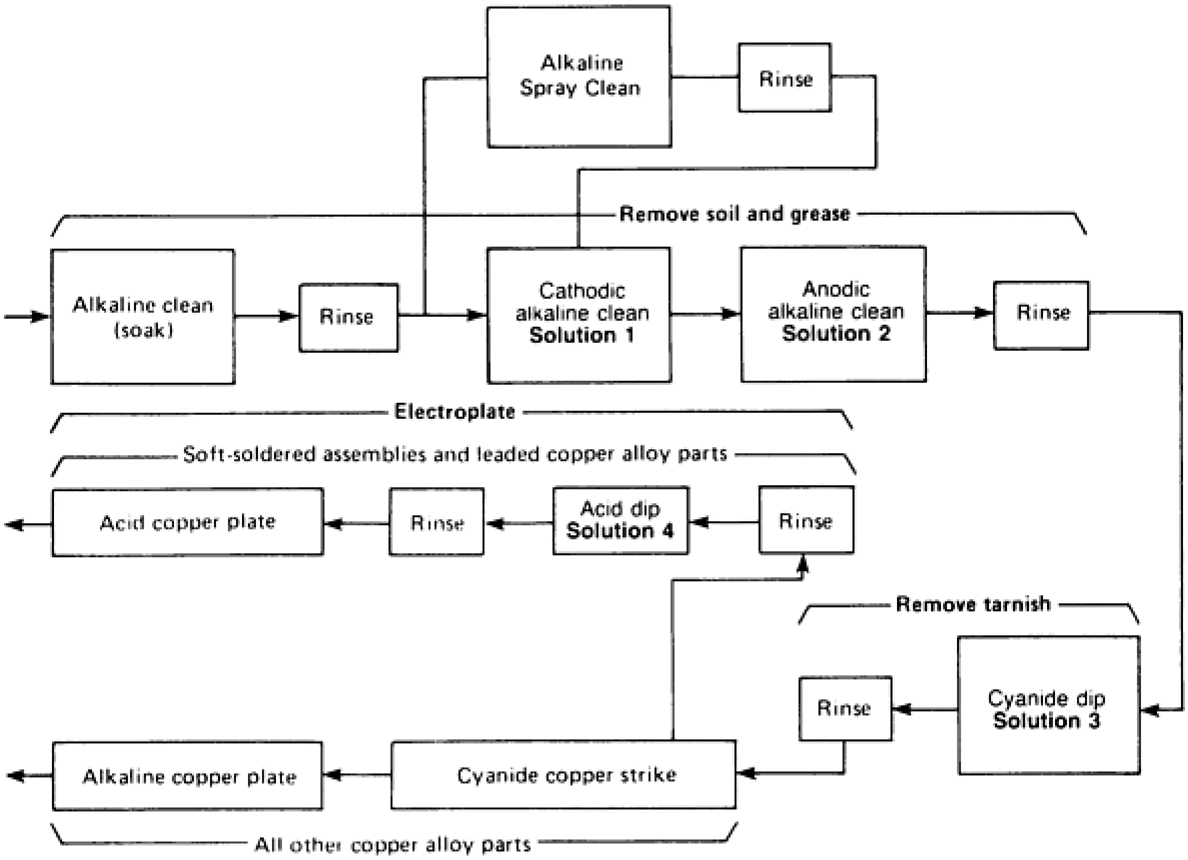
Racks and baskets that are used during the application of chromate chemical conversion coatings should not be used in alkaline cleaning solutions. Contamination of the cleaning solution with as little as 10 ppm of hexavalent chromium can cause poor adhesion and blistering of subsequent metal deposits. To avoid the effects of accidental contamination when chromate treatments are used, sodium hydrosulfite should be added to the cleaning solution at the rate of 14 g ($\frac{1}{2}$ oz) per 380 L (100 gal). The sodium hydrosulfite reduces hexavalent chromium to trivalent chromium, which does not affect subsequent plating. Periodic additions are required because trivalent chromium is reoxidized to hexavalent by the oxygen released at the anode.

**Ultrasonic cleaning** of copper-base materials is used when the size of particles remaining on the surface is less than 5 to 10 μm (0.2 to 0.4 mils) in any one direction and for removing dirt and chips that cause smudge, as indicated by a white cloth wipe test. Remove much of the surface contamination by other more economical cleaning procedures before ultrasonic cleaning. This increases the life of the ultrasonic cleaning solution and maintains production efficiency. After ultrasonic cleaning, the parts may be rinsed in deionized or distilled water and dried with warm filtered air or in a vacuum oven.

Ultrasonic cleaning is used with alkaline cleaning solutions, solvents, vapor degreasing solutions, or acid pickling solutions to increase the rate of cleaning or to complete the removal of soil from areas not completely cleaned by soak or spray procedures. An example of the need for ultrasonic assistance is the cleaning of fine internal threads on brass parts. An alkaline solution containing 15 to 30 g/L (2 to 4 oz/gal) of cleaner may be used for ultrasonic cleaning of such parts.

## Plating and Coating

**Preparation for Plating.** Before copper alloys are plated, surface oxides are removed and the surfaces chemically activated for adherence of the plate. Heavy oxide scales are usually removed at the mill, so descaling is not normally a part of the preplate treatment. Figures 1 and 2 show sequences of operations required for preparing the surfaces of copper alloys. These operations apply to both lead-free and leaded materials and to soft-soldered assemblies. For many plating operations, where the copper alloy is relatively clean, free of oils, and uncontaminated by buffing compounds, the process can be simplified by eliminating the alkaline soak. If the surface contains buffing compounds, it may require precleaning by soaking in emulsion cleaners. Many plating processes do not use the anodic alkaline clean, especially when an acid dip is used after the cathodic alkaline clean. The acid dip suffices to remove any smut or stain. An acid dip may be simply 15% sulfuric acid or, if the surface needs additional pickling, a bright dip may be used. There are a number of bright dips for copper alloys on the market based on the sulfuric acid-hydrogen peroxide system (see Table 1), in addition to the example in Fig. 2. A chromate bright dip should not be used before plating because of possible chromium contamination of the plating bath, which could lead to blistering, pitting, and peeling of the electrodeposit.



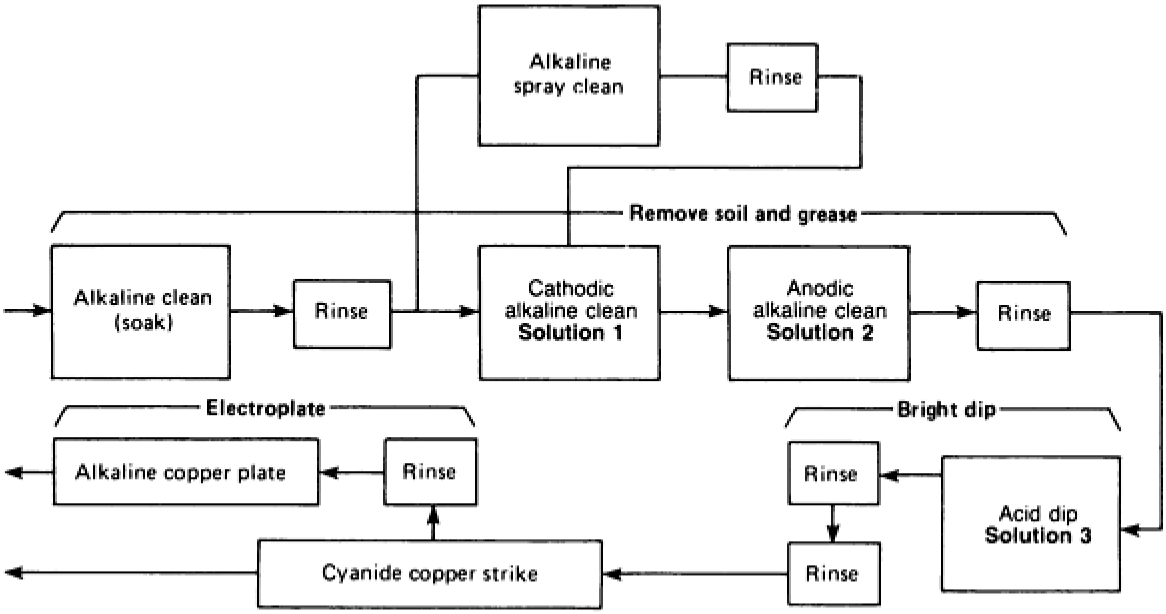
| Solution No. | Type of solution | Composition of solution[(a)] | Operating temperature | | Cycle time,s |
|---|---|---|---|---|---|
| | | | °C | °F | |
| 1 | Cathodic alkaline cleaner[(b)] | $Na_2CO_3H_2O$, 40-50%; $Na_3PO_4 \cdot 12H_2O$, 25-40%; NaOH, 10-25%; $Na_2SiO_3$, 15-40% | 60-71 | 140-160 | 60-180 |
| 2 | Anodic cleaner[(b)] | Same as Solution 1 | 60-71 | 140-160 | 5-10 |
| 3 | Cyanide dip | NaCN, 15-45 g/L (2-6 oz/gal) | Room | Room | 30 |
| 4 | Acid dip | $HBF_4$, 5-10% | Room | Room | 5-10 |

(a) By volume, except where otherwise noted.

(b) Current density 1 to 3 A/dm$^2$ (10 to 30 A/ft$^2$), 3 to 4 V

**Fig. 1 Surface preparation required for removal of buffing compounds and tarnish before plating of copper**

**alloys. If the buffing compound is hard and dry, an additional presoak in a solvent emulsion cleaner can be used.**



| Solution No. | Type of solution | Composition of solution[(a)] | Operating Temperature | | Cycle time,s |
|---|---|---|---|---|---|
| | | | °C | °F | |
| 1 | Cathodic alkaline cleaner[(b)] | $Na_2CO_3 \cdot H_2O$, 40-50%; $Na_3PO_4 \cdot 12\ H_2O$, 25- 40%; NaOH, 10-25%; Surface active agent, 1% | 60-71 | 140-160 | 60-180 |
| 2 | Anodic cleaner[(b)] | Same as solution 1 | 60-71 | 140-160 | 5-10 |
| 3 | Bright dip[(c)] | $H_2SO_4$, 65-75%; $HNO_3$, 20-35%; HCl, 1.1 g/L ($\frac{1}{6}$ oz/gal); $H_2O$, 5-10% | Cool | Cool | 5-10 |

(a) By volume, except where noted.

(b) Current density, 1 to 3 A/dm$^2$ (10 to 30 A/ft$^2$), 3 to 4 V.

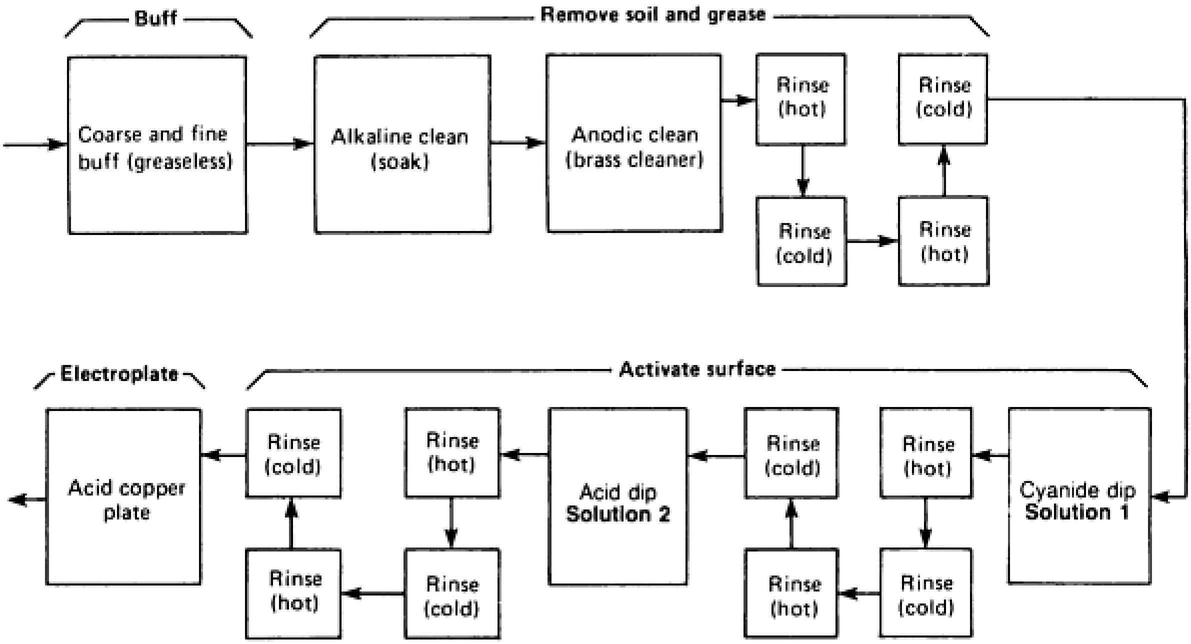
(c) Constant agitation of work

**Fig. 2 Surface preparation required for the removal of buffing compounds and for bright dipping before plating of copper alloys**

Oxides can be removed from cast or heat-treated copper alloys by either abrasive or chemical cleaning procedures. Castings always require abrasive cleaning; however, they do not necessarily require subsequent pickling or bright dipping for the removal of oxides. If acid treatment is required, thorough rinsing is mandatory to prevent spotting of the plating by entrapped acid. Stampings and drawn parts can be treated in the same manner as castings; however, it may be less expensive to pickle the parts before abrasive finishing if heavy oxides are present. Screw-machine parts made of leaded copper alloys usually require no treatment for oxide removal before plating, but abrasive cleaning can be used when required.

***Beryllium Copper.*** Surface preparation procedures for beryllium copper are the same as for other copper alloys, unless the beryllium copper has been heat treated and still contains surface oxides resulting from that heat treatment. Such oxides on beryllium copper are more difficult to remove than normal oxides on other copper alloys. They can be best removed in strong, hot caustic solutions followed by a good bright dip. The procedure outlined in Fig. 2 should be sufficient if the bright dip cycle is increased to 10 to 15 s. The sulfuric-peroxide bright dips also work well on beryllium copper. The alkaline soak clean and the anodic alkaline clean may or may not be required, depending on the degree of surface contamination resulting from heat treatment. In rare cases, the plater is required to remove scale resulting from high-temperature (>400 °C, or 750 °F) heat treatments such as in solution annealing. The parts must be soaked in a 50% solution of sodium hydroxide at 130 °C (265 °F) for 1 or 2 min before acid pickling in a good bright dip.

***Powder Metallurgy Parts.*** Technology has advanced to a level where parts sintered from metal powders are not as porous and can be easily electroplated. A sequence of operations for surface preparation of powder metallurgy (P/M) parts before electroplating is shown in Fig. 3. Because P/M parts are made from different alloys and because porosity varies, a suitable surface preparation and electroplating technique must be developed for each part.



| Solution No. | Type of solution | Composition of solution | Operating temperature | Cycle time, s |
|---|---|---|---|---|
| 1 | Cyanide dip | NaCN, 7.5 g/L (1 oz/gal) | Room temperature | 30-60 |
| 2 | Acid dip | $H_2SO_4$, 3-5 vol% | Room temperature | 5-10 |

**Fig. 3 Surface preparation of brass powder metallurgy parts before plating**

The methods applicable to porous cast parts can be used for low-porosity P/M parts with densities more than 95% of theoretical. P/M strip stock bonded to steel is an example of low-porosity material. The surface preparation and plating techniques vary for higher-porosity parts with densities 85 to 90% of theoretical.

During plating of P/M parts, the pores act as thermal pumps. Solutions are released from or absorbed by the pores, depending on whether the solution is hotter or colder than the part. Deep and interconnecting pores are likely to entrap cleaning or rinsing solutions, which are released slowly during plating. Porosity must be determined before cleaning, and suitable techniques must be used to prevent solution entrapment. Entrapped solutions may cause precipitation of metal compounds on the work surfaces during plating. The porous nature of P/M parts causes contamination and depletion of all solutions and necessitates that the solutions be closely controlled.

Spotty plating is caused by entrapped solutions that seep out of the pores and stain the plated surface as it dries. Spots may not develop for several days after plating or may appear to be insignificant immediately after plating and subsequently enlarge with time.

A continuous plated coating can seldom be attained on P/M parts unless the pores are closed. Methods for closing the pores include buffing, rolling, burnishing, heat treating, and impregnation. Buffing, rolling, or burnishing are used when appearance is important and dimensional tolerances are not critical. These techniques can be applied either before or after plating. Heat treating is one of the most satisfactory methods for closing pores when surface quality and size are more important than appearance. Occasionally, green compacts are electroplated and then sintered. Another technique is to sinter fully, then to plate and heat treat. This procedure requires washing and acid dipping the parts to neutralize alkalinity prior to heat treating.

Impregnation with copper, lead, tin, waxes, resins, or oils is another method for closing the pores of P/M parts before plating. Thermosetting polyester styrene and silicone resins are suitable impregnating materials. When the polyester-styrene resin is used, the parts are degreased, baked to remove moisture, then impregnated under vacuum and pressure. An emulsion cleaner can be used to remove excess resin from blind holes and threads prior to curing the resin at 120 to 150 °C (250 to 300 °F). Tumbling or polishing can be used to remove excess cured resin.

When silicone resin is used, the surfaces of the powder compact are coated with a thin water-repellent film. Then the compact is heated in air to 205 °C (400 °F), quenched in a solution of 4% silicone (type 200) and 96% perchloroethylene, and baked again for $\frac{1}{2}$ to 2 h. After being pickled in acid, the part can be plated in the conventional manner, preferably in an alkaline bath.

Before being impregnated with oil, the parts are heated in a vapor degreaser and, while hot, immersed in cold oil. After cooling in the oil, the parts are removed, drained of oil, and then rinsed in cold solvent. Parts impregnated with oil have been coated with copper by conventional electroplating processes with resultant satisfactory bonding of the coating.

**Evaluation of Cleanness Prior to Plating.** The degree of cleaning required for a copper alloy part depends on its intended end use. In some cases visual observation of the cleaned part is sufficient to determine if adequate cleaning has been accomplished. However, cleaning conducted prior to deposition processes must be very thorough, and methods of evaluating the surface cleanness are often required. For metal that has been degreased, this evaluation can be best achieved by spraying the part with water from an atomizer; areas that are clean show up as a continuous film, while areas that have been inadequately cleaned are covered with small water droplets.

Another technique for evaluating the cleanness of small parts involves suspending them in the mouth of a beaker containing a few mils of 10% ammonium sulfide. After an exposure time of 5 to 10 s, a uniform tarnish film will appear over clean areas. Nonuniformity in the color of the tarnish film indicates the presence of residual soils. With practice, the tarnishing test can provide a rapid assessment of the efficiency of a particular cleaning process. For safety reasons the test must be conducted in a fume hood.

It is often difficult to determine if residual oxides remain on a copper alloy surface following pickling operations, particularly if the oxides are of the refractory type. One evaluation method consists of first immersing the part in rosin flux and then in 60-40 tin-lead solder held at 246 °C (475 °F) for 5 s. The resultant solder coating is compared to the solder coating on a part that is known to be clean. Areas still covered with oxide will appear as areas not wet by the solder.

## Electroless Plating

Electroless plating involves the reduction of a metal salt to its metallic state by electrons supplied from the simultaneous oxidation of a reducing agent. The electroless plating solutions are compounded so that the concentration of the reducing salts, metal salts, buffering salts, and the pH controls the rate of reduction of the metal salt and of the oxidation of the reducing agent. If these reactions are not controlled, the metal deposit is reduced spontaneously to a fine powder. The metal to be plated acts as a catalyst and localizes the deposit of the plate to the part itself. Electroless plating completely plates uniform deposits to any thickness desired over intricately shaped parts or assemblies and into deep recesses and long tubular holes. Fine and close-fitting threads can be plated uniformly over the entire threaded area.

On copper-base materials, the process is limited to the plating of nickel, tin, gold, and silver deposits. Solutions for plating these deposits are affected adversely by contaminants, such as cyanides, lead, zinc, manganese, and cadmium. Tin may render the nickel plating solution inoperative; therefore, tin-containing copper alloys must be plated with copper or gold before a final nickel coating is applied.

Because copper is more noble than nickel, it will not act as a catalyst to start the deposition of nickel. This condition is alleviated by contacting the copper workpiece with an active metal such as iron or aluminum that causes the deposition of a thin nickel coating on the workpiece. The nickel coating is of sufficient thickness to continue the oxidation-reduction reaction for further nickel deposition after the activating metal is removed. Another procedure for starting the deposition of nickel is to make the part cathodic and apply a current briefly to the part as it is held in the electroless bath. Electroless nickel plating is particularly useful for coating deep recesses and holes that cannot be adequately electroplated. The article "Electroless Nickel Plating" in this Volume contains further information on the operating conditions of electroless nickel baths.

Electroless plating processes are used to plate copper with gold and silver for decorative purposes. Nickel, gold, and silver are frequently applied to copper electronic components to prevent tarnishing during subsequent processing and to aid in the soldering of semiconductors. Electroless tin plating has been used for copper tubes to prevent corrosion by carbonated waters.

## Immersion Plating

Immersion plating, sometimes called galvanic plating, depends on the position that the base metal occupies in the electromotive series with respect to the metal to be deposited from solution. Plating occurs when the metal from a dissolved metal salt is displaced by a more active, less noble metal that is immersed in the solution. As the depositing metal is displaced from the bath, metal from the workpiece dissolves in the solution and becomes a contaminant in the bath. Depleted baths are never replenished, but are replaced with fresh solution.

When immersion plating copper-base materials, only those metals more noble than copper can be displaced from solution, thereby limiting this process to metals such as gold and silver. Immersion-plated deposits are thin, usually in the range of 0.050 to 0.50 μm (0.002 to 0.02 mil).

Compositions and operating temperatures of solutions for immersion plating of gold and silver are:

| **Gold plating** | |
|---|---|
| Potassium gold cyanide | 4 g/L ($\frac{1}{2}$ oz/gal) |

| | |
|---|---|
| Potassium or sodium cyanide | 25 g/L ($3\frac{1}{2}$ oz/gal) |
| Sodium carbonate | 30 g/L (4 oz/gal) |
| Temperature of solution | 60 to 80 °C (140 to 180 °F) |
| **Silver plating** | |
| Silver cyanide | 7.5 g/L (1 oz/gal) |
| Sodium or potassium | 15 g/L (2 oz/gal) |
| Temperature of solution | 18 to 38 °C (65 to 100 °F) |

## Electroplating

Metals such as gold, silver, rhodium, nickel, chromium, tin, and cadmium are electrodeposited on copper and copper alloys. Copper electroplating with these metals is used primarily for decorative purposes and for preventing tarnish or corrosion.

**Chromium** is occasionally plated directly onto copper and copper alloys as a low-cost decorative coating and color match. A plated nickel undercoat is applied when quality plating of chromium is required to produce color depth and resistance to corrosion, abrasion, and dezincification.

***Decorative chromium deposits*** are characteristically thin and porous. Galvanic action between the chromium and base metal may occur during exposure to aggressive environments and result in accelerated corrosion. With copper alloys of high zinc content, dezincification and eventual lifting and flaking of the deposit may result. For added protection, chromium deposits plated directly on the base metal are coated with clear lacquers or with the more durable combination coatings of silicone and acrylic thermosetting organic resins.

Decorative chromium deposits are usually 0.25 to 0.50 μm (0.01 to 0.02 mil) thick. When chromium is deposited directly onto the base metal, the thickness of the deposit is seldom less than 38 μm (1.5 mils), and for many applications a minimum of 50 μm (2 mils) is specified. Additional information can be found in the article "Decorative Chromium Plating" in this Volume.

***Hard chromium deposits*** are used primarily to improve wear resistance and friction characteristics. Because most of the copper-base materials are soft and ductile, the base metal lacks sufficient hardness to support thick deposits of hard chromium against heavy pressures without the risk of scoring or flaking. Hard chromium is electroplated from solutions under conditions similar to those used for decorative chromium plating; however, the deposits are much thicker, frequently dull in appearance, and generally deposited directly on the base metal. To conform to exact dimensional tolerances and to avoid buildup of deposit at corners, an excess of deposit is plated and the final dimension is attained by grinding or lapping. Further information can be found in the article "Industrial (Hard) Chromium Plating" in this Volume.

**Cadmium.** Copper-base materials are easily electroplated with cadmium from conventional plating baths. A typical bath has the following composition:

| | |
|---|---|
| Cadmium oxide | 22 to 33 g/L (3.0 to 4.5 oz/gal) |
| Sodium cyanide | 85 to 110 g/L (11.5 to 15.0 oz/gal) |
| Sodium hydroxide | 16 to 24 g/L (2.1 to 3.2 oz/gal) |
| Brightening agent | As required |

Usually, applying an undercoat prior to the deposition of cadmium is unnecessary. Cadmium plating is used to minimize galvanic corrosion between copper-base materials and other cadmium-plated metals in the same assembly. Cadmium-plated copper parts are used in aircraft, marine, and military applications involving atmospheric exposure; however, the use of cadmium is being curtailed because of health and safety concerns associated with its use.

**Gold** is usually applied over an electroplated undercoating of nickel or silver, but may be electroplated directly on the copper alloy. In the electronics industry, nickel is plated to copper before gold plating. The nickel barrier stops migration of copper into the gold layer. The gold thickness is about 2.5 μm (0.1 mil). The nickel barrier is normally a minimum of 1.3 μm (0.05 mil) thick; however, exposure of the gold-plated part to elevated temperatures for extended periods of time may require a nickel barrier 127 μm (5 mils) thick. If silver is the barrier, government specifications for electronic applications usually require a minimum thickness of 5 μm (0.2 mil) of silver and 1.3 μm (0.05 mil) of gold.

When gold is plated directly on copper alloy, a deposit of 3 μm (0.1 mil) or more is needed because of rapid diffusion, especially at elevated temperatures. This rapid diffusion destroys the electrical and decorative properties of the deposit by interdiffusion between the coating and the base metal. Total coverage and freedom from porosity are necessary for corrosion protection.

For greatest adhesion, the part should be plated with a gold strike before the final deposit of gold. One satisfactory strike solution consists of potassium gold cyanide 0.8 g/L (0.1 troy oz/gal as gold) and potassium cyanide 45 g/L (6 oz/gal). To avoid tarnishing, the struck part should be transferred immediately to the plating solution with the current flowing as the work enters the solution. An alternate procedure is to rinse the struck work, then acid dip, rinse, and plate with a suitable current density.

Current density for racked parts varies from 0.2 to 1 A/dm$^2$ (2 to 10 A/ft$^2$), depending on the solution used. The rate of deposition depends on the solution and varies from 100 mg/A · min (0.3 A/dm$^2$, or 3 A/ft$^2$, for 14.4 min deposits 3 μm, or 0.1 mil, of gold) in most cyanide and neutral solutions to one-third of this rate in most acid solutions. For barrel plating, the limiting current density for all solutions is about one-;third of that used in rack plating.

Cyanide solutions are the most efficient and have the best throwing power, whereas deposits from acid and neutral solutions are less porous and are not stained by incompletely removed solution.

Patented solutions for plating gold contain 0.03 kg (1 troy oz) of gold per gallon, usually added as potassium gold cyanide, and proprietary brightening agents. Insoluble anodes are used with these solutions. The patent-free hot gold cyanide solution is extremely sensitive to impurities, and the deposits lack brightness. The solution is limited in application. Gold metal anodes are used with this solution.

The proprietary solutions are brightened or colored by codeposited base metals, especially silver, nickel, cobalt, and copper. These base metals may be classed as impurities for some applications. When gold deposits of less than 0.33 μm (0.013 mil) are used on a plated item, the deposit should be protected by lacquer or a chromate passivation.

**Nickel** is plated onto copper-base materials for decorative purposes and as an undercoating for increased corrosion resistance of nickel-chromium coating systems. Because nickel deposits have a yellow cast and tarnish easily, many nickel-plated parts are finished with electroplated chromium. Costume jewelry, lipstick cases, hardware for doors and windows, automotive hub caps, air valves, and plumbing fixtures are examples of copper-base parts regularly plated with nickel, either as a final coat or an undercoat.

Nickel electrodeposits from some solutions reproduce the irregularities in the base metal surface to a marked degree. The base metal must be polished and buffed before plating if a smooth uniform plated surface is required. Polishing and buffing are not required when nickel is to be plated on a reasonably smooth surface from solutions that produce a high degree of leveling of the deposit as it builds up in thickness. Deposits from these solutions are smooth and bright. Nickel plating with high leveling and brightness can provide an attractive mirrorlike finish. Proprietary leveler brighteners are added to the nickel bath to achieve high leveling with nickel deposits as thin as 7.6 to 10 μm (0.3 to 0.4 mil).

Numerous types of nickel electroplating solutions are available. The solutions differ in basic composition, preferred operating conditions, and quality of the deposit. These are described in the article "Nickel Plating" in this Volume.

Most decorative plating is done in solutions that yield bright or semibright deposits. Although dull nickel deposits may be buffed to a high luster, the cost of buffing limits dull nickel to nondecorative or functional uses.

Black nickel is a decorative finish only. It should be plated over a deposit or base metal that is corrosion resistant. Very thin deposits of black nickel are recommended because thick deposits lack the ductility and adhesiveness required to withstand shock.

**Rhodium.** An undercoat of nickel is used when copper alloys are to be plated with rhodium. For decorative purposes, the thickness of rhodium is usually about 0.25 μm (0.01 mil). Deposits of 25 μm (1 mil) or more are used for functional purposes, but these heavier deposits do not have the brightness or color characteristics of the decorative finishes. Rhodium plating solutions are of the sulfuric acid or phosphoric acid type. Formulas and operating conditions are given in the article "Platinum-Group Metals Plating" in this Volume.

**Silver** plating is used for decorative and functional purposes. Its useful characteristics for functional applications include:

- High surface conductivity for radio frequencies. A minimum of 3 μm (0.1 mil) of silver is required for these applications.
- Low resistance for electrical contacts. The thickness of silver used for electrical contacts ranges from very thin deposits, such as those produced by immersion coating to electroplates 13 μm (0.5 mil) thick.
- Antiseizing or antigalling properties for wear surfaces.

Silver can be deposited as a dull plate from cyanide solutions or as a bright plate from baths containing suitable brighteners. Details of electrolyte compositions and operating conditions are contained in the article "Silver Plating" in this Volume. Plating times for the deposition of 25 μm (1 mil) of silver, as a function of current density, are:

| Current density | | Plating time, min |
|---|---|---|
| A/dm$^2$ | A/ft$^2$ | |
| 1 | 10 | 38 |
| 2 | 20 | 18 |
| 3 | 30 | 13 |
| 4 | 40 | 9 |

Pollution free, proprietary acid silver sulfate plating baths are now also available.

**Tin.** As a protective coating, tin is not necessarily anodic to copper alloys. A copper alloy may not always be fully protected against a corrosive environment at the expense of tin. Some corrosion products of tin are more noble than copper and can create the type of galvanic conditions that lead to pitting corrosion. Tin can be plated from alkaline stannate baths or from sulfate or fluoborate acid baths. For compositions and operating conditions of tin electrolytes, see the article "Tin Plating" in this Volume.

**Tin-Copper Alloys.** The 40 to 50% Sn alloy, speculum metal, has been used as a decorative coating because of its silverlike color. The bronze alloy coatings containing 10 to 20% Sn are producible to match the color of gold and have been used as decorative deposits for this reason. Information on plating bronze alloys is given in the article "Tin Alloy Plating" in this Volume.

**Tin-lead alloys** can be plated on copper alloys in almost any proportion from a fluoborate bath. An alloy of 7% Sn and 93% Pb has been used for corrosion resistance, especially to sulfuric and chromic acids. The 60% Sn, 40% Pb eutectic alloy has excellent solderability and good electrical properties and corrosion resistance. The eutectic alloy may be applied also by hot dipping, but control of thickness is as difficult as with hot dipping in pure tin.

Compositions of solutions for plating 7Sn-93Pb and 60Sn-40Pb (solder) are given in Table 14.

### Table 14 Bath compositions and operating conditions for tin-lead plating

Conditions for operating include a cathode current density of 3 A/dm$^2$ (30 A/ft$^2$); anode to cathode ratio is 2 to 1; solution has maximum pH of 0.2 and is mildly agitated at a temperature of 16 to 38 °C (60 to 100 °F); air agitation cannot be used because it will oxidize the tin.

| Constituent | Total tin | | Stannous tin | | Lead | | Free fluoboric acid | | Free boric acid | | Peptone | | Anode Composition |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | g/L | oz/gal | g/L | oz/gal | g/L | oz/gal | g/L | oz/gal | g/L | oz/gal | g/L | oz/gal | |
| 7Sn-93Pb | 7.0 | 0.94 | 6.0 | 0.80 | 88.4 | 11.8 | 100.0 | 13.4 | 25 | 3.4 | 0.50 | 0.067 | 7Sn-93Pb |

**Chemical or electrolytic polishing** imparts a smooth bright finish and removes burrs selectively from certain areas. Usually the same solution will accomplish both purposes, although variations in operating conditions may be desirable, depending on which feature is required.

For electropolishing, the parts are racked and made the anode in an acid solution. Direct current is applied and the process selectively removes more metal from the high points of the surface than from the low. This results in a high polish and the removal of burrs.

Chemical polishing imparts a finish similar to that obtained by electropolishing, but electropolished surfaces are usually smoother and brighter.

Electropolishing for 4 to 6 min will reduce the surface roughness to between one-third and one-half the original value. Electropolishing and chemical polishing will remove minor scratches and defects, as well as burrs.

Selection of these processes is influenced by the following considerations:

- For complex parts, electropolishing and chemical polishing are easier and less expensive than mechanical polishing.
- Copper-base materials that are polished either electrolytically or chemically do not require the use of buffing or polishing compounds. Thus, they do not encounter the difficulties associated with removal of

entrapped compounds and usually do not require any additional cleaning operations other than rinsing.
- Parts racked for electropolishing may be electroplated in the same racks, which results in considerable savings in handling costs.
- Electrolytically or chemically polished surfaces tarnish less readily than mechanically polished surfaces. Some chemical polishing baths can offer passivation and prevent copper from tarnishing during storage.
- Parts that might deform during mechanical polishing or tumbling will not be deformed by electrolytic or chemical polishing.
- Mechanical polishing may result in a deformed surface layer that differs from the base metal and does not accept plating uniformly. Electroplate on electropolished base metal has adhesion superior to that on mechanically finished surfaces

Parts that are electropolished include fishing lures, plumbing fixtures, furniture arms and legs, lamps and lighting fixtures, wire goods, brass appliance parts, jewelry, nameplates, and bezels. Copper-plated parts, such as automobile tail pipes, die castings that have not been buffed, and high-altitude oxygen bottles are electropolished effectively for an improved finish. The thickness of copper plate should be in excess of 20 μm (0.8 mil) before electropolishing. Most of the commercial solutions used for electropolishing copper alloys contain phosphoric acid with additional agents.

A sequence of operations for electropolishing consists of:

- Racking the parts
- Cleaning to remove oil, grease, dirt, and oxide
- Double rinsing in water at room temperature
- Electropolishing for 2 to 4 min at about 65 °C (150 °F), using a current density of 30 A/dm$^2$ (300 A/ft$^2$)
- Double rinsing in water at room temperature and drying

If the parts are to be electroplated after electropolishing, the drying operation in the above sequence is omitted and the process continues with anodic alkaline cleaning until the surface is light brown in color. Then the parts are rinsed in water at room temperature, dipped in 5% sulfuric acid solution, double rinsed in water at room temperature, immersed in the cyanide copper strike solution, and plated.

The quality of an electrolytically or chemically polished surface is affected by the following factors:

- *Composition of the material*. Most copper alloys are suitable except those containing appreciable amounts of lead, such as the free-machining alloys. Materials successfully treated include copper, beryllium copper, single-phase bronzes, and single-phase nonleaded brasses.
- *Condition of the initial surface*.
- *Grain size of the metal*. The smaller the grain size the better the finish. A grain size of 0.004 mm (0.0002 in.) yields excellent results; satisfactory results are produced with grain sizes up to about 0.01 mm (0.0004 in.).

## Passivation

Passivation refers to the process of forming a protective film on metal. The blue-green patina of copper developed during atmospheric exposure of copper alloys is a protective coating that is aesthetically pleasing. The patina may be artificially produced or accelerated by a solution, developed by the Copper and Brass Research Association, having the formulation:

| | |
|---|---|
| Ammonium sulfate | 2.7 kg (6 lb) |

| | |
|---|---|
| Copper sulfate | 85 g (3 oz) |
| Ammonia (technical grade, 0.90 sp gr) | 39.6 $cm^3$ (1.34 fl oz) |
| Water | 25 L (6.5 gal) |
| Total solution | 27 L (7.3 gal) |

A fine spray of the solution should be applied to a chemically clean surface. The film should be permitted to dry before the part is sprayed a second time. Five or six repetitions of the spraying and drying sequence are required. The color begins to develop in about 6 h and at first is somewhat bluer than natural patina. A more attractive color develops as the surface is exposed to natural weathering.

Small copper parts may be coated with an imitation patina by dipping them in or brushing them with the following solution:

| **Ingredient** | **Parts by weight** |
|---|---|
| Copper | 30 |
| Nitric acid, concentrated | 60 |
| Acetic acid, 6% | 600 |
| Ammonium chloride | 11 |
| Ammonium hydroxide (technical grade, 0.90 sp gr) | 20 |

When preparing the solution, copper is dissolved in the nitric acid, and as soon as the action ceases, the remaining three constituents are added. The solution is allowed to stand several days before use. Parts treated with this solution are coated with linseed oil.

## Coloring

Copper-base materials may be surface treated to produce a variety of colors, ranging from dark reds to black. The final color depends on base metal composition, solution composition, immersion time, and operator skill. Coloring is primarily an art, and practical experience is necessary to develop the skill required to produce uniform finishes consistently. Copper alloys are colored chemically to enhance the appearance of a product, to provide an undercoating for subsequent organic finishes as with brass, and to reduce light reflection in optical systems. Chemical coloring produces a thin layer of a compound on the surface of the base metal. This layer retains some of the characteristics of the metal surface prior to coloring, such as smooth and lustrous or dull.

The procedures for artificial coloring of metals utilize many of the reactions that occur more slowly under natural conditions. Some colored films not found in nature can be produced artificially. Additional color combinations, such as oxidized and highlighted finishes, can be produced by successive chemical and mechanical operations, to emphasize or to remove partially the chemically colored film.

Coloring copper alloys is essentially a process for coloring copper, because zinc and tin compounds are colorless. These constituents and their concentrations greatly affect many of the chemical reactions and color tones of the coatings formed. A copper content of less than 85% is required to produce a good blue-black finish on brass by an ammoniacal copper sulfate or ammoniacal copper carbonate blackening or blue dip solution. Other solutions are more suitable for coloring high-copper alloys.

After machining and mechanical surface preparation have been completed, the parts should be thoroughly cleaned to remove dirt, oil, grease, and oxide films. Cleaning is important for the development of a uniform film in chemical coloring. The cleaning and deoxidizing procedures should be selected so that the structure of the metal at the surface undergoes a minimum of undesirable change. Acid dipping or bright dipping using nitric-sulfuric acid solution may be necessary to remove oxides and to activate the surface for chemical coloring. A certain amount of trial and error is usually required to establish the most suitable techniques for surface preparation.

**Coloring Solutions.** Many types of chemical solutions are used for coloring copper alloys. The formulations and conditions commonly used in commercial applications to produce colors are given in Table 15.

**Table 15 Solutions for coloring copper alloys**

| Desired color | Solution composition | Process conditions | Comments |
|---|---|---|---|
| **Solutions for alloys containing $\geq$ 85% Cu** | | | |
| Dark red | Molten potassium nitrate | Temperature, 650-700 °C (1200-1300 °F); immersion time, $\leq$ 20 s; hot water quench | Parts must be lacquered. |
| Black[(a)] | Solution A: liquid sulfur, 28 g (1 oz); sulfurated potash, 57 g (2 oz); ammonium hydroxide (sp gr 0.89), 7 g ($\frac{1}{4}$ oz); water, 4 L (1 gal) | Room temperature | Produces a dull black finish; a reddish bronze to dark brown finish can be obtained by dry scratch brushing with a fine wire or cloth wheel. |
| | Solution B: sulfurated potash, 1.9 g/L ($\frac{1}{4}$ oz/gal) of water | . . . | Solution strength should be adjusted to blacken the part in approximately 1 min; too rapid formation of coloring film can result in a nonadherent and brittle film. |
| | Solution C: potassium sulfide, 3.7-7.5 g/L ($\frac{1}{2}$-1 oz/gal) of water | Immersion time, $\leq$ 10 s | Parts must be lacquered. |
| Steel black | Arsenious oxide (white arsenic), 113 g (4 oz); hydrochloric acid (sp gr 1.16), 240 cm$^3$ (8 fl oz); water, 4 L (1 gal) | Temperature of solution, ~82 °C (180 °F) | Immerse parts in the solution until a uniform color is obtained; scratch brush while wet, then dry and lacquer. |
| Black | Sodium hydroxide, 45 g | Temperature, 82-99 °C (180-210 °F); | Adequate ventilation is required. After |

| | | | |
|---|---|---|---|
| anodizing | (16 oz); water, 4 L (1 gal) | current density, 0.2-1 A/dm$^2$ (2-10 A/ft$^2$); anode-to-cathode ratio, 1:1; voltage, 6 V; cathodes, steel, carbon, or graphite; anodizing time, 45 s to 3.75 min; tank material, steel | anodizing, the parts are washed in hot and cold water, rinsed in hot water, dried, buffed lightly with a soft cloth wheel, and lacquered, if desired. |
| Reddish bronze to dark brown (statuary bronze) | Sulfurated potash, 57 g (2 oz); sodium hydroxide, 85 g (3 oz); water, 4 L (1 gal) | Temperature, 77 °C (170 °F); immersion time depends on final color desired | Parts are usually scratch brushed with a fine wire wheel; lacquering is required. |
| Verde antique | Solution A: copper nitrate 113 g (4 oz); ammonium chloride, 113 g (40 oz); calcium chloride, 113 g (4 oz); water, 4 L (1 gal) | . . . | Verde antique finishes are also known as patina. They are stippled on brass or copper and dried. Parts made of copper or copper plated are usually treated in a sulfide solution to produce a black base color, which results in a dark background. The use of sodium salts in the verde antique solution results in a yellowish color, while ammonium salts impart a bluish cast. Stippling can be repeated, and when the antique green color appears, immersion in boiling water will produce several different color effects. Other color effects are obtained by using some dry colors such as light and dark chrome green, burnt and raw sienna, burnt and raw umber, ivory drop white, and drop black, or Indian red. After coloring, the surface should be lacquered or waxed. A semiglossy appearance of the lacquered surface can be produced by brushing with paraffin, beeswax, or carnuba wax on a goats-hair brush rotated at about 750 rev/min. |
| | Solution B: acetic acid, 2 L ($\frac{1}{2}$ gal); ammonium chloride, 570 g (20 oz); sodium chloride, 200 g (7 oz); cream of tartar, 200 g (7 oz); copper acetate, 200 g (7 oz); water, 2 L ($\frac{1}{2}$ gal) | . . . | |
| Light brown | Barium sulfide, 16 g ($\frac{1}{2}$ oz); ammonium carbonate, 7 g ($\frac{1}{4}$ oz); water, 4 L (1 gal) | Room temperature | . . . |
| Brown | Potassium chlorate, 155 g ($5\frac{1}{2}$ oz); nickel sulfate, 78 g ($2\frac{3}{4}$ oz); copper sulfate, 680 g (24 oz); water, 4 L (1 gal) | Temperature, 90-100 °C (195-212 °F) | . . . |
| **Solutions for alloys containing <85% Cu** | | | |
| Black | Solution A: copper sulfate, 85 g (3 oz); sodium thiosulfate, 170 g (6 oz); water, 11-19 L (3-5 gal) | Brass parts are placed in oblique tumbling barrel made of stainless steel. The parts are covered with water; the copper sulfate and sodium thiosulfate are dissolved in warm water and added to the contents of the barrel. The parts are tumbled for 15 to 30 min to obtain finish, the solution is drained from | Parts must be lacquered. |

| | | | |
|---|---|---|---|
| | | barrel, and the parts are washed thoroughly in clean water. The parts are then removed from the barrel and dried in sawdust or air blasted. | |
| | Solution B: copper carbonate, 16 g ($\frac{1}{2}$ oz); ammonium hydroxide (sp gr 0.89), 113 g (4 oz); sodium carbonate, 7 g ($\frac{1}{4}$ oz); water, 4 L (1 gal) | Temperature, 88-93 °C (190-200 °F) | . . . |
| Statuary bronze | Copper carbonate, 16 g ($\frac{1}{2}$ oz); ammonium hydroxide (sp gr 0.89), 113 g (4 oz); sodium carbonate, 7 g ($\frac{1}{4}$ oz); water, 4 L (1 gal) | Temperature, 88-93 °C (190-200 °F). Immerse the parts in the hot solution for 10 s; rinse in cold water and dip in solution of dilute sulfuric acid; rinse in hot and then cold water; clean with soft cloth or sawdust. | Parts must be coated with clear lacquer. |
| Blue black | Copper carbonate, 0.45 kg (1 lb); ammonium hydroxide (sp gr 0.89), 1 L (1 qt); water, 3 L (3 qt) | Temperature, 54-79 °C (130-175 °F) | Excess copper carbonate should be present; proper color should be obtained in 1 min. |
| Brown | Part 1: copper sulfate, 113 g (4 oz); potassium chlorate, 227 g (8 oz); water, 4 L (1 gal). Part 2: liquid sulfur, 28 g (1 oz), or sulfurated potash, 57 g (2 oz); water, 4 L (1 gal) | Immerse parts in Part 1 for 1 min; without rinsing, immerse parts in Part 2 for a short time; rinse in cold water; repeat dipping operation in both solutions until desired color is obtained; rinse work in hot water; dry in hot sawdust or with an air blast; scratch brush with fine wire wheel and lacquer | . . . |
| Light brown (old English finish) | Part 1: liquid sulfur, 14 g ($\frac{1}{2}$ oz), or sulfurated potash, 28 g (1 oz); water, 4 L (1 gal). Part 2: copper sulfate, 57 g (2 oz); water, 4 L (1 gal) | Immerse parts in Part 1; without rinsing, immerse in Part 2; rinse in cold water; repeat dipping operations until light color is obtained. For uniform finish, scratch brush and repeat dipping operations until desired color is obtained; rinse parts in cold and hot water; dry in sawdust; scratch brush on a fine wire wheel; and lacquer. | . . . |
| Antique green on brass | Nickel ammonium sulfate, 227 g (8 oz); sodium thiosulfate, 227 g (8 oz); water, 4 L (1 gal) | Temperature, 71 °C (160 °F) | . . . |
| Hardware green on brass | Ferric nitrate, 28 g (1 oz); sodium thiosulfate, 170 g (6 oz); water, 4 L (1 gal) | Temperature, 71 °C (160 °F) | . . . |

| | | | |
|---|---|---|---|
| Brown on brass or copper | Potassium chlorate, 155 g ($5\frac{1}{2}$ oz); nickel sulfate, 78 g ($2\frac{3}{4}$ oz); copper sulfate, 680 g (24 oz); water, 4 L (1 gal) | Temperature, 91-100 °C (195-212 °F) | . . . |
| Light brown on brass or copper | Barium sulfide, 14 g ($\frac{1}{2}$ oz); ammonium carbonate, 7 g ($\frac{1}{4}$ oz); water, 4 L (1 gal) | . . . | Color is made more clear by wet scratch brushing and redipping. |

(a) Alloys blackened by these solutions include silicon bronzes; beryllium coppers; bronzes containing up to 8% Sn; phosphor bronzes of all types; and brasses, leaded or unleaded, with zinc contents up to 35%. Several other proprietary processes are also available for producing a satisfactory black finish.

***Post-Treatment.*** Many chemical films must be scratch brushed to remove excess or loose deposits. In addition, contrast in colors can be obtained by relieving by scratch brushing with a slurry of fine pumice, hand rubbing with an abrasive paste, mass finishing, or buffing to remove some or all of the colored film from the highlights. Clear lacquers are usually necessary for adequate life and service of chemical films used as outdoor decorative finishes. Finishes for exposure indoors are often used without additional protection to the conversion coating.

## Organic Coatings

Information on the materials and methods commonly used for organic finishing of metal surfaces with clear or pigmented coatings is given in the article "Painting" in this Volume. Tarnishing or discoloration of copper alloys can be retarded or delayed indefinitely by the application of a lacquer. Lacquers should be selected and applied on the basis of the intended service environment of a given product. For exterior service, a dry film thickness of 38 to 50 μm (1.5 to 2 mils) is recommended. In less severe indoor service, a dry film thickness of about 13 to 18 μm (0.5 to 0.7 mil) performs satisfactorily.

**Air-Drying and Thermosetting Lacquers.** The performance of thermosetting or heat-cured lacquers is superior to that of air-drying lacquers. The use of the thermosetting types is preferred if ovens are available. Distinction should be made, however, between true thermosetting and forced drying. All lacquers can be force dried after a suitable air-flash period to facilitate handling, but thermosetting materials must be heated to an appropriate temperature, 120 to 205 °C (250 to 400 °F) or higher, for 5 to 60 min, to cross-link the polymers present in them and to develop their inherent characteristics.

The catalytic activity of copper is such that essentially complete curing of thermosetting lacquers is obtained at temperatures lower than those required with inert substrates. Consequently, many thermosetting lacquers discolor copper alloys severely when heated to temperatures recommended by their suppliers. Such discoloration can be minimized by curing at lower temperatures.

Resins are chosen on the basis of service requirements and include:

- Alkyds
- Acrylics
- Cellulosics, such as cellulose nitrates, ethyl cellulose, and cellulose acetate butyrates
- Epoxies
- Phenolics
- Polyesters

- Silicones
- Urea and melamine formaldehydes
- Vinyls
- Urethanes

An epoxy, cellulose nitrate, or alkyd resin provides satisfactory protection for an inexpensive container, such as a lipstick container. The use of a heat-resisting melamine provides satisfactory service at moderately elevated temperatures. Silicone formulated for high-temperature service provides the best heat resistance, but is a more costly material. If resistance to degradation by weather is important, high-quality acrylics provide the best results. General characteristics of these resins are given in the article "Painting" in this Volume.

# Surface Engineering of Magnesium Alloys

**Revised by James E. Hillis, Dow Chemical Company**

## Introduction

SURFACE TREATMENTS are applied to magnesium parts primarily to improve their appearance and corrosion resistance. Many factors may be involved in selecting a suitable surface treatment or finishing system, including surface conductivity, wear resistance, the service environment, alloy composition, and the presence (or absence) of dissimilar metals in the assembly.

Environmental exposures involving salt water or condensing moisture in the presence of chlorides, as well as other salts, have in the past proven very aggressive to magnesium alloys. The higher-purity alloys introduced in the mid-1980s, however, exhibit significantly reduced sensitivity to such environments. For example, die cast alloys AZ91D and AM60B, with controlled levels of iron, nickel, and copper contamination, have been used in increasing volumes in automotive applications as a result of their improved road salt corrosion durability, combined with their castability and light weight. In both painted and unpainted applications these alloys provide salt-water corrosion performance equal to or better than that of die cast aluminum and carbon steel. (See the article "Corrosion of Magnesium and Magnesium Alloys" in *Corrosion,* Volume 13 of *ASM Handbook,* and Ref 1, 2, 3, and 4.)

Figure 1 illustrates the contrast in performance of the old AZ91B die cast alloy versus the higher-purity AZ91D alloy, after 240 h of ASTM B 117 salt-spray testing. Figure 2 compares the performance of painted AZ91D and cold-rolled carbon steel after five years at a marine atmospheric exposure site on the Texas Gulf coast. The coating system in both cases consisted of an iron-phosphatizing pretreatment (without a chrome rinse) plus 12 to 20 μm (0.5 to 0.8 mil) each of cathodic epoxy and a spray acrylic top coat. Alloys AZ91E, WE54A, and WE43A are three sand cast alloys introduced since 1985 that offer similarly improved performance in gravity, or low-pressure cast applications (Ref 5, 6).

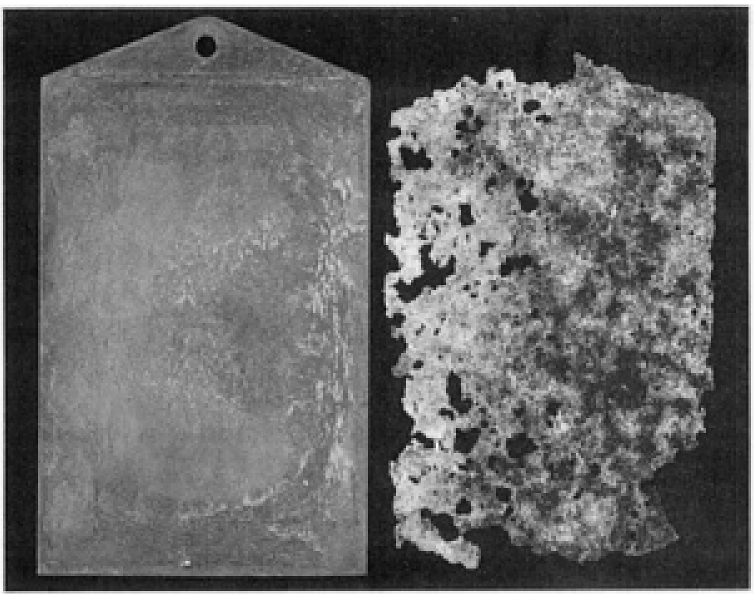


**Fig. 1 Ten-day ASTM B 117 salt-spray corrosion performance of high-purity AZ91D (0.1 mm/yr, or 4 mils/yr, left) versus AZ91B (17 mm/yr, or 680 mils/yr, right). Source: Ref 3, 6**

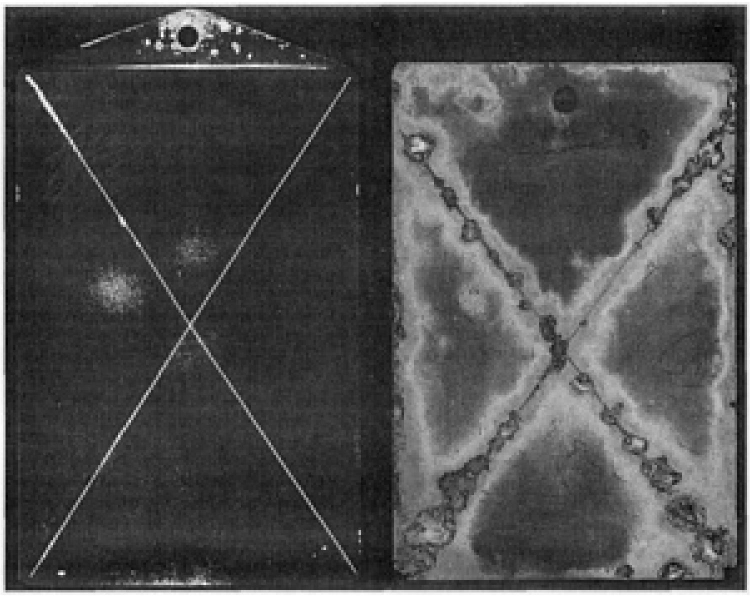


**Fig. 2 Five-year Gulf Coast corrosion performance of coated AZ91D die cast magnesium (left) versus cold-rolled carbon steel (right). Both panels were cleaned, iron phosphatized, coated with 18 μm (0.7 mil) of baked cathodic epoxy primer and 12 to 20 μm (0.5 to 0.8 mil) of acrylic lacquer. The test was conducted at the ASTM Brazos River site near Freeport, TX using scribed panels per ASTM D 1654. Source: Ref 1**

The following environments are listed in the order of increasing corrosiveness: oil immersion, indoor, rural, industrial, and marine. Magnesium alloys are afforded increasing protection in the following order: bare, pickled, chromate conversion coated, anodized, electroplated, and coated with organic finishes. Anodic coatings are porous and provide no corrosion protection unless sealed with a paint. Table 1 relates applications of various degrees of severity to finishing systems used. It should be noted that damaged paint films allow moisture to migrate through porous anodic coating, resulting in corrosion. Painting over the damage will seal in the moisture, creating further problems.

**Table 1 Finishing systems applied to magnesium for various applications**

| | |
|---|---|
| **Systems for specific parts** | |
| Aircraft auxiliary component housings, sand cast | Sand blasted, sulfuric acid pickle, anodize or dichromate treatment (No. 7), epoxy sealed, baked epoxy primer, and top coat |
| Automotive engine brackets, die cast | Wet bowl abraded, no additional finishing |
| Automotive interior brackets, die cast | Chopped aluminum wire blast |
| Automotive valve/cam covers, die cast | Wet abraded, alkaline cleaned, iron phosphate treated, electrostatic powder coated (acrylic, polyester, or epoxy-polyester hybrid) |
| Chain saws, die cast | Wet barrel or bowl abraded, electrostatic powder coated (polyester or epoxy-polyester hybrid) |
| Computer disk drive component, extruded | Dichromate treatment No. 7 per Fig. 3; no additional finish |
| Dock boards, wrought | No finish applied |
| Electronic housing, die cast | Modified chrome pickle No. 20 per Fig. 4; sprayed acrylic, polyester, or urethane exterior coating |
| Foundry flasks | No finish applied |
| Line trimmer | Wet abraded, alkaline clean, phosphate treated, and powder coated |
| Lawnmower deck, die cast | Alkaline cleaned, phosphate pretreated, electrostatic powder coated (polyester) |
| Luggage frame, extruded | Acid pickled, phosphate treated, powder coated (polyester) |
| Missile exteriors, wrought | System A: dichromate, vinyl butyrate zinc chromate wash primer, baked phenolic epoxy varnish, 2 coats, enamel, 2 coats |
| | System B: chrome pickle or anodizing depending on alloy, phenolic epoxy paint, 2 coats |
| Satellites | System A: dichromate |
| | System B: anodize |
| | System C: zinc immersion coating, flash copper plate, 9.1 μm (0.36 mil), silver 0.0025 μm (0.0001 mil), gold, 0.0025 μm (0.0001 mil) |
| **General systems--indoor exposures** | |

| | |
|---|---|
| System A | Phosphate pretreat, epoxy, vinyl, epoxy hybrid urethane, polyester, or acrylic finish coat 8-20 μm (0.3-0.8 mil) |
| System B | Light to medium anodize or chromate pretreat, epoxy or epoxy hybrid, 8-20 μm (0.3-0.8 mil) |
| System C | Electroplate, 25 μm (1 mil) |
| **Systems for marine or similarly corrosive exposures** | |
| System A | High purity alloy; phosphate pretreat, epoxy, vinyl, epoxy-hybrid, urethane, or polyester coating 12-25 μm (0.5-1.0 mil) |
| System B | Standard alloy; chrome pickle or light anodize, vinyl wash primer, vinyl or epoxy chromate primer, 2 coats, baked enamel 1 or 2 coats |
| System C | Standard alloy; anodize, penetrating epoxy sealer, 2-3 coats, epoxy chromate primer, 2 coats, lacquer or synthetic enamel 2 or more coats |

Because of its high position in the electromotive series, magnesium is more susceptible than other common metals to galvanic corrosion. However, galvanic corrosion is possible only if bare magnesium is in electrical contact with another bare metal and if the surface of the two metals is bridged by a conductive aqueous electrolyte. Because in many applications such conditions are difficult to avoid, galvanic corrosion is controlled through the use of compatible metals (e.g. aluminum alloys 5052 or 6061, or zinc, cadmium, or tin electroplated coatings on steel fasteners). With dissimilar metal components assembled to magnesium parts, paint, plastic tape, organic sealants, or compatible metal shims, such as 5000 or 6000 series aluminum, are used to prevent direct electrolyte bridging of the components at the interface. (See the article "Corrosion of Magnesium and Magnesium Alloys" in *Corrosion,* Volume 13 of *ASM Handbook,* and Ref 7 and 8.)

Proper and adequate cleaning is an important prerequisite to the successful application of finishing systems to magnesium alloy products. Failure to follow suitable cleaning procedures causes future problems of corrosion and product degradation. Mechanical and chemical cleaning methods are used singly or in combination, depending on the specific application and product involved. Cleaning processes of either type require suitable control to ensure repetitive reliability.

## Acknowledgements

Special thanks are due to David L. Hawke, Hydro Magnesium, for his helpful comments and suggested revisions.

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## Mechanical Cleaning

Mechanical cleaning of magnesium alloy products is accomplished by grinding and rough polishing, dry or wet abrasive blast cleaning, wire brushing, and wet barrel or bowl abrading (vibratory finishing).

**Grinding and Rough Polishing.** Grinding with belts, wheels, and rotary files is used for cleaning sand castings. Belt grinding, however, usually is used as a finishing operation for the removal of flash and surface imperfections from die castings, or of die marks and scratches from significant surfaces of extrusions. No great danger of surface contamination exists, and no special abrasive or belt backings are necessary.

The possibility of fire resulting from the polishing of magnesium may be virtually eliminated by following the recommendations set forth by the producers of magnesium. These recommendations are summarized in the section "Health and Safety" in this article.

**Dry Abrasive Blast Cleaning.** Sand blasting is the method of dry abrasive blast cleaning most frequently used on magnesium alloys. Many foundries use flint silica sand with a fineness of 25 or 35 AFS. Occasionally, however, steel grit is used. Usually, castings are blasted immediately after shakeout to reveal any major surface defects. After gates, sprues, and risers are sawed off and other operations are performed to prepare the castings for shipment, a final abrasive blast with sand or steel grit is given just before pickling. Under conventional operating conditions, the two types of abrasives yield equally satisfactory results; but if excessive blast pressure is used, steel grit is more likely to cause surface corrosion, because of the embedding of steel particles in the magnesium surface.

Dry blasting with any abrasive is followed by acid pickling to remove the harmful effects of blasting. Table 2 describes two pickling baths, aqueous solutions of sulfuric acid and of nitric and sulfuric acids, frequently used for this purpose, and indicates conditions for their use.

**Table 2 Acid pickling treatments for magnesium alloys**

| Treatment | Principal applications | Metal removed | | Solution | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Constituents | Amount | | Operating temperature | | Immersion time, min | Tank material or lining |
| | | µm | mils | | g/L | oz/gal | °C | °F | | |
| **For cast or wrought alloys** | | | | | | | | | | |
| Chromic acid | Remove oxide, flux, corrosion products | None | | $CrO_3$ | 180 | 24 | 21-100[(a)] | 70-212[(a)] | 1-15 | Stainless steel, 1100 aluminum, lead |
| Ferric nitrate[(b)] | Bright finish; maximum corrosion | 8 | 0.3 | $CrO_3$ | 180 | 24 | 16-38 | 60-100 | $\frac{1}{4}$-3 | Type 316 stainless steel, |

|  |  |  |  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|
| nitrate(b) | resistance of bare metal; finishing of die castings |  |  | $Fe(NO_3)_3 \cdot 9H_2$ | 40.0 | 5.3 |  | 100 |  | vinyl, polyethylene |
|  |  |  |  | O | 3.5 | 0.47 |  |  |  |  |
|  |  |  |  | NaF |  |  |  |  |  |  |
| Hydrofluoric acid | Active surface for chemical treatment | 3 | 0.1 | 50% HF | 230 | 31 | 21-32 | 70-90 | $\frac{1}{2}$-5 | Type 316 stainless steel, lead, rubber |
| Nitric acid | Prepickle for ferric nitrate treatment(c) | 13-25 | 0.5-1.0 | 70% $HNO_3$ | 50 | 6.7 | 21-32 | 70-90 | $\frac{1}{5}$ - $\frac{1}{2}$ | Stainless steel |
| **For wrought alloys only** |  |  |  |  |  |  |  |  |  |  |
| Acetic-nitrate | Remove mill scale; improve corrosion resistance of bare metal | 13-25 | 0.5-1.0 | $CH_3COOH$ | 192 | 25.6 | 21-27 | 70-80 | $\frac{1}{2}$-1 | 3003 aluminum, ceramic, lead |
|  |  |  |  | $NaNO_3$ | 50.0 | 6.7 |  |  |  |  |
| Glycolic-nitrate | Remove mill scale or surface oxides; improve corrosion resistance(d) | 12-25 | 0.5-1.0 | 70% | 230 | 31 | 16-49 | 60-120 | $\frac{1}{2}$-1 | Rubber |
|  |  |  |  | $CH_2OHCOOH$ | 40 | 5.3 |  |  |  |  |
|  |  |  |  |  | 40 | 5.3 |  |  |  |  |
|  |  |  |  | 70% $HNO_3$ |  |  |  |  |  |  |
|  |  |  |  | $NaNO_3$ |  |  |  |  |  |  |
| Chromic-nitrate | Remove mill scale, burned-on graphite; preclean for welding | 13 | 0.5 | $CrO_3$ | 180 | 24 | 21-32 | 70-90 | 3 | Stainless steel, lead, rubber, vinyl |
|  |  |  |  | $NaNO_3$ | 30 | 4 |  |  |  |  |
| Chromic sulfuric | Preclean for spot welding | 8 | 0.3 | $CrO_3$ | 180 | 24 | 21-32 | 70-90 | 3 | Stainless steel, 1100 aluminum, ceramic, rubber |
|  |  |  |  | 96% $H_2SO_4$ | 0.4 | 0.05 |  |  |  |  |
| **For cast alloys only** |  |  |  |  |  |  |  |  |  |  |
| Nitric sulfuric | Remove effects of blasting from sand | 50 | 2.0 | 70% $HNO_3$ | 77.0 | 10.3 | 21-32 | 70-90 | $\frac{1}{6}$ - $\frac{1}{4}$ | Ceramic, rubber, glass |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| sulfuric | castings | | | 96% $H_2SO_4$ | 20 | 2.7 | | | $\frac{1}{6}$ - $\frac{1}{4}$ | glass |
| Phosphoric acid | | | | | | | | | | |
| Step 1 | Remove surface segregation from die castings | 13-25 | 0.5-1.0 | 85% $H_3PO_4$ | 425-866 | 57-116 | 21-27 | 70-80 | 10-15 s | Fiber-reinforced plastic, polyvinyl chloride, polyethylene |
| Step 2[e] | | | | NaOH | 80-120 | 11-16 | 21-27 | 70-80 | 30 s | Carbon steel |
| Sulfuric acid | Remove effects of blasting from sand castings | 50 | 2.0 | 96% $H_2SO_4$ | 30 | 4 | 21-32 | 70-90 | $\frac{1}{6}$ - $\frac{1}{4}$ | Ceramic, rubber, lead, glass |

(a) For removal of flux, solution must be 88 - 100 °C (190 - 212 °F).

(b) For most uniform appearance, die castings must be mechanically finished before being pickled, because the ferric nitrate solution accentuates flow marks and segregation on die-cast surfaces.

(c) Use of nitric acid prepickle increases solution life and decreases treatment time in ferric nitrate pickling.

(d) Nonvolatile glycolic acid reduces costs compared to acetic acid.

(e) No rinsing between steps

**Wet abrasive blast cleaning** of magnesium alloys is used for final finishing before electroplating, producing a matte surface before chemical treatments, removing carbonaceous or heavy corrosion products, and removing residual paint after stripping operations. Equipment, abrasives, and process controls are the same as those used for many other materials (see the article "Mechanical Cleaning Systems" in this Volume). Remove any contamination by acid pickling, using the sulfuric or nitric-sulfuric baths described in Table 2.

**Barrel or Bowl Abrading.** Magnesium die cast components are often cleaned of charred and uncharred die lubricants and other surface contaminants using wet barrel, or vibratory bowl, abrading in combination with detergents and surface treatment formulations. The ceramic media employed in these operations serve to both clean and smooth parts. It is important that a good flow of solution is continuously applied to the media in order to keep contaminants from accumulating and recontaminating part surfaces. Abrading is used as both a stand-alone finishing operation with high-purity alloy parts (see the section "Mechanical Finishing," below) and as a pretreatment/cleaning operation prior to painting parts used in applications such as chain saws, lawn and garden equipment, and power hand tools.

**Wire Brushing.** Magnesium alloy sheet is wire brushed for in-process cleaning and for the removal of oxides before arc or resistance welding. The wire-brushing machine should be adjusted as to the amount of pressure exerted on the sheet. The machine should be designed so that it does not gouge the sheet. The final surface smoothness depends also on the coarseness and composition of the wire. Safety precautions should be observed when wire brushing magnesium as indicated in the section "Health and Safety" in this article.

## Chemical Cleaning

Chemical methods for cleaning magnesium alloys are vapor degreasing, solvent cleaning, emulsion cleaning, alkaline cleaning, and acid pickling.

**Solvent cleaning and vapor degreasing** are used to remove oils, forming lubricants, waxes, quenching oils, corrosion-protective oils, polishing and buffing compounds, and other soluble soils and contaminants. Solid particles such as machining dust or chips are removed by the washing action of the solvent as it dissolves the oil or grease that holds the metal fines to the part. These processes must be used before painting, plating, and chemical treatments, as well as before and after machining and forming.

The same methods, equipment, and solvents are used for magnesium as for other metals (see the article "Solvent Cold Cleaning and Vapor Degreasing" in this Volume). Trichloroethylene and perchloroethylene are the solvents most often used. Methylene chloride is effective in removing the excess organic-resin impregnants from the surface of the castings without removing the compound from the pores in the metal.

**Emulsion cleaning** may be used for the removal of oils and buffing compounds (see the article "Emulsion Cleaning" in this Volume). The emulsion cleaner should be neutral or alkaline, with a pH of 7.0 or above, so as not to etch magnesium surfaces. Emulsion cleaners incorporating water with the solvent should be tested before use to avoid possible attack or pitting of the metal.

**Alkaline cleaning** is the most frequently used method of cleaning magnesium alloys preparatory to painting, chemical treatments, or plating. Alkaline cleaners are also used to remove chromate films from magnesium.

Most magnesium alloys are not attacked by common alkalis except pyrophosphates and some polyphosphates, and even these alkalis do not appreciably attack magnesium alloys above a pH of 12.0. Nearly any heavy-duty alkaline cleaner suitable for low-carbon steel performs satisfactorily on magnesium alloys. The pH of alkaline cleaners for magnesium alloys should be 11.0 or higher.

Soak cleaners are usually based on alkali hydroxides, carbonates, phosphates, and silicates, preferably in combinations of two or more, and also contain natural resinates or synthetic surfactants as emulsifying agents. Soak cleaners are used in concentrations of 30 to 75 g/L (4 to 10 oz/gal) and at 71 to 100 °C (160 to 212 °F). Alkaline cleaners used for spray cleaning cannot use a surface-active wetting agent, because the foaming problem would be too great. In this case, the mechanical force of the spray helps dislodge soils.

Cathodic cleaning uses the work as the cathode in the cleaning solution at approximately 6 V dc. Anodic cleaning is not recommended because of the formation of undesirable oxide or hydroxide films. Pitting of the surface of the magnesium may also result from prolonged anodic cleaning.

A simple aqueous bath for soak or electrolytic cleaning of magnesium alloys is made and used as follows:

| | |
|---|---|
| Trisodium phosphate ($Na_3PO_4 \cdot 12H_2O$), g/L (oz/gal) | 30 (4) |
| Sodium carbonate ($Na_2CO_3 \cdot 10H_2O$), g/L (oz/gal) | 30 (4) |
| Wetting agent, g/L (oz/gal) | 0.7 (0.1) |
| Operating temperature, °C (°F) | 82-100 (180-212) |

| | |
|---|---|
| Immersion time, min | 3-10 |

Another formula for soak or electrolytic cleaning, which can be used before electroplating, consists of the following:

| | |
|---|---|
| Sodium carbonate ($Na_2CO_3 \cdot 10H_2O$), g/L (oz/gal) | 22.5 (3) |
| Sodium hydroxide (NaOH), g/L (oz/gal) | 15 (2) |
| Wetting agent, g/L (oz/gal) | 0.7 (0.1) |
| Operating temperature, °C (°F) | 82-100 (180-212) |
| Immersion time, min | 3-10 |

When either of these baths is used as an electrolytic cleaner, parts are made the cathode at a current density of 1 to 5 $A/dm^2$ (10 to 50 $A/ft^2$) at 6 V dc. Many proprietary compounds are better cleaners than the above formulas.

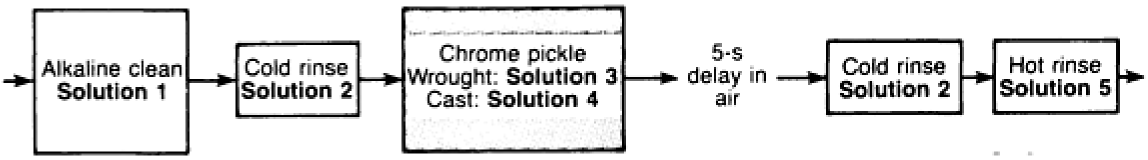
Hard-to-remove soils, such as graphitic lubricants used in the hot forming of magnesium alloy sheet products or in the fabrication of impact extrusions, can best be removed by soaking in the heavy-duty caustic cleaner:

| | |
|---|---|
| Sodium hydroxide (NaOH), g/L (oz/gal) | 98 (13) |
| Wetting agent, g/L (oz/gal) | 0.7 (0.1) |
| Operating temperature, °C (°F) | 87-100 (190-212) |
| Immersion time, min | 10-20 |

A chromic acid pickle, as shown in Table 2, usually is used after cleaning in the above solution. Cleaners containing more than 2% NaOH attack ZK60A; therefore, the above solution should not be used on this alloy.

**Acid pickling** is required for removal of contamination that is tightly bound to the surface or insoluble in solvents or alkalis. These contaminants include natural oxide tarnish, embedded sand or iron, chromate coatings, welding residues, and burned-on lubricants.

In selecting an acid pickling treatment, consider the type of surface contamination to be removed, the type of magnesium alloy to be treated, and the dimensional loss allowable, as well as the desired surface appearance. Table 2 gives details of acid pickling treatments used for magnesium alloys. Confining these treatments to alloy types indicated avoids the formation of a powdery black smut on pickled surfaces.



| Solution No. | Type of solution | Constituents | Amount, g/L (oz/gal) | Operating temperature, °C (°F) | Cycle time, min | Tank material |
|---|---|---|---|---|---|---|
| 1 | Alkaline cleaner | [a] | [a] | 88-100 (190-212) | 3-10 | Low-carbon steel |
| 2 | Cold rinse | Water | . . . | Ambient | [b] | Low-carbon steel |
| 3 | Chrome pickle[c] | $Na_2Cr_2O_7 \cdot 2H_2O$<br>$HNO_3$ (sp gr 1.42)<br>Water[d] | 180 (24)<br>180 (24)<br>bal | 21-32 (70-90) | $\frac{1}{2}$-2[e] | [f] |
| 4 | Chrome pickle[g] | $Na_2Cr_2O_7 \cdot 2H_2O$<br>$HNO_3$ (sp gr 1.42)<br>$Na_2HF_2$, $KHF_2$, or $NH_4HF_2$<br>Water[d] | 180 (24)<br>120-180 (16-24)<br>15 (2.0)<br>bal | 21-32 (70-90)<br>49-60 (120-140)[h] | $\frac{1}{2}$-2[i] | Type 316 stainless steel[j] |
| 6 | Hot rinse | Water | . . . | 71-82 (160-180)[k] | . . . | Low-carbon steel |

(a) Type and strength of solution used governed by degree of surface contamination.

(b) Rinse thoroughly with adequate inflow of fresh water; agitate.

(c) For wrought materials, all alloys, not to be hot formed, and for wrought materials, all alloys, for which tolerances permit removal of approximately 15 μm (0.6 mil) of stock. When treatment is used on alloys M1A and ZK60A to provide paint base, use fresh solutions.

(d) Use water from steam condensate or water treated by ion exchange, when available, instead of well or hard tap water.

(e) For well-controlled bath, 1 min is standard.

(f) Tank material can be of stainless steel or low-carbon steel lined with glass, ceramic, synthetic rubber, or vinyl-based materials. Racks and baskets for use with Solution 3 may be stainless steel or Monel.

(g) For sand and permanent mold castings of all alloys for which tolerances permit stock removal of approximately 15 μm (0.6 mil); die castings, all alloys, of 3 to 8 μm (0.1 to 0.3 mil). Dip die castings for 15 to 30 s in water 71 to 82 °C (160 to 180 °F) before immersing in solution.

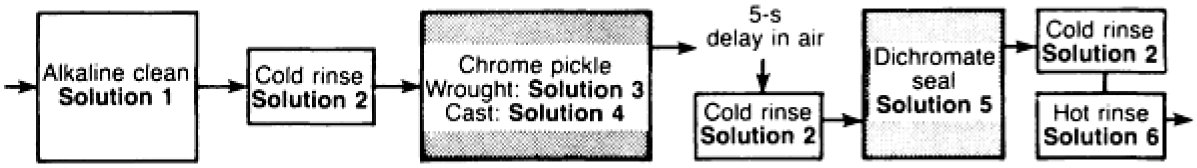
(h) For die castings.

(i) For well-controlled bath, 1 min is standard on all products except die castings. Immerse die castings only 10 s.

(j) Racks and baskets for use with Solution 4 can be type 316 stainless steel or phosphor bronze.

(k) Immerse long enough to heat parts sufficiently to facilitate rapid drying; keep rinse clean with inflowing fresh water.

**Fig. 3 Chrome pickle treatment (chemical treatment No. 1; MIL-M-3171, type I). Applicable to all alloys and product forms. Used to provide a base for paint or short-time protection for shipment or storage**



| Solution No. | Type of solution | Constituents | Amount, g/L (oz/gal) | Operating temperature, °C (°F) | Cycle time, min | Tank material |
|---|---|---|---|---|---|---|
| 1 | Alkaline cleaner | [a] | [a] | 88-100 (190-212) | 3-10 | Low-carbon steel |
| 2 | Cold rinse | Water | . . . | Ambient | [b] | Low-carbon steel |
| 3 | Chrome pickle[c] | $Na_2Cr_2O_7 \cdot 2H_2O$<br>$HNO_3$ (sp gr 1.42)<br>Water[d] | 180 (24)<br>180 (24)<br>bal | 21-32 (70-90) | $\frac{1}{2}$-2[e] | [f] |
| 4 | Chrome pickle[g] | $Na_2Cr_2O_7 \cdot 2H_2O$<br>$HNO_3$ (sp gr 1.42)<br>$NaHF_2$, $KHF_2$, or $NH_4HF_2$<br>Water[d] | 180 (24)<br>120-180 (16-24)<br>15 (2)<br>bal | 21-32 (70-90)<br>49-60 (120-140)[h] | $\frac{1}{2}$-2[i] | Type 316 stainless steel[j] |
| 5 | Dichromate seal | $Na_2Cr_2O_7 \cdot 2H_2O$<br>$CaF_2$ or $MgF_2$<br>Water[d] | 120-180 (16-24)<br>2.47 (0.33)<br>bal | 99-100 (210-212) (boiling) | 30 | Low-carbon steel |
| 6 | Hot rinse | Water | . . . | 71-82 (160-180) | [k] | Low-carbon steel |

(a) Type and strength of solution used governed by degree of surface contamination.

(b) Rinse thoroughly with adequate inflow of fresh water; agitate.

(c) For wrought materials, all alloys, not to be hot formed, and for wrought materials, all alloys, for which tolerances permit removal of approximately 15 μm (0.6 mil) of stock. When treatment is used on alloys M1A and ZK60A to provide paint base, use fresh solutions.

(d) Use water from steam condensate or water treated by ion exchange, when available, instead of well or hard tap water.

(e) For well-controlled bath, 1 min is standard.

(f) Tank material can be of stainless steel or low-carbon steel lined with glass, ceramic, synthetic rubber, or vinyl-based materials. Racks and baskets for use with Solution 3 may be stainless steel or Monel.

(g) For sand and permanent mold castings of all alloys for which tolerances permit stock removal of approximately 15 μm (0.6 mil); die castings, all alloys, of 3 to 8 μm (0.1 to 0.3 mil). Dip die castings for 15 to 30 s in water 71 to 82 °C (160 to 180 °F) before immersing in solution.

(h) For die castings.

(i) For well-controlled bath, 1 min is standard on all products except die castings. Immerse die castings only 10 s.

(j) Racks and baskets for use with Solution 4 can be type 316 stainless steel or phosphor bronze.

(k) Immerse long enough to heat parts sufficiently to facilitate rapid drying; keep rinse clean with inflowing fresh water.

**Fig. 4 Sealed chrome pickle treatment. Applicable to all alloys and product forms. Used as a substitute for dichromate coating or for more protection than is provided by the chrome pickle treatment**

When a magnesium alloy product is used bare or with a clear finish, it is desirable to improve the corrosion resistance of the metal surface in addition to providing an attractive appearance. This can be accomplished by the use of ferric nitrate, acetic-nitrate, or phosphoric acid pickle (Table 2). The ferric nitrate pickle deposits an invisible chromium oxide film that passivates the surface and improves corrosion resistance. The acetic-nitrate and phosphoric acid pickles act as sequestering agents that effectively remove even invisible traces of other metals from the magnesium surface and thus prevent localized galvanic corrosion. Although all of these methods are effective in improving corrosion resistance, ferric nitrate and phosphoric acid pickles give best results.

## Mechanical Finishing

Depending on required appearance, the most frequently used methods of mechanical finishing are barrel tumbling, polishing and buffing, vibratory finishing, fiber brushing, and shot blasting. Shot blasting with 0.10 to 0.25 mm (0.003 to 0.009 in.) glass spheres produces a satin finish. Plastic and chopped aluminum wire blasting media are also used. Sand or steel shot blasting should be excluded as means for producing a desired mechanical finish. If these media are used, heavy pickling (1 to 2 mils of metal removal) is required to restore corrosion resistance, and such pickling can seriously alter the mechanical finish produced. Surface contamination by plastic, chopped aluminum, or glass bead media is less damaging and the effects can be easily removed by subsequent mild etching treatments such as ferric nitrate pickling. Wet blasting with glass beads or aluminum oxide is less contaminating than any dry blasting process. (See the article "Corrosion of Magnesium and Magnesium Alloys" in *Corrosion,* Volume 13 of *ASM Handbook,* and Ref 3, 5, and 9.)

**Mass (Barrel) Finishing.** The use of dry barrel finishing is usually limited to the production of a final finish on magnesium alloy parts that are small and relatively thin and for which metal removal must be held to a minimum. Wet barrel finishing is used for deburring, grinding, polishing, burnishing, and coloring. Procedures used in wet and dry barrel finishing are discussed in the article on mass finishing.

**Vibratory finishing** combines smoothing and brightening with cleaning to remove dirt, oxides, thin flash, and casting skin. Ceramic and other media are used depending on the surface condition of the part and the finish required. Acid additives etch magnesium surfaces and should never be used. Proper rinsing and drying are important.

**Polishing and buffing** are not used for final finishing, but for preparing magnesium alloy surfaces for other finishes, such as chemical treatments, anodizing, plating, or painting. As shown in Table 3, the procedures used to produce a highly polished or buffed surface on magnesium alloys are similar to those used for aluminum-base alloys. However, because most magnesium alloys are appreciably harder than aluminum alloys and tend to drag or tear to a lesser degree, it is unnecessary to use as much lubrication as is usually required with aluminum alloys. When polishing die castings, the metal removal is kept at a minimum to preserve the relatively thin nonporous outer layer of the casting.

### Table 3 Procedures for polishing and buffing magnesium alloys

| Operation | Abrasive grit size | Wheel | | | | |
|---|---|---|---|---|---|---|
| | | Type | Diam | | Speed | |
| | | | mm | in. | m/s | sfm |
| Rough polishing[a] | 60-100[b] | Canvas, felt, sheepskin | 150-360 | 6-14 | 15.3-25.5 | 3000-5000 |
| Medium polishing[c] | 100-320[b] | Built-up cloth | 150-360 | 6-14 | 20.4-30.6 | 4000-6000 |
| Fine polishing | 240-400 | Cloth or sheepskin | 250-360 | 10-14 | 22.9-38.2 | 4500-7500 |
| Satin finishing[d] | 50-320[e] | Full-disk buffs[f] | 150-300 | 6-12 | 15.3-25.5 | 3000-5000 |
| Buffing[g] | [h] | Cotton buffs | 150-410 | 6-16 | 20.4-40.8 | 4000-8000 |

(a) For rough surfaces only, such as sand castings.

(b) Aluminum oxide or silicon carbide; grease stick may be used.

(c) For less severe surface condition and before buffing.

(d) For final finish or before plating.

(e) Greaseless compound.

(f) Loose or folded cotton cloth.

(g) A cutdown operation to produce a smooth finish with an intermediate degree of brightness.

(h) Tripoli or aluminum oxide buffing compound

Standard polishing wheels and abrasive belts are used to remove rough surfaces, parting lines, and other surface imperfections from magnesium alloy pieces. Aluminum oxide or silicon carbide abrasives are used, in grit sizes from 60 to 320, depending on the surface roughness and the final finish desired.

Particles of free iron or other heavy metals must not be used in abrasives for the polishing of magnesium alloys, because these metals, when embedded in the surface, can cause cell corrosion effects while parts are in storage or cause a pitting condition in pickling processes used before chemical treatments or electroplating.

Large castings require polishing of significant surfaces before buffing. Fine polishing belts are used on parts with little contour. Parts with more intricate contour are polished on setup wheels or on cloth wheels, using a greaseless compound. Grit sizes from 220 to 320 are most commonly used in polishing operations prior to buffing.

Satin finishing or flexible-wheel polishing is also used on magnesium alloys. This finish is produced by applying a greaseless compound to the surface of a clot wheel as it is slowly revolved. No lubricant is required.

Magnesium alloys can be buffed to a smooth, bright finish using aluminum oxide or tripoli compounds on a light-count sewed wheel. For color buffing, a dry lime compound may be used. Buffing compounds containing free iron or other heavy metal abrasives should not be used.

A ferric nitrate bright pickle, as shown in Table 2, is used on polished or buffed surfaces prior to the application of a clear organic coating. Using a ferric nitrate bright pickle produces a bright, passive surface that increases the adhesion and corrosion protection of the coating; it also serves to prevent blemishes such as spotting, blooming, and worm tracking in the coating after it has dried.

Precautions that must be exercised in the polishing and buffing of magnesium alloys are discussed in the section "Health and Safety" in this article.

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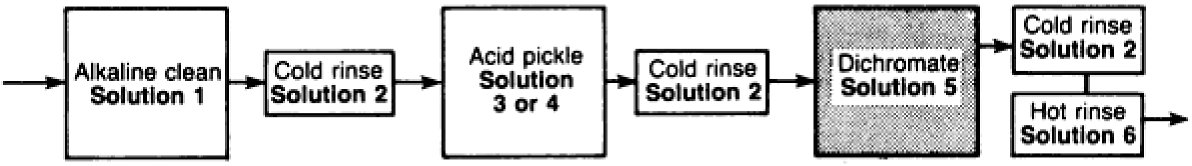
## Chemical Finishing Treatments

Chemical finishing treatments for magnesium alloys are used either to provide short-time protection against corrosion and abrasion during shipment and storage, or as pretreatments to additional finishing systems.

Figures 3, 4, 5, and 6 present flow charts of processing steps in four frequently used chemical treatments; tabular data accompanying each of these charts indicate operating conditions and applicability of the respective treatments. Note that the chrome pickle and sealed chrome pickle treatments cannot be used on close-tolerance machined parts unless tolerances will permit or allowances for metal removal have been made. The dichromate treatment (Fig. 5) involves no appreciable dimensional changes. Moreover, when a hydrofluoric-sulfuric acid pretreatment and brief exposure to the chrome pickling solution are used, the modified chrome pickle treatment (Fig. 6) involves no appreciable dimensional changes.



| **Solution** | **Type of solution** | **Constituents** | **Amount, g/L (oz/gal)** | **Operating temperature, °C (°F)** | **Cycle time, min** | **Tank material** |
|---|---|---|---|---|---|---|
| 1 | Alkaline cleaner | (a) | (a) | 88-100 (190-212) | 3-10 | Low-carbon steel |
| 2 | Cold rinse | Water | . . . | Ambient | (b) | Low-carbon steel |
| 3 | Acid pickle(c) | 60% HF<br>water(d) | 180 (24)<br>bal | 21-32 (70-90) | 5(e) | Low-carbon steel(f) |
| 4 | Acid pickle(g) | $NaHF_2$, $KHF_2$, or<br>water(d) | 50 (6.7) | 21-32 (70-90) | 5 | Low-carbon steel(f) |
| 5 | Dichromate | $Na_2Cr_2O_7 \cdot 2H_2O$<br>$CaF_2$ or $MgF_2$<br>water(d) | 120-180 (16-24)<br>2.48 (0.33)<br>bal | 99-100 (210-212) (boiling) | 30(h) | Low-carbon steel |
| 6 | Hot rinse | Water | . . . | 71-82 (160-180) | (i) | Low-carbon steel |

Note: Racks and baskets for use with all tank materials should be Monel, type 316 stainless steel, or phosphor bronze.

(a) Type and strength of solution used governed by degree of surface contamination.

(b) Rinse thoroughly with adequate inflow of fresh water; agitate.

(c) This bath may be used for all treatable alloys in all forms. This bath must be used for castings that have not been pickled after being sand blasted.

(d) Water from steam condensate or water treated by ion exchange should be used when available instead of well or hard tap water.

(e) For AZ31A and B, $\frac{1}{2}$ to 1 min.

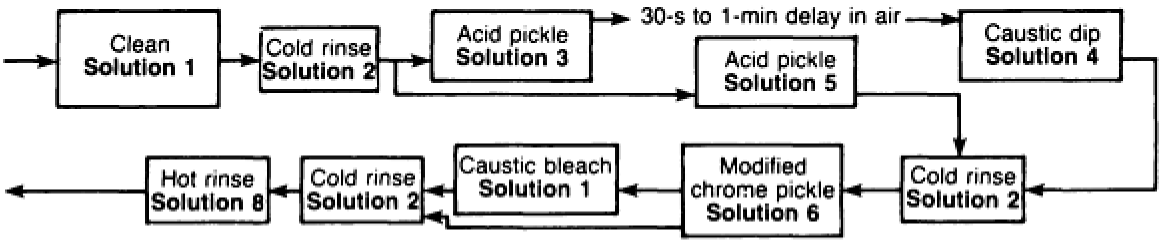
(f) Line tanks with lead or with natural or synthetic rubber.

(g) This pickle is preferred for AZ31B and C; an alternate pickle for wrought products and for castings that have been pickled after being sand blasted.

(h) For ZK60A. 15 min.

(i) Immerse long enough to heat parts sufficiently to facilitate rapid drying; keep rinse clean with inflowing fresh water.

**Fig. 5 Dichromate treatment (chemical treatment No. 9; MIL-M-3171, Type III). Used for maximum corrosion protection and to provide a paint base. Results in no appreciable change in dimensions and can be used on finish-machined wrought and cast products of all alloys except EK30A, EK41A, HK31A, and M1A**



| Solution No. | Type of solution | Constituents | Amount, g/L (oz/gal) | Operating temperature, °C (°F) | Cycle time, min | Tank material |
|---|---|---|---|---|---|---|
| 1 | Cleaner[a] | $Na_4P_2O_7$<br>$Na_2B_4O_7 \cdot 10H_2O$<br>NaF<br>Water[b] | 30 (4)<br>68 (9)<br>8 (1)<br>bal | 77-82 (170-180) | 2-5 | Low-carbon steel |
| 2 | Cold rinse | Water | . . . | Ambient | [c] | Low-carbon steel |
| 3 | Acid pickle[d] | 100% $H_3PO_4$<br>Water[b] | 481-820 (65-110)<br>bal | 21-32 (70-90) | $\frac{1}{6}$ - $\frac{1}{4}$ | Low-carbon steel[e] |
| 4 | Caustic dip | NaOH | 50 (6.6) | 21-82 (70-180) | $\frac{1}{2}$ | Low-carbon steel |

| | | | | | | |
|---|---|---|---|---|---|---|
| 5 | Acid pickle(f) | 100% HF<br>$H_2SO_4$<br>Water(b) | 143-196 (20-25)<br>48 (6.4)<br>bal | 21-32 (70-90) | 2-5 | Low-carbon steel(e) |
| 6 | Modified chrome pickle(g) | $NaHF_2$<br>$NaCr_2O_7 \cdot 2H_2O$<br>$Al_2(SO_4) \cdot 14H_2O$<br>$HNO_3$ (sp gr 1.42)<br>Water(b) | 15 (2)<br>180 (24)<br>10 (1.3)<br>120 (16)<br>bal | 21-32 (70-90) | $\frac{1}{12}$-2 | Type 316 stainless steel or low-carbon steel with vinyl |
| 7 | Caustic bleach(h) | NaOH, 5-10% | . . . | 82-100 (180-212)(i) | $\frac{1}{2}$ | Low-carbon steel |
| 8 | Hot rinse(j) | Water | . . . | 71-82 (160-180) | (k) | Low-carbon steel |

(a) Vapor degreasing, solvent washing, or conventional alkaline cleaning may be used instead of this special mild-etching cleaner. Metal removal in 5 min, 2.5 to 5.0 μm (0.1 to 0.2 mil).

(b) Use water from steam condensate or water treated by ion exchange, when available, instead of well or hard tap water.

(c) Rinse thoroughly with adequate inflow of fresh water; agitate.

(d) Acid pickle using this solution is preferred pretreatment if metal loss of 13 μm (0.5 mil) can be tolerated.

(e) Lined with rubber or vinyl.

(f) Alternative treatment; for use if metal loss of 13 μm (0.5 mil) is unacceptable.

(g) Metal removal rate, 1.2 μm (0.5 mil) per min.

(h) Optional; provides bright appearance.

(i) For castings; wrought products are best treated in a room-temperature solution.

(j) Oven drying, at temperatures not exceeding 150 °C (300 °F),may be substituted for hot water rinse.

(k) Immerse long enough to heat parts sufficiently to facilitate rapid drying; keep rinse clean.

**Fig. 6 Modified chrome pickle treatment (chemical treatment No. 20). Used to provide a base for paint or for protection during shipment or storage. Provides a more uniform coating than chrome pickle treatment. Applicable to all alloys and product forms, particularly die castings, for which slight metal losses are acceptable**

Traditionally chrome-free phosphates have not been recommended for use with magnesium components, however with the introduction of the new higher-purity die cast alloys (AZ91D, AM50A, AM60B, and AS41B; see Ref 10) a number of commercial phosphatizing treatments and simple phosphate formulations have been found to provide performance competitive with the best chromate-based surface treatments. These chrome-free treatments have been employed commercially with increasing frequency in finishing magnesium parts for a variety of markets including automotive, sporting goods, and power lawn equipment (Ref 1, 2, 9).

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10. Standards B93-94 and B94-94, Aluminum and Magnesium Alloys, Vol 02.02, *Annual Book of ASTM Standards,* ASTM, in press

## Anodic Treatments

Of the many anodizing treatments developed for magnesium, only a few have achieved commercial significance. Chemical Treatment No. 9 (galvanic anodizing) is a low-voltage dc treatment that produces a thin black conversion coating, which is used mainly as a paint base. Chemical Treatment No. 17 and HAE treatment produce more substantial coatings (thicknesses of 5 to 30 μm) and are more widely used, primarily as bases for heavy-duty paint systems for rigorous service conditions, such as in military and aerospace applications. The heavier anodized coatings also provide significant resistance to abrasion. The Cr-22 treatment is a high-voltage process that is not currently used, but derivative proprietary processes are commercially available. Anodized coatings have varying degrees of porosity and must be sealed for use in severely corrosive salt environments. The coatings can be infused with various polymers to produce special properties such as lubricity.

Two proprietary chrome-free anodizing treatments have been introduced recently. Both have been demonstrated to provide excellent wear resistance, and when evaluated for a military application, one was found superior to both the HAE and No. 17 anodizing treatments in coated corrosion performance (Ref 11, 12, 13).

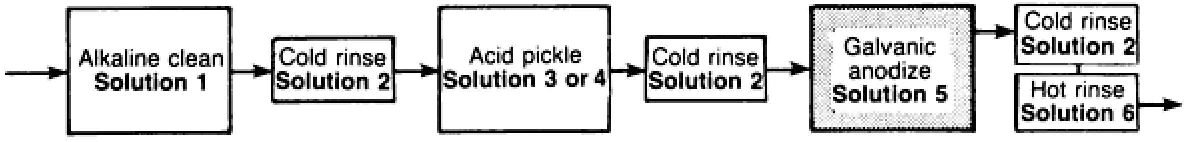
**Surface Preparation.** Before conversion coating, all surfaces must be scrupulously clean and free of contamination. Remove oil, grease, and other organic contaminants with suitable solvent cleaners, or with hot alkaline cleaning solutions such as those previously described in the section on chemical cleaning. Scales, oxides, burned-on drawing lubricants, and inorganic corrosion products should be removed in acid pickling solutions of prescribed composition and in accordance with the recommendations given in Table 2.

Parts that have been fabricated by stamping should be deburred to ensure that a coating is not applied to feathered edges that might break off and expose bare metal. Sharp edges and round corners should be made smooth before anodizing. Wherever close dimensional tolerances are entailed, adequate provision for buildup that results from coating should be made.

**Chemical Treatment No. 9.** A galvanic anodizing treatment in which a source of electric power is not required, Chemical Treatment No. 9 is applied to all forms and alloys of magnesium to produce a protective black coating with good paint-base characteristics. Parts with attachments of other metals may also be treated. Because this process does not result in appreciable dimensional change, the parts are machined to close tolerances before treatment.

Proper galvanic action requires the use of racks, made of stainless steel, Monel, or phosphor bronze. When the workpieces are immersed in the anodizing solution, they are made the anodes, and the tank, if made of low-carbon steel, acts as cathode. If the tank is equipped with a nonmetallic lining, separate steel cathodes must be used.

A processing diagram, together with details of solution compositions and operating conditions for Chemical Treatment No. 9, is presented in Fig. 7



| Solution No. | Type of solution | Constituents | Amount, g/L (oz/gal) | Operating temperature, °C (°F) | Cycle time, min | Tank material |
|---|---|---|---|---|---|---|
| 1 | Alkaline cleaner | (a) | (a) | 88-100 (190-212) | 3-10 | Low-carbon steel |
| 2 | Cold rinse | Water | . . . | Ambient | (b) | Low-carbon steel |
| 3 | Acid pickle(c) | 60% HF<br>Water(d) | 180 (24)<br>bal | 21-32 (70-90) | 5(e) | Low-carbon steel(f) |
| 4 | Acid pickle(g) | $NaHF_2$, $KHF_2$, or $NH_4HF_2$<br>Water(d) | 50 (6.6)<br>bal | 21-32 (70-90) | 5 | Low-carbon steel(f) |
| 5 | Galvanic anodize(h) | $(NH_4)_2SO_4$<br>$Na_2Cr_2O_7{\cdot}2H_2O$<br>$NH_4OH$ (sp gr 0.880)<br>Water(d) | 30 (4)<br>30 (4)<br>2.2 (0.3)<br>bal | 49-60 (120-140) | 10-30(i) | (j) |
| 6 | Hot rinse | Water | . . . | 71-82 (160-180) | (k) | Low-carbon steel |

Note: Racks and baskets for use with all tank materials may be stainless steel, Monel, or phosphor bronze.

(a) Type and strength of solution governed by degree of surface contamination.

(b) Rinse thoroughly; agitate.

(c) May be used for all alloys in all forms; must be used for castings that have not been pickled after being sand blasted.

(d) Water from steam condensate or water treated by ion exchange should be used, when available, instead of well or hard tap water.

(e) For AZ31A and B, $\frac{1}{2}$ to 1 min.

(f) Lined with lead or with natural or synthetic rubber.

(g) An alternative pickle for wrought products and for castings that have been pickled after sand blasting; preferred for AZ31B and C.

(h) Current density should not exceed 1 A/dm$^2$ (10 A/ft$^2$); at least 753 A · min/m$^2$ (70 A · min/ft$^2$) is required for uniform coating.Maintain solution at pH 5.6 to 6.0 by adding solution containing 5% $CrO_3$ and concentrated $H_2SO_4$.

(i) Treat parts until a uniform black coating is obtained.

(j) If made of low-carbon steel, the tank acts as a cathode. If tank is made of or lined with nonmetallic material, use steel cathode plates.

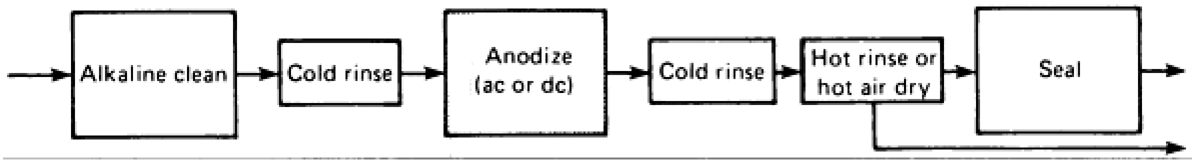
(k) Immerse long enough to sufficiently heat parts to facilitate rapid drying; keep rinse clean with adequate flow of fresh water.

**Fig. 7 Chemical treatment No. 9 (MIL-M-3171A) galvanic anodizing**

**Chemical Treatment No. 17,** which can be applied to all forms and alloys of magnesium, produces a two-phase, two-layer coating. A light green or greenish tan undercoating, about 5.0 μm (0.2 mil) thick, forms at lower voltages. This is covered by a much heavier, second-phase coating about 30.4 μm (1.2 mils) thick, vitreous, and dark green. The second-phase coating is relatively brittle and highly abrasion resistant. Formed at higher voltages, its corrosion resistance and paint-based properties are excellent. However, according to ASTM D 1732, the dark green, thick coating is preferable to the light green thin coating only when:

- Preliminary removal of surface contamination is not convenient.
- The highest degree of abrasion resistance is required from the coating.
- A dimensional increase of about 0.02 mm (0.001 in.) can be tolerated.
- The part is not to be subjected in service to severe impact, deformation, or flexing, which can cause spalling of the coating.

Details of solution compositions and operating conditions for this treatment are given in Fig. 8, which also shows a flow diagram of the processing steps.



| Operating conditions | Alternating current treatment | Direct current treatment |
|---|---|---|
| **For coatings of both colors and thicknesses** | | |

| | | |
|---|---|---|
| Composition of aqueous anodizing solution[a]: | | |
| $NH_4HF_2$, g/L (oz/gal) | 240 (32) | 360 (48) |
| $Na_2Cr_2O_7 \cdot 2H_2O$, g/L (oz/gal) | 100 (13.3) | 100 (13.3) |
| 85% $H_3PO_4$, mL/L (fl oz/gal) | 90 (12) | 90 (12) |
| Operating temperature[b], °C (°F) | 71-82 (160-180) | 71-82 (160-180) |
| Current density, A/dm$^2$ (A/ft$^2$) | 0.5-5 (5-50) | 0.5-5 (5-50) |
| **For light green coating, thin[c]** | | |
| Current consumption[d], A · min/m$^2$ (A · min/ft$^2$) | 860-1075 (80-100) | 540-645 (50-60) |
| Terminating voltage[d], V | 75 | 75 |
| Treatment time[d], min | 4-5 | $2\frac{1}{2}$-3 |
| **For dark green coating, thick[e]** | | |
| Current consumption[d], A · min/m$^2$ (A · min/ft$^2$) | 4950 (460) | 3230 (300) |
| Terminating voltage[d], V | 100 | 100 |
| Treatment time[d], min | 23[f] | 15[f] |
| **Sealing post-treatment[g]** | | |
| Aqueous solution, sodium tetrasilicate ($Na_2Si_4O_9$), g/L (oz/gal) | 53 (7) | |
| Temperature, °C (°F) | 93-100 (200-212) | |
| Immersion time, min | 15 | |

(a) Use water from steam condensate or water treated by ion exchange, when available, instead of well or hard tap water.

(b) Solution will not operate below 60 °C (140 °F). It may be operated up to the boiling point without adversely affecting results.

(c) Formed in first phase of treatment. Usual thickness, 5.0 μm (0.2 mil); range, 2.5 to 7.5 μm (0.1 to 0.3 mil).

(d) Terminating voltage and treatment time vary, but the number of ampere minutes per unit area remains constant for any one alloy.

(e) Formed in second phase of treatment. Usual thickness 30.4 μm (1.2 mils); range, 23 to 38.1 μm (0.9 to 1.5 mils).

(f) A denser coating is produced by maintaining the voltage, allowing the current to decrease for 20 min (ac) or 15 min (dc) after the indicated minimum amperage per square metre (foot) has been applied.

(g) Optional; to increase corrosion resistance, apply to parts not to receive organic finishes. Immerse in solution,rinse parts in cold, then in hot, water. Air dry.

**Fig. 8 Chemical treatment No. 17 (MIL-M-45202) anodizing treatment. Conditions for cleaning and rinsing same as for galvanic anodizing treatment**

***Bath Preparation.*** Half the amount of water required should be heated to 71 °C (160 °F), then slowly add ammonium acid fluoride. Add other chemicals and the remainder of the water. The solution should be heated to 82 °C (180 °F), and stirred vigorously for 5 to 10 min. Reheating to 82 °C (180 °F) and stirring should be repeated each time the solution cools to room temperature.

***Bath Replenishment.*** Rise of terminating voltage indicates depletion of bath. Usually, an adjustment in bath composition is required after about 0.5 $m^2$/L (20 $ft^2$/gal) of bath has been treated. The amounts of ingredients added are determined by standard methods of chemical analysis of the depleted solution.

***Equipment.*** The anodizing tank and heating coils usually are made of low-carbon steel. However, tanks lined with synthetic rubber or a vinyl-based material may be used, provided the cathodes are of low-carbon steel and a sufficient distance is allowed between the work and the sides of the tank to prevent contact and burning.

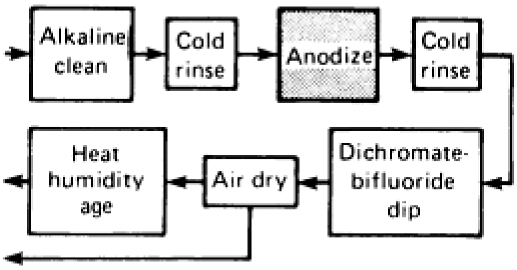
Most racks are made of magnesium alloys, and the coating formed on these racks during anodizing can be stripped in an aqueous solution containing 20% chromic acid. Aluminum alloys 5052, 5056, and 220 are also acceptable rack materials, but to avoid chemical attack, these alloys must not be immersed in the solution on open circuit.

Motor generators may be used to supply power for either alternating-current or direct-current installations. Rectifiers are suitable for supplying direct current only. A saturable reactor may be used to generate alternating current.

**HAE treatment** also produces a two-phase coating and is applied to all forms and alloys of magnesium, provided they contain no attachments or inserts of other metals. A light tan subcoating, about 5.0 μm (0.2 mil) thick, is produced at lower voltages. The thicker phase, formed at higher voltages, is normally dark brown in color and usually about 30 μm (1.2 mil) thick. Both phases have excellent paint-based characteristics.

The dark brown coating is hard and exhibits exceptionally good abrasion resistance, but it spalls under compressive deformation and can adversely affect the fatigue strength of a base metal less than about 2.5 mm (0.1 in.) thick. The subcoating has no effect on fatigue strength and does not spall.

Solution compositions and operating conditions for the HAE treatment are given in the table that accompanies the flow chart for the process in Fig. 9. The dichromate-bifluoride post-treatment that is part of the HAE treatment, as shown in Fig. 9, provides the coating with high resistance to corrosion.



| **Anodizing**[a] | |
|---|---|
| Composition of solution, g/L (oz/gal): | |
| Potassium hydroxide (KOH) | 165 (22) |
| Aluminum hydroxide ($Al(OH)_3$) | 34 (4.5)[b] |
| Potassium fluoride ($K_2F_2$) | 34 (4.5) |
| Trisodium phosphate ($Na_3PO_4$) | 34 (4.5) |
| Potassium manganate ($K_2MnO_4$)[c] | 19 (2.5) |
| Water | bal to 3.7 L (to 1 gal) |
| Operating temperature, °C (°F) | Room temperature to 25 (to 77) |
| Current density, A/dm$^2$ (A/ft$^2$) | 1.5-2.5 (15-25) |
| Terminating voltage, V: | |
| First-phase coating | 65-70 |
| Second-phase coating | 80-90 |
| Treatment time[d], min: | |
| First-phase coating | 7-10 |
| Second-phase coating | 60 |

| | |
|---|---|
| **Dichromate-bifluoride dip** | |
| Composition of solution, g/L (oz/gal): | |
| Sodium dichromate, ($Na_2Cr_2O_7 \cdot 2H_2O$) | 20 (2.7) |
| Ammonium bifluoride ($NH_4HF_2$) | 100 (13.3) |
| Water | bal to 3.7 L (to 1 gal) |
| Operating temperature, °C (°F) | 21-32 (70-90) |
| Immersion time, min | 1 |
| **Heat-humidity aging**[e] | |
| Temperature, °C (°F) | 77-85 (170-185) |
| Relative humidity, % | ~85 |
| Time, h | 7-15 |

(a) Acid pickling is not required before anodizing because of the chemical action of the anodizing bath on the alkaline-cleaned surface. Use alternating current for anodizing. Coatings are deposited in two phases: first a light tan coating 5.0 μm (0.2 mil) thick, then a dark brown coating usually 30.4 μm (1.2 mils) thick.

(b) For an exceptionally hard, abrasion resistant, dark brown coating, use 45 to 53 g/L (6 to 7 oz/gal) $Al(OH)_3$.

(c) An equal weight of potassium permanganate ($KMnO_4$) may be used instead of potassium manganate; dissolve the permanganate completely in water before adding to the solution; an additional 43 g (1.5 oz) of potassium hydroxide must also be added.

(d) Treatment time varies with current density. Increasing current density decreases treatment time; for uniform coating, 2 A/dm$^2$ (20 A/ft$^2$) is recommended.

(e) Improves corrosion resistance of coated parts

**Fig. 9 HAE anodizing treatment (MIL-C-13335, amendment 1; MIL-M-45202). Conditions for cleaning and rinsing same as for galvanic anodizing treatment**

***Bath Preparation.*** As the first step in preparing the HAE solution, the anhydrous potassium fluoride and trisodium phosphate are dissolved in about half the amount of water required. To this is added an aqueous solution of potassium hydroxide in which aluminum hydroxide has been dissolved. It is difficult to dissolve commercially obtained aluminum hydroxide in a potassium hydroxide solution at room temperature, but it can be dissolved by boiling it in the potassium hydroxide solution for 15 to 20 min.

Metallic aluminum may be dissolved in potassium hydroxide in place of aluminum hydroxide. The reaction, which should be performed under an exhaust hood or in a well-ventilated location, forms a clear liquid and black residue; only the clear liquid is added to the main solution.

Either potassium manganate or potassium permanganate, which is unstable in alkaline solutions and converts to the manganate, is added last. Conversion of the permanganate is evidenced by a color change from purple to green. Conversion can be accelerated by dissolving the permanganate in boiling water and then adding this solution to the bath, or by adding it to the potassium hydroxide solution and boiling. Finally, water is added to make the required volume of solution; continuous agitation is necessary to put all ingredients into solution.

***Bath Replenishment.*** Expensive analyses are not required for maintaining the bath, because depletion of the manganese compound is indicated by a lightening of the characteristic dark brown color of the coating and serves as a bath control. It should be noted, however, that coatings of the lighter brown color have the same properties as those of dark brown color. To maintain the dark brown color of the coating, bath adjustments should be made after about 0.4 $m^2$/L (15 $ft^2$/gal) of bath has been treated.

To replenish, 3.7 to 7.5 g/L (0.5 to 1 oz/gal) of potassium manganate or permanganate is added while the bath is being constantly agitated. Additions of aluminum are made at 15 to 20% of the original quantities or aluminum hydroxide (11 g/L, or $1\frac{1}{2}$ oz/gal to solution) as previously described. The fluoride and phosphate ingredients deplete at a very slow rate and may be added at six-month intervals if the bath is used continually at the rate of 15 to 20% of original quantities.

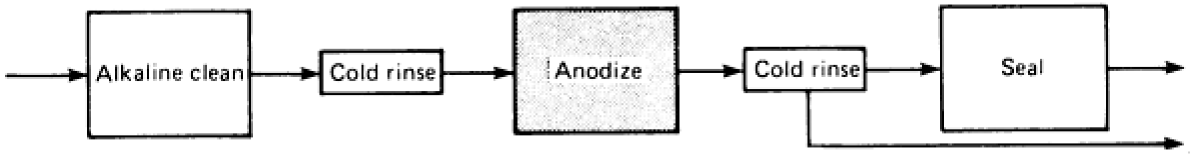
***Post-Treatment.*** After anodizing, parts are rinsed thoroughly in water and immersed for 1 min in an aqueous solution containing 77 g (2.7 oz) of sodium dichromate and 377 g (13.3 oz) of ammonium bifluoride per 3.7 L (1 gal) of water. To dry parts, hot air may be used, without rinsing, and parts may be aged in an oven for 7 to 15 h. Aging at about 79 °C (175 °F) and about 85% relative humidity greatly improves the corrosion-protective quality of the coating. Heating of parts, particularly those with thick wall sections, should be done at low humidity until the surface is hot, after which aging is continued at higher humidity.

***Equipment.*** The anodizing tank of double-welded construction and cooling plates or coils are made of black iron. Racks should be of magnesium alloy and should be protected by a suitable vinyl tape at solution level. Steel clamps can be used to clamp the racks to busbars. Galvanized iron, brass, bronze, tin, zinc, and rubber should not be used for equipment that comes in contact with the bath.

Alternating current at 60 Hz is supplied from a constant current regulator capable of delivering the required current over a range of 0 to 110 V.

The post-treatment dip tank must be lined with polyethylene or similar inert material. An oven or humidity cabinet, capable of maintaining temperatures to 86 °C (185 °F) and humidity to 85%, is used for aging.

**Cr-22 Treatment.** A flow chart of processing steps for the Cr-22 treatment is presented in Fig. 10, together with a table listing bath compositions and operating conditions. The green and black coatings obtainable by varying solution composition, operating temperature, and current density may be applied to all alloys, and although intended primarily as bases for organic finishes, these coatings provide excellent corrosion resistance to unpainted parts when sealed as described in Fig. 10. Inclusions or residual stresses in the magnesium surface occasionally result in the appearance of small nodules in the Cr-22 coating, but the presence of these nodules has no apparent effect on the corrosion protection provided by the coating. Heavier coatings produced by the Cr-22 treatment, like those produced by Chemical Treatment No. 17 and HAE treatments, spall under compressive deformation.



| **Operating conditions** | **Type of coating** | |
|---|---|---|
| | **Green**[a] | **Black**[b] |
| Composition of anodizing solution: | | |
| $CrO_3$, g/L (oz/gal) | 25 (3.3) | 50 (6.7) |
| 50% HF (sp gr, 1.20), mL/L (fl oz/gal) | 36 (4.7) | 35 (4.7) |
| 85% $H_3PO_4$ (sp gr, 1.70), mL/L (fl oz/gal) | 50 (6.7) | 50 (6.7) |
| $NH_4OH$ (sp gr, 0.90), mL/L (fl oz/gal) | 220 (29) | 220 (28) |
| Water[c] | bal | bal |
| Operating temperature, °C (°F) | 88-91 (190-195)[d] | 85 (185)[d] |
| Current density | 1.5 (15)[e] | 2.5 (25)[f] |
| Terminating voltage, V | | |
| For normal thickness | 320 | 320 |
| For heavy coatings | 350-380 | 350-380 |
| Treatment time, min | 12-15 | 12-15 |
| Sealing post-treatment[g] | | |
| Solution, vol% sodium silicate (42° Bé) | 10 | |
| Temperature, °C (°F) | 85-100 (185-212) | |
| Immersion time, min | 2 | |

(a) Green coating, conforming to MIL-M-45202, type II, class B, ranges in thicknesses from 10 to 28 μm (0.4 to 1.1 mil); usual thickness, 20 μm (0.8 mil).

(b) Black coating, conforming to MIL-M-45202; type II, class C, ranges in thickness from 5 to 25 μm (0.2 to 1.0 mil); usual thickness, 13 μm (0.5 mil).

(c) Use water from steam condensate or water treated by ion exchange, when available, instead of well or hard tap water.

(d) Recommended; effective range, 74 to 93 °C (165 to 200 °F).

(e) Recommended; effective range, 1.0 to 3.0 A/$dm^2$ (10 to 30 A/$ft^2$).

(f) Recommended; effective range, 2.0 to 3.0 A/$dm^2$ (20 to 30 A/$ft^2$).

(g) Optional for both types; to increase corrosion resistance, apply to parts not to receive organic finishes

**Fig. 10 Cr-22 (MIL-M-45202) anodizing treatment. Conditions for cleaning and rinsing same as for galvanic anodizing treatment**

***Bath Preparation.*** To half the required volume of water, the constituents of the bath are added in the order listed in Fig. 10, stirring continuously. When the chemicals are completely dissolved, water is added to bring the bath to the required volume, then sufficient ammonium hydroxide is added to raise the pH to 8.

***Bath replenishment*** can be affected by adding the initial preparation chemicals in quantities determined by conventional chemical analyses for ammonia, phosphorus, fluorine, and hexavalent chromium. Replenishment after the anodizing of 0.6 $m^2$/L (30 $ft^2$/gal) of electrolyte, at 1.5 A/$dm^2$ (15 A/$ft^2$), has been found satisfactory. To minimize vapor losses at the high operating temperature of Cr-22 baths, polyethylene floats are used to cover bath surfaces.

***Equipment.*** Tanks and heating coils should be made of low-carbon steel. Do not use copper, brass, or zinc for equipment that will come into contact with the bath. Racks should be made of magnesium alloys, and as in all anodizing treatments, electrical contact points should be clean and firm.

The power supply should be capable of delivering a current of 1.5 A/$dm^2$ (15 A/$ft^2$) of work area at a maximum of 350 V (60 cycles/s, alternating current).

**Repair of Damaged Anodic Coatings.** Touch-up procedures depend on the nature and extent of damage. Minor damage, scratches, or very small areas where magnesium metal is exposed can be treated as follows:

1. Clean damaged area with organic solvent.
2. Brush with chrome pickle solution (Fig. 3, solution 4); or with a solution containing 9.7 g/L (1.3 oz/gal) of chromic acid with water and 28 g (1 oz) of calcium sulfate, added in that order and stirred vigorously for 15 min.
3. Apply suitable primer and finish paint coat after thoroughly rinsing and drying.

Larger areas, several square inches, can be reanodized without removing the old coating, or the old coating can be stripped in a 20% solution of chromic acid and the entire part reanodized.

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12. C. Jurey, Magoxid-Coat, A Hard Anodic Coating for Magnesium, *Proc. Int. Magnesium Association* (Washington, DC), 1993
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## Process Control of Chemical and Anodic Treatments

To achieve desired results with any acid pickle, chemical, or anodic treatment, proper control of temperature and concentration must be maintained. In these treatments, solution temperature governs the rate of metal removal or of film formation. Acid pickles and chemical treatments are conventionally formulated to be used at room temperature to avoid the expense of heating or cooling. Elevated temperatures are required only when chemical action is too slow at ambient temperature, as in alkaline cleaning, chromic acid pickling, and anodizing.

The rate of metal removal by acid pickling also increases with acid concentration. Solutions are usually formulated so that the pickling rate is fast enough to be economical, but not so fast that metal removal is difficult to control or that localized pitting results. As the bath is used, magnesium is dissolved and acid is consumed. Concentrated acid must be added periodically to replenish what is consumed and to maintain the solution within recommended composition limits. As the magnesium content of the solution increases, the pickling rate becomes slower, and eventually the rate becomes too slow, no matter how high the acid content. Chemical treatments cause staining when the magnesium content of solutions used is too high. These conditions can be avoided by discarding solution when its magnesium content reaches about 30 g/L (4 oz/gal).

When only one acid is present in a pickling solution, its concentration may be determined analytically by titration with standard sodium hydroxide solution. Magnesium content can be determined rapidly with atomic absorption spectroscopy or a flame photometer. Other components of the chemical baths can be determined by standard analytical procedures. In the absence of analytical facilities, it is necessary to fortify pickling solutions periodically to maintain the desired reaction rate; solutions for chemical treatment may be maintained by periodically replacing one-fourth of the volume with fresh solution.

Table 4 summarizes process control for various acid pickling, chemical, and anodic treatments and indicates the unfavorable effects that result when operating variables are above or below recommended ranges.

**Table 4 Effects of lack of control of process variables in acid pickling, chemical, and anodic treatments**

| Treatment | Solution constituent or condition | Recommended range | Effect of operating out of recommended range | |
|---|---|---|---|---|
| | | | Too low | Too high |
| **Acid pickling treatments** | | | | |
| Acetic-nitrate | Glacial acetic acid | 115-300 g/L (15-40 oz/gal) | Slow rate | Uneconomical |
| | Sodium nitrate | 30.0-75 g/L (4-10 oz/gal) | Smut | Slow rate |
| Chromic acid | Chromic acid | 115-375 g/L (15-50 oz/gal) | Slow rate | Uneconomical |

| | | | | |
|---|---|---|---|---|
| Chromic-sulfuric | Chromic acid | 150.4-240.6 g/L (20-32 oz/gal) | Unknown(a) | Unknown(a) |
| | 96% sulfuric acid | 0.37-0.60 g/L (0.05-0.08 oz/gal) | Unknown(a) | Unknown(a) |
| | pH | 0.4-1.0 | Unknown(a) | Unknown(a) |
| Ferric nitrate(b) | Chromic acid | 150.4-225 g/L (20-30 oz/gal) | Rapid rate; yellow stain | Slow rate |
| | Ferric nitrate | 22.5-45.1 g/L (3-6 oz/gal) | Slow rate; rough or frosted | Rapid rate; yellow stain |
| | Sodium fluoride | 2.2-6.7 g/L (0.3-0.9 oz/gal) | Slow rate; smut; rough or frosted appearance | Rapid rate; yellow or gray film |
| Glycolic-nitrate | 70% glycolic acid | 115-375 g/L (15-50 oz/gal) | Poor corrosion resistance | Uneconomical |
| | 70% nitric acid | 22.5-90.2 g/L (3-12 oz/gal) | Slow rate | Rapid rate |
| | Sodium nitrate | 30.0-75.2 g/L (4-10 oz/gal) | Smut | Slow rate |
| Hydrofluoric acid | 50% hydrofluoric acid | 190-565 g/L (25-75 oz/gal) | Powdery dichromate treatment; incomplete $MgF_2$ film | Uneconomical |
| Nitric acid | 70% nitric acid | 30.0-75.2 g/L (4-10 oz/gal) | Slow rate | Rapid rate; rough surface |
| Nitric-sulfuric | 70% nitric acid | 30.0-90.2 g/L (4-12 oz/gal) | Smut | Rapid rate |
| | 96% sulfuric acid | 9.5-30.0 g/L (1.3-4 oz/gal) | Slow rate | Rapid rate |
| Phosphoric acid(c) | 85% phosphoric acid | 865-965 g/L (115-128 oz/gal) | Rapid rate | . . . |
| Sulfuric acid | 96% sulfuric acid | 15.0-45.1 g/L (2-6 oz/gal) | Slow rate | Rapid rate; rough surface |
| **Chemical treatments** | | | | |

| | | | | |
|---|---|---|---|---|
| Chrome pickle and sealed chrome pickle | Sodium dichromate | 135.3-205 g/L (18-27 oz/gal) | Powdery coating | Shallow etch |
| | 70% nitric acid | 60.1-180.4 g/L (8-24 oz/gal) | Shallow etch | Powdery coating |
| | Temperature | 21-49 °C (70-120 °F) | Shallow etch | Powdery coating |
| | Magnesium | 30.0 g/L max (4 oz/gal max) | . . . | Shallow etch |
| | Prerinse delay in air | 5 s max(d) | . . . | Powdery coating |
| Dichromate | Sodium dichromate | 120-205 g/L (16-27 oz/gal)(e) | Nonuniform or no coating | Uneconomical |
| | Calcium fluoride | | Powdery coating | No problem |
| | Free fluoride | 0.2% max | . . . | No coating(f) |
| | pH(g) | 4.1-5.5 | Heavy or powdery coating | Nonuniform or no coating |
| | Temperature | 93-100 °C (200-212 °F) | No coating | . . . |
| Modified chrome pickle(h) | Sodium acid fluoride | 11.2-15.0 g/L (1.5-2 oz/gal) | Powdery smut | Powdery coating |
| | Sodium dichromate | 135.3-205.0 g/L (18-27 oz/gal) | Pale color; too reactive | Slow rate |
| | Aluminum sulfate | 7.5-11.2 g/L (1.0-1.5 oz/gal)(i) | Poor coating color on castings | Rapid rate; poor etch |
| | 70% nitric acid | 22.5-120.3 g/L (3-16 oz/gal) | Poor etch; slow rate | Pale color; poor etch |
| | Temperature | 21-38 °C (70-100 °F) | Slow rate | Too reactive |
| **Anodic treatments** | | | | |
| Chemical Treatment No. 9 | Ammonium sulfate | 16.5-24.0 g/L (2.2-3.2 oz/gal)(j) | Slow rate | Powdery coating |
| | Sodium dichromate | 16.5-24.0 g/L (2.2-3.2 | Thin coating | Slow rate |

| | | | | |
|---|---|---|---|---|
| | | oz/gal)(k) | | |
| | pH(l) | 5.6-6.0 | Powdery coating | Slow rate |
| | Temperature | 49-60 °C (120-140 °F) | Slow rate | Rapid rate |
| Chemical Treatment No. 17 | Ammonium acid fluoride(m) | 300.8-451.2 g/L(n) (40-60 oz/gal) | Local pitting | Insoluble |
| | Sodium dichromate(m) | 53-120 g/L (7-16 oz/gal) | Thin coating | Uneconomical |
| | 85% phosphoric acid(m) | 53-105.2 g/L (7-14 oz/gal) | Soft coating | Uneconomical |
| | Chloride contamination | 3% max | . . . | Soft coating |
| | Current density | 0.5-5 A/dm$^2$ (5-50 A/ft$^2$) | Attack at liquid level | Pitting or burning |
| | Temperature | 71-82 °C (160-180 °F) | No coating | No problem |
| HAE | Potassium hydroxide | 105-190 g/L (14-25 oz/gal) | Pitting; burning; nonuniformity | Pitting; burning; roughness |
| | Potassium fluoride(o) | 15.0-150.4 g/L (2-20 oz/gal) | Spottiness; nonuniformity | Uneconomical |
| | Trisodium phosphate(p) | 15.0-225.6 g/L (2-30 oz/gal) | Light and dark areas | Uneconomical |
| | Aluminum hydroxide(p) | 7.5-53 g/L (1-7 oz/gal)(q) | Coating hardness lowered | Hard, rough coating |
| | Potassium manganate | 3.7-22.5 g/L (0.5-3 oz/gal) | Light brown coating | Dark brown, rough coating |
| | Current density | 0.5-5 A/dm$^2$ (5-50 A/ft$^2$) | Slow rate | Nonuniformity in recesses(r) |
| | Temperature | 25-38 °C (77-100 °F)(s) | . . . | Lower corrosion resistance |
| Cr-22 | Chromic acid(t) | 22.5-30.0 g/L (3-4 oz/gal) | Nonuniform or pale coating | Dark coating |

| | | | | |
|---|---|---|---|---|
| | 50% hydrofluoric acid(t) | 30.0-53 g/L (4-7 oz/gal) | Low voltage, nonuniform coating | Pale coating |
| | 85% phosphoric acid(t) | 45.1-90.2 g/L (6-12 oz/gal) | Nonuniform coating | Uneconomical; rough coating |
| | pH(u) | 6.0-6.5 | . . . | Uneconomical |
| | Current density | 1.0-3.0 A/dm$^2$ (10-30 A/ft$^2$) | Slow rate | Dark coating |
| | Temperature | 74-93 °C (165-200 °F) | Slower corrosion resistance | . . . |

(a) Effects of operation outside recommended ranges are not known. Depletion of solution is indicated by the formation of a brassy film and by a pH in excess of 1.0; at this point, add chromic and sulfuric acids, or discard solution.

(b) Discard solution when depleted or periodically add one fourth of volume of solution.

(c) Dragout loss prevents excessive salt buildup.

(d) Do not allow surface to dry out before rinsing.

(e) Limited solubility regulates fluoride.

(f) Add 0.2% calcium chromate if fluoride is too high.

(g) Correct pH with additions of sodium hydroxide or chromic acid.

(h) Fortify bath by additions of sodium dichromate to restore original concentration of 180.4 g/L (24 oz/gal) of nitric acid to maintain concentration of used bath at 60 g/L (8 oz/gal) and of 28 g (1 oz) of sodium acid fluoride for every 310 g (11 oz) of nitric acid added. Bath is considered depleted when concentration of nitric acid is below 22.5 g/L (3 oz/gal) and is indicated by poor color and nonuniformity of coating.

(i) For fresh bath; no additions required when fortifying.

(j) As $H_2SO_4$.

(k) As $CrO_3$.

(l) Control of pH achieved by additions of a solution containing, by weight, 5% $CrO_3$ and 5% $H_2SO_4$ (concentrated).

(m) Fortify after preparing 0.4 $m^2/L$ (20 $ft^2/gal$) of solution.

(n) Local pitting begins at 1020 g (36 oz), particularly with thorium-containing alloys.

(o) Anhydrous.

(p) Fortify after treating 0.3 $m^2/L$ (15 $ft^2/gal$) of solution to maintain dark brown color of coating.

(q) 2.2 to 15.0 g/L (0.3 to 2 oz/gal) as Al.

(r) Use 1.5 $A/dm^2$ (15 $A/ft^2$) for uniformity of coating in recesses.

(s) Ideal temperature, 27 °C (80 °F); 38 °C (100 °F) is satisfactory for alloys containing aluminum.

(t) Fortify after treating 0.7 $m^2/L$ (36 $ft^2/gal$) to maintain deposition rate.

(u) Control of pH achieved by adding 28% solution of ammonium hydroxide

**In-Process Corrosion.** During periods of high humidity, magnesium parts in process often exhibit corrosion products, even though protected with a chrome pickle. This is especially true of sand castings. The corrosion products are readily removed by treating the parts in a boiling dichromate solution as shown in Fig. 5. The parts are then protected from further corrosion by slushing oil.

## Difficulties with Chemical and Anodic Treatments

Difficulties experienced with chemical and anodic treatments result from the lack of control of processing variables. One difficulty common to all treatments, chemical or anodic, is nonuniformity of coating or actual failure to coat on certain areas of a part. This is most likely to occur on complex parts and is caused by the entrapment of air in pockets or blind holes. The remedy is to agitate parts when first placing them in the bath and to reposition them periodically to make sure the bath is brought into contact with all areas.

Other difficulties and their corrections vary for each chemical or anodic treatment. Tables 5, 6, and 7 describe the usual appearance of coatings produced by the chrome pickle, sealed chrome pickle, dichromate, Chemical Treatment No. 9, Chemical Treatment No. 17, and HAE treatments, and list common difficulties, as evidenced by deviations from usual coating appearance, together with causes of these difficulties and procedures to be followed for their correction.

**Table 5 Causes and corrections of difficulties with coatings produced by the chrome pickle and sealed chrome pickle treatments**

Normal appearance of coating, matte gray to yellow red iridescent

| Difficulty | Cause | Corrective procedure |
|---|---|---|
| Pale color, shallow etch, slow reaction of solution with metal | Depletion of the chrome pickle bath. Paleness of color should not be confused with the lack of color from insufficient exposure to air during transfer to rinse | Revivify bath by additions of nitric acid and sodium dichromate to restore to proper operating level. Control bath by periodic chemical analysis of ingredients |

| | | |
|---|---|---|
| Bright, brassy--smooth surface with occasional pits(a) | Excess of nitric acid in the bath | Adjust with additions of sodium dichromate to restore proper ratio of dichromate to acid |
| | Buildup of excessive amount of magnesium nitrate in the bath | Bath has been revivified too many times; discard and use fresh bath |
| Brown, nonadherent, powdery coatings | Work held in air too long before rinsing | Delay in air; 5 s max; surface should not dry before rinsing |
| | Ratio of acid to sodium dichromate concentration too high | Adjust concentrations to restore proper ratio |
| | Solution too hot because of small volume in relation to work | Cool solution or increase volume of solution used |
| | Metal not properly degreased | Use recommended cleaning method |
| | Oil film on solution | Prevent by using recommended cleaning procedures(b) |
| | Solution revivified too often | Discard; use fresh solution |

Note: When viewed under magnification, coating exhibits a network of pebbled etching. The appearance of a properly applied chrome pickle coating is influenced to some degree by the age of the solution and by the composition and temper of the alloy treated.

(a) When examined under magnification.

(b) Correct by skimming off oil and adding small amount, 0.05%, of fluorinated-hydrocarbon wetting agent

## Table 6 Causes and corrections of difficulties with dichromate coatings

Normal appearance varies from light to dark brown, depending on alloy composition

| **Difficulty** | **Cause** | **Corrective procedure** |
|---|---|---|
| Abnormally heavy coatings | pH of dichromate bath too low, below 4.1 | Raise pH by addition of NaOH |
| | Contact between work and tank | Insulate parts and rack from tank |
| Loose, powdery coatings | Acid fluoride or HF bath too dilute | Adjust fluoride content |
| | pH of dichromate bath <4.1 | Raise pH by addition of NaOH |
| | Parts oxidized, corroded, or flux-contaminated | Chromic acid clean parts prior to dichromating |

| | | |
|---|---|---|
| | Contact between work and tank | Insulate parts and rack from tank |
| Failure to coat, or nonuniform coatings | pH of dichromate bath >5.5 | Lower pH by addition of $CrO_3$ |
| | Dichromate concentration too low | Do not allow dichromate to fall below 120 g/L (16 oz/gal); maintain as high as economical |
| | Oily matter not removed; previous chrome pickle coating not completely removed | Careful rinsing after alkaline cleaning; use chromic acid pickle to supplement alkaline cleaning for complete removal of chrome pickle coating |
| | Part not fluoride treated | Give part acid fluoride or HF pickle before dichromating |
| | Part is made of EK30A, EK41A, HK31A, HM21A, HM31A, or M1A | Dichromate treatment does not coat these alloys; use another treatment |
| | Dichromate bath not kept boiling during treatment period | Solution should actually boil; minimum bath temperature, 93 °C (200 °F) |
| | High carryover of acid fluoride or HF into dichromate bath | Thoroughly rinse parts after acid fluoride or HF pickle |
| | Hydrofluoric acid dip too long | Use $\frac{1}{2}$ to 1 min for AZ31A and B; if 5 min dip is used, extend cold water rinse to 5.7 min |
| Pitting or other attack on aluminum inserts or attachments | Hydrofluoric acid dip reacts on aluminum | Use sodium, potassium, or ammonium acid fluoride solution in place of hydrofluoric acid dip |

## Table 7 Causes and corrections of difficulties with coatings produced by anodizing treatments

| **Difficulty** | **Cause** | **Corrective procedure** |
|---|---|---|
| **Chemical treatment No. 9**[(a)] | | |
| Grayish, nonuniform appearance | Insufficient or improper cleaning of work before treatment | Use proper methods for adequate cleaning |
| | Treating solutions depleted | Check pickling bath, HF or acid fluoride, for proper pH[(b)] |
| Failure to coat on certain alloys[(c)] | Lack of good external electrical contact of work with tank or cathode plates | Ensure good external electrical contact between work and cathode |
| | Work touching tank walls or bottom (or cathode plates) | Prevent work from contacting cathode in electrolyte |

| | | |
|---|---|---|
| **Chemical treatment No. 17(d)** | | |
| Deviation from characteristic appearance | Improper balance in content of bath ingredients(e) | Adjust bath ingredients to proper operating range; use chemical analysis to determine need |
| Spalling of dark green coating | Unusually thick coatings may spall when substrate is bent or otherwise deformed | Spalling can be minimized by sealing coating with an organic finish having low surface tension, low viscosity, and slow drying rate |
| **HAE anodizing treatment(f)** | | |
| Significant color lightening | Depletion of the chemical ingredients of the bath(e) | Adjust aluminum and manganese contents to proper level(g) |

(a) Usual appearance of thin coating; light tan; thick coating; dark brown.

(b) Galvanic anodizing bath is maintained at a pH of 5.6 to 6.0 with additions of a solution containing, by weight, 5% $H_2SO_4$ (concentrated).

(c) Especially alloys without aluminum content such as EK30A, EK41A, HK31A, HM21A, HM31A, and HZ32A.

(d) Usual appearance of a thin coating: light green; thick coating: dark green. A clear, colorless coating can also be deposited by Chemical treatment No. 17 by use of 40 V as terminal voltage.

(e) Solution unbalance may occur after treatment of as little as 0.4 $m^2$/L (20 $ft^2$/gal) of solution; however, when applying clear or thin coatings, 2 to 2.6 $m^2$/L (100 to 130 $ft^2$/gal) of solution usually can be treated before bath adjustment is indicated.

(f) Usual appearance of thin coating: light tan; thick coating: dark brown.

(g) Fluoride and phosphate become depleted at an extremely low rate and require adjustment only every few months in production.

For example, the adhesion of paint films applied to dichromated parts can be adversely affected by the presence of a dusty material on the parts after final rinsing and drying. Chemical analysis might indicate this material to be a sulfate precipitated from the domestic water that was being used to replace evaporation losses in the dichromating solution. The problem can be solved by recycling: storing the steam condensate obtained from heating the solution and installing an automatic level-control system to feed this condensate into the dichromating tank.

Although dichromating usually treats the metal satisfactorily, another example of special difficulties might involve a residue of dye-penetrant developer that can remain on the surfaces of castings and interfere with the adhesion of paint films. In this situation, vapor degreasing, either before or after the dichromating treatment, would only set the developer, rather than effect its removal. Thorough cleaning of parts to remove all developer residue immediately after penetrant inspection, and before vapor degreasing, can solve the problem. This cleaning would entail the use of an alkaline cleaner and, if necessary, scrubbing with a bristle brush.

Another example involves corrosion products that were observed surrounding stainless steel hardware that had been inserted into sand castings of alloy AZ91A before dichromating. The parts were free from corrosion immediately after application of the finish; corrosion occurred while parts were in storage.

The corrosion of the magnesium was found to be the result of a galvanic couple set up between the magnesium and stainless steel, caused by the entrapment of acid solution during dichromating. This condition was eliminated by applying the dichromate treatment to the castings before inserting the stainless steel parts, and by applying a coating of zinc chromate primer to the stainless steel parts just before inserting them into the castings.

Precision-machined parts that were given a chromic acid pickle might present another example of difficulty if the parts were found to have an etched surface. Analysis of the bath might indicate the presence of a high concentration of chloride and sulfate ions, 0.5 g/L (0.07 oz/gal), of Cl, as NaCl, and 1.7 g/L (0.2 oz/gal) of $SO_4$, as $H_2SO_4$,the source of which might be traced to the prepared water. Because chloride and sulfate ions cannot be readily removed, the bath would probably be discarded. To prevent further loss of parts, baths must be checked frequently and test panels treated for 15 to 30 s and examined; an evolution of gas during treatment and a dimensional change indicate that a bath is contaminated and must be discarded.

As another example, spacecraft parts were only given a Chemical Treatment No. 17 anodize for corrosion protection. Although this treatment was satisfactory during indoor in-plant processing, white corrosion appeared during stand-by in the salt air and fog atmosphere at the launch pad. This attractive anodic coating is porous and not corrosion-protective. Parts were sealed with a paint system to correct the problem.

**Inspection Methods.** Examine coatings on treated parts visually for complete and uniform coverage and for color peculiar to the type of treatment being checked. Buildup caused by the coating is determined most simply and reliably by measurement of the parts, before and after treatment, with a micrometer accurate to 2.5 μm (0.1 mil). If this is not possible, measure test panels that have been treated simultaneously with the parts before and after treatment.

Process test panels together with panels through all the steps of cleaning, pretreatment coating, and where applicable, post-treatment. Post-treatment should not consist of an additional film of coating, organic or inorganic, applied either by spraying or dipping. After processing for the time required to produce the coating, test panels should be subjected to the following tests:

- *Abrasion resistance:* The test panels should be rubbed by the tip of a 4.7 mm ($\frac{3}{16}$ in.) diam Pyrex rod, the end of which has been heated in a blast flame until it is fire polished and hemispherical. Press the rod against the coating and rub back and forth by hand with just enough pressure to abrade the surface of the rod. The coating should not break or show scratches that penetrate to the base metal.
- *Salt spray (fog) exposure:* The treated test panels, when exposed to salt spray in accordance with Federal Test Method 151 for a specified number of hours, rinsed in tap water, and air dried, should show an average of no more than eight corrosion spots, none larger than 0.8 mm ($\frac{1}{32}$ in.) in greatest dimension. Corrosion appearing at the electrical-contact area or at the edges of the test panels may be disregarded.

## Plating

All commercial plating systems can be applied to magnesium alloys after proper preplating operations. However, zinc and nickel are the only metals that can be plated directly on magnesium. These deposits are not used commercially, but instead serve as undercoatings upon which other commonly plated metals are deposited. Standard practice for plating magnesium involves surface conditioning, zinc immersion plating (zincate solution), and a cyanide copper strike to a thickness of 8 μm (0.3 mil), followed by any standard plating process.

The preparation of magnesium for electroplating is similar in principle to that prescribed for many other metals. First, magnesium must be cleaned to remove all surface contaminants. Then, depending on the surface finish desired, it must be conditioned. This may be accomplished by one or more of the following finishing methods: glass or plastic bead blasting, pickling, barrel finishing, and polishing and buffing. Surface contaminants resulting from these treatments must be removed by additional cleaning. Depending on the type of soil, suitable cleaning methods include vapor degreasing, emulsion cleaning, alkaline soak cleaning, and water rinsing. Finally, the magnesium surface must be activated chemically before it can accept either of the recommended metal undercoatings.

**Nickel Undercoating.** The deposition of nickel on magnesium must be preceded by two acid etching treatments, one in a chromic-nitric acid solution and another in a solution of hydrofluoric acid. These pretreatments of magnesium, in combination with the deposition of a nickel undercoating, are generally referred to as the chemical-etching process.

Figure 11 illustrates the successive steps involved in alkaline cleaning, etching, and nickel plating. Operating conditions and pertinent data are given in the accompanying table. The nickel undercoating may be deposited from either an electrolytic, acid-fluoride, plating bath, or an electroless immersion bath as shown:

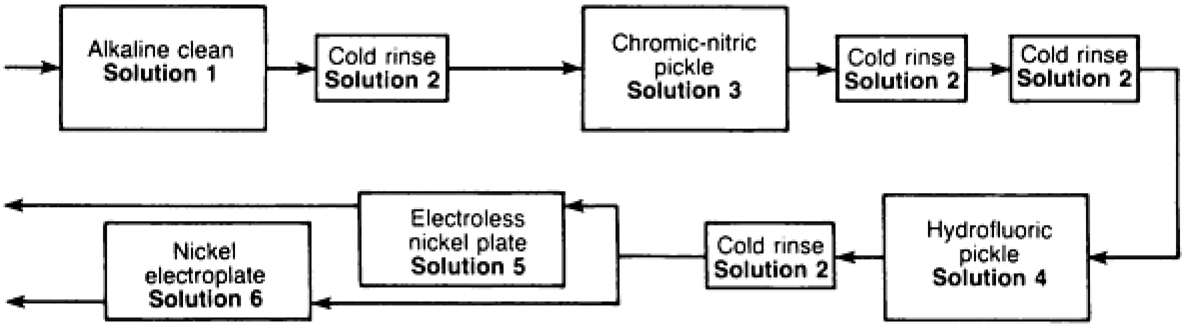
| **Constituent or condition** | **Value or range** |
|---|---|
| **Electroless nickel** | |
| Basic nickel carbonate, g/L (oz/gal) | 9.7 (1.3) |
| Hydrofluoric acid as 70% HF, mL/L (fl oz/gal) | 6.4 (0.85) |
| Citric acid, mL/L (fl oz/gal) | 5.2 (0.7) |
| Ammonium acid fluoride, g/L (oz/gal) | 15 (2.0) |
| Sodium hypophosphite, g/L (oz/gal) | 20.3 (2.7) |
| Ammonium hydroxide, mL/L (fl oz/gal) | 30.4 (4.06) |
| Water | bal |
| pH (colorimetric) | 4.5-6.8[a] |
| Operating temperature, °C (°F) | 76-82 (170-180) |
| Agitation required | Mild mechanical |
| Rate of deposition (approx), μm/h (mil/h) | 20 (0.8) |
| **Nickel electroplate** | |
| Basic nickel carbonate, g/L (oz/gal) | 120 (16.0) |
| Hydrofluoric acid as 100% HF, mL/L (fl oz/gal) | 43 (5.7) |

| | |
|---|---|
| Citric acid, g/L (oz/gal) | 40.6 (5.4) |
| Wetting agent[b], g/L (oz/gal) | 0.7 (0.1)[c] |
| Water | bal |
| pH (colorimetric) | 3.0 |
| Operating temperature, °C (°F) | 48-60 (120-140) |
| Current density, A/dm$^2$ (A/ft$^2$) | 3-10 (30-100) |
| Cathode-rod agitation, m/s (ft/min) | 0.06-0.08 (12-16) |

(a) Preferred, 6.5.

(b) Example, sodium lauryl sulfate.

(c) 1 g/L (0.134 oz/gal)



| Solution No. | Type of solution | Composition | Amount | Operating temperature, °C (°F) | Cycle time, min | Tank material |
|---|---|---|---|---|---|---|
| 1 | Alkaline cleaner[a] | [b] | [b] | 82-100 (180-212) | 3-10 | Low-carbon steel |
| 2 | Cold rinse | Water | . . . | Ambient | $\frac{1}{2}$-1 | Low-carbon steel[e] |

|  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|
| 3 | Chrome-nitric pickle(c) | $CrO_3$ | 125 mL/L (16 fl oz/gal)(d) | 21-32 (70-90) | $\frac{1}{2}$-2 | . . . |
|  |  | 70% $HNO_3$ | 110 mL/L (14 fl oz/gal)(d) |  |  |  |
| 4 | Hydrofluoric pickle | 70% HF | 220 mL/L (28.2 fl oz/gal)(f) | 21-32 (70-90) | 10 | Low-carbon steel(g) |
| 5 | Electroless nickel(h) | Basic nickel carbonate | 9.7 g/L (1.3 oz/gal) | 77-82 (170-180) | (i) | Low-carbon steel(j) |
|  |  | Hydrofluoric acid (as 70% HF) | 6.2 mL/L (0.8 fl oz/gal) |  |  |  |
|  |  | Citric acid | 5.2 g/L (0.7 oz/gal) |  |  |  |
|  |  | Ammonium acid fluoride | 15 g/L (2.0 oz/gal) |  |  |  |
|  |  | Sodium hypophosphite | 20.3 g/L (2.7 oz/gal) |  |  |  |
|  |  | Ammonium hydroxide | 30.4 mL/L (4.0 fl oz/gal) |  |  |  |
|  |  | Water | bal |  |  |  |
|  |  | pH (colorimetric) | 4.5-6.8(k) |  |  |  |
| 6 | Nickel electroplate(l) | Basic nickel carbonate | 120 g/L (16.0 oz/gal) | 49-60 (120-140) | (i) | Low-carbon steel(m) |
|  |  | Hydrofluoric acid (as 100% HF) | 43 mL/L (5.7 fl oz/gal) |  |  |  |
|  |  | Citric acid | 40 g/L (5.4 oz/gal) |  |  |  |
|  |  | Wetting agent(n) | 0.7 g/L (0.01 oz/gal)(o) |  |  |  |
|  |  | pH (colorimetric) | 3.0 |  |  |  |

(a) Alkaline cleaning may be preceded by vapor degreasing, emulsion cleaning, or mechanical cleaning.

(b) Type and strength of solution governed by degree of surface contamination.

(c) Solution must be ventilated.

(d) For aluminum-containing alloys. For alloys containing no aluminum, concentrations are 226 g (8 oz) $CrO_3$ and 326 g (11.5 oz) of 70% $HNO_3$ and water to make 3.8 L (1 gal).

(e) Stainless steel or low-carbon steel lined with polyethylene.

(f) For alloys containing more than 5% Al. For all other alloys, solution contains 195 g (6.9 oz) 70% HF and water to make 3.8 L (1 gal).

(g) Lined with polyethylene, synthetic rubber, or vinyl-based material.

(h) Agitation of work is recommended.

(i) Time determined by required thickness of nickel deposit.

(j) Lined with polyethylene, saran, or Lucite.

(k) Preferred, 6.5.

(l) Direct current required; agitation of cathode bar recommended.

(m) Lined with synthetic rubber or vinyl-based material.

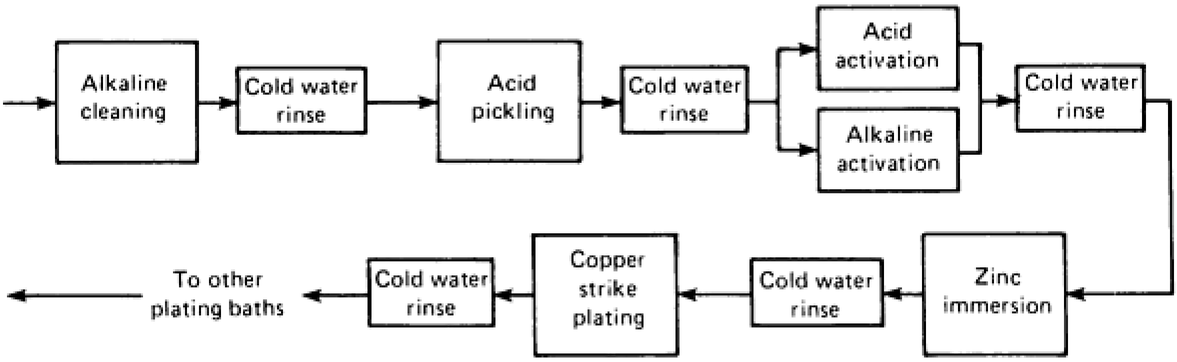
(n) Example, sodium lauryl sulfate.

(o) 1 g/L (0.13 oz/gal)

**Fig. 11 Preparing magnesium alloys for nickel plating**

To some extent, the two etching treatments undercut surface pits to provide mechanical anchorage for the plated deposits. After a nickel undercoating is applied to this roughened surface, the surface of the coating is not as bright or as smooth as that obtained with the zinc immersion process. However, in common with zinc coating, nickel coating can accept any of the standard electrodeposits, including cadmium, zinc, copper, brass, nickel, black nickel, chromium, gold, silver, and rhodium. Electroless deposits, such as gold or copper, also may be applied over the initial nickel plate.

**Zinc Undercoating.** After being alkaline cleaned, acid pickled, and surface-activated, magnesium can be prepared for plating by being immersed in a nonelectrolytic chemical bath that produces a thin deposit of zinc directly on the base metal. The basic steps, operating conditions, and tank materials required for the zinc immersion process are summarized in the flow chart and table of Fig. 12. After the immersion treatment, the very light zinc coating about 2.5 μm (0.1 mil) thick must be protected by a copper strike plate before any other standard electrodeposit may be applied. The following are the various steps that comprise the zinc immersion process, as well as the various solutions used.



| Operation | Cycle time, min | Solution temperature | | Tank material |
|---|---|---|---|---|
| | | °C | °F | |
| Alkaline cleaning[a] | 3-10 | 87-100 | 190-212 | Low-carbon steel |
| Acid pickling | $\frac{1}{2}$-1 | 21-32 | 70-90 | Ceramic or stainless steel[b] |
| Acid activation | 1-5 | 21-32 | 70-90 | Rubber, polyethylene, or vinyl plastisol |
| Alkaline activation | 2-5 | 76 | 170 | Stainless steel |
| Zinc immersion | 1-3 | 79-85[c] | 175-185[c] | Stainless steel |
| Copper strike plating[d] | 6-10 | 65-71 | 150-160 | Low-carbon steel; rubber |
| Cold water rinses | $\frac{1}{2}$-1 | Ambient | Ambient | Low-carbon steel |

(a) May be preceded by solvent cleaning, mechanical cleaning, or both.

(b) Mixtures containing fluorides require polyethylene, vinyl-based or synthetic rubber linings.

(c) Automatic temperature control preferred.

(d) Cathode agitation, constant filtration, and automatic temperature control preferred

**Fig. 12 Preparing magnesium alloys for copper plating. See text for details of solution composition and other**

**operating conditions.**

***Alkaline cleaning,*** as used in the electroplating of magnesium, consists of soak cleaning or cathodic electrocleaning, or a combination of both. These processes are described in detail in the article on alkaline cleaning in this Volume. Strong caustic solutions are used to remove segregated metal, graphite, and other surface contaminants. The composition and operating conditions for one water solution of this type are:

| | |
|---|---|
| Sodium hydroxide ($NaOH$), g/L (oz/gal) | 120-720 (1-6) |
| Temperature, °C (°F) | 99-170 (210-340) |
| Time, min | 10-20 |

Follow this treatment by an acid dip to remove the heavy film of hydroxide.

***Acid Pickling.*** Depending on magnesium alloy composition and product form, the following acid pickling solutions can be used prior to plating. All standard alloys and forms of magnesium can be pickled and chemically brightened by the use of the aqueous solution that follows:

| | |
|---|---|
| Chromic trioxide ($CrO_3$), g/L (oz/gal) | 180 (24.0) |
| Ferric nitrate ($Fe(NO_3)_3 \cdot 9H_2O$), g/L (oz/gal) | 40 (5.3) |
| Potassium fluoride ($KF$), g/L (oz/gal) | 3.5-7 (0.05-0.9) |
| Temperature, °C (°F) | Room temperature, 21-32 (70-90) |
| Time, min | $\frac{1}{4}$-2 |

All magnesium alloys and forms can be pickled under the following conditions:

| | |
|---|---|
| Phosphoric acid, 85% $H_3PO_4$ | No dilution |
| Temperature, °C (°F) | Room temperature, 21-32 (70-90) |

| | |
|---|---|
| Time, min | $\frac{1}{4}$-5 |

Sheet, extrusions, and forgings can be pickled in the following aqueous solution:

| | |
|---|---|
| Glacial acetic acid ($CH_3COOH$), mL/L (fl oz/gal) | 280 (37.4) |
| Sodium nitrate, g/L (oz/gal) | 80 (10.7) |
| Temperature, °C (°F) | Room temperature, 21-32 (70-90) |
| Time, min | $\frac{1}{2}$-2 |

Where little or no dimensional change is permitted, parts may be pickled in an aqueous solution of chromic acid, 180 g/L (24.0 oz/gal) of chromic trioxide of water at any temperature from room to boiling temperatures. This dip removes graphite, oxides, and other soils without removing an appreciable amount of metal.

***Surface Activation.*** To obtain an adherent and uniform coating of zinc on magnesium, the surface of the magnesium must be activated by immersion in a special acid or alkaline solution. The acid activating bath removes thin oxide or chromate films left by prior pickling or cleaning operations with a minimum of etching of the base metal. It also produces an equipotentialized surface on which the zinc immersion coating can deposit uniformly. The composition and operating characteristics of an aqueous acid activating solution in common use are:

| | |
|---|---|
| Phosphoric acid, 85% $H_3PO_4$, mL/L (fl oz/gal) | 200 (26.7) |
| Ammonium acid fluoride ($NH_4HF_2$), g/L (oz/gal) | 100 (13.3) |
| Temperature, °C (°F) | Room temperature, 21-32 (70-90) |
| Time | 25 s to 2 min |

Operation of acid fluoride activating baths at appreciably below 21 °C (70 °F) may result in poor adhesion of the electroplated deposit.

An alkaline pyrophosphate activating solution also removes oxides and other films; by virtue of its alkalinity, it does not dissolve the metals employed for rack contacts. Thus, there is little or no danger that metals such as iron or copper can plate out by immersion at locations adjacent to rack contacts. This form of stray plating prevents the proper deposition of the subsequent zinc immersion coating. The composition and operating characteristics of the alkaline solution are:

| | |
|---|---|
| Tetrasodium pyrophosphate ($Na_4P_2O_7$), g/L (oz/gal) | 40 (5.3) |
| Sodium tetraborate ($Na_2B_4O_7$), g/L (oz/gal) | 70 (9.3) |
| Sodium fluoride (NaF), g/L (oz/gal) | 20 (2.7) |
| Temperature, °C (°F) | 76 (170) |
| Time, min | 2-5 |

The bath should not be operated much above 76 °C (170 °F), as the alkaline solution has a tendency to dry on the parts prior to rinsing. For this reason, the transfer from hot activator to water rinse should be as rapid as possible.

***Zinc Immersion Coating.*** Standard zinc immersion baths (Table 8) are based on aqueous solutions of pyrophosphate, a zinc salt, a fluoride salt, and, if required, a small amount of carbonate for adjusting alkalinity to the proper range. The pyrophosphate dissolves oxide and hydroxide films to form water-soluble complexes. By effecting film removal under specific conditions of pH, temperature, and bath concentration, a thin, adherent coating of metallic zinc is deposited. Fluoride is added to control the rate of zinc deposition. To a considerable extent, the quality and adhesion of the zinc deposit depends on the rate of deposition; too rapid a rate usually produces less adherent coatings.

**Table 8 Composition of zinc immersion bath**

| Activator | Constituent | Concentration | | | |
|---|---|---|---|---|---|
| | | Nominal | | Range | |
| | | g/L | oz/gal | g/L | oz/gal |
| Acid | Oxalic acid $(CO_2H)_2$ | 5 | 0.7 | 2-10 | 0.3-1.3 |
| Alkaline | Potassium pyrophosphate ($K_4P_2O_7$) | 60 | 8 | 50-150 | 6.5-10.0 |
| | Sodium carbonate ($Na_2CO_3$) | 15 | 2 | 10-20 | 1.3-2.6 |

The most commonly used zinc immersion solution has composition and pH as follows:

| | |
|---|---|
| Zinc sulfate monohydrate ($ZnSO_4 \cdot H_2O$), g/L (oz/gal) | 30 (4.0) |

| | |
|---|---|
| Tetrasodium pyrophosphate ($Na_4P_2O_7$), g/L (oz/gal) | 120 (16.0) |
| Sodium fluoride (NaF), g/L (oz/gal) | 5 (0.7) |
| **or** | |
| Lithium fluoride (LiF), g/L (oz/gal) | 3 (0.4) |
| Sodium carbonate ($Na_2CO_3$), g/L (oz/gal) | 5 (0.7) |
| pH | 10.0-10.6 (10.2-10.4 preferred) |

Within limits, the bath constituents can vary from the above formula provided the ratio of pyrophosphate to zinc is kept to the proper range and fluoride concentration is maintained at the level indicated. Water for preparing the bath should be reasonably free from iron and other heavy-metal salts. Ordinary tap water may be used, but deionized water is preferred.

The bath is prepared by first dissolving the zinc sulfate monohydrate in water at room temperature. The solution is then heated to 60 to 82 °C (140 to 180 °F), and tetrasodium pyrophosphate is added slowly, while stirring. The white, fluffy precipitate (sodium zinc pyrophosphate) that first forms dissolves after further stirring for 5 to 10 min or longer, depending on the degree of agitation and temperature. Next, fluoride is added and then carbonate. The amount of carbonate added is the average required to produce the proper pH and should be determined by the actual pH of the solution. Sulfuric or phosphoric acid can be added to reduce pH, when necessary. The pH values given above are those determined by colorimetric methods; electrometric values, using a standard glass electrode, are 0.5 pH lower.

The bath is operated at 79 to 85 °C (175 to 185 °F). Mild agitation is used to prevent stratification, particularly when water is added to replace evaporation losses. Immersion time depends on alloy composition, bath temperature, surface preparation, and other variables; usually it ranges from 1 to 3 min, but it may be as long as 10 min for aluminum-containing alloys.

As indicated in Fig. 12, the tank should be made of stainless steel. Low-carbon steel, unless it is heavily nickel plated, will cause excessive iron contamination of the solution.

The zinc immersion bath has a fairly long life and can be maintained by analysis and regular additions. Eventually, it becomes contaminated with dissolved magnesium and other impurities and must be discarded.

***Copper strike plating*** in a cyanide bath should follow immediately after the application of the zinc coating. The work should make electrical contact with the cathode bar before being immersed in the plating bath. If the work is to be subsequently plated in an alkaline bath or in a modified noncorrosive fluoride nickel bath, flash copper deposits of 3 $\mu$m (0.1 mil) or less are adequate. However, if an acid bath is to be used, copper deposits of 8 μm (0.3 mil) minimum are required to protect the base metal from chemical attack, and the work must be thoroughly neutralized and rinsed after the flash plating cycle.

In some applications, because of the complexity of the parts or porosity of the base metal, increasing the minimum thickness of the copper strike plate could be necessary. Castings, because of porosity, generally require a slightly higher minimum thickness of copper when the subsequent plating bath is to be an acid type.

A high current density 3 to 4 A/dm$^2$ (30 to 40 A/ft$^2$) is applied for $\frac{1}{2}$ to 1 min, and then reduced to 1.5 to 2.5 A/dm$^2$ (15 to 25 A/ft$^2$). Prolonged strike plating at high current density causes poor adhesion and blistering. Any other metal usually electrodeposited can be applied after flash copper plating is completed.

**Zinc Undercoating for Die Castings.** Whereas AZ91 with 9% Al is frequently used for die castings, any surface areas with aluminum-rich segregates are difficult to zincate. The best compromise for castability and plating characteristics is the AZ71 composition with a lower aluminum content of 7%. The section of this article on surface activation outlines normal practice of either an acid or alkaline activation after acid pickling and before zinc immersion plating (Fig. 12). Hot chamber magnesium die castings can be successfully plated using an acid activation followed by an alkaline activation. The patented process follows:

1. Acid activation, 0.3 to 1 min, 21 to 29 °C (70 to 85 °F)
2. Cold water rinse, minimum 1 min
3. Alkaline activation, 0.3 to 1 min, 60 to 65 °C (140 to 150 °F)
4. Cold water rinse
5. Zinc immersion bath, 60 to 65 °C (140 to 150 °F)

Acid copper is more efficient than semi-bright nickel for leveling and filling pits in the castings.

**Uses of Plated Magnesium.** Copper-nickel-chromium plating systems on magnesium satisfy decorative and protective requirements for interior and mild exterior environments. They have not found application for parts exposed to severe marine or salt splash conditions because of the accelerated galvanic corrosion that can occur wherever small areas of magnesium may be exposed by porosity or mechanical damage to the plating. Hard chromium plating provides excellent wear resistance and long working life for magnesium photoengraving plates. Electroless nickel plating on magnesium has found use in the computer and electronics industries for applications requiring corrosion and wear resistance, solderability, and stable electronic contacts; copper plus hot-flowed tin plating are also used. Gold over electroless nickel is used in space applications of magnesium.

**Corrosion Resistance.** Satisfactory corrosion resistance, especially in marine exposures or with salt-spray testing, is obtained only when the plated deposit is pore-free. Porosity in the base metal promotes porosity in the plated deposits; consequently, corrosion resistance of plated magnesium alloy parts having appreciable surface porosity is less than that of parts that have a minimum of surface porosity. This is evident from the results of salt-spray corrosion studies of plated wrought and sand cast alloys. Less total plate thickness is required to give comparable corrosion resistance over wrought alloys than over cast alloys. The results with wrought alloys are much more consistent over a number of tests than are those with cast alloys, undoubtedly because of the amount of variation in surface porosity or surface quality of the sand castings tested.

In general, on the same type of base metal, either wrought or cast, corrosion resistance is a function of total plate thickness. Service tests should be conducted to determine the best systems and plate thicknesses to give satisfactory corrosion resistance. Suggested minimum total plate thicknesses for decorative chromium plating and copper-nickel-chromium are shown in Table 9.

**Table 9 Minimum total plate thicknesses for decorative chromium plating**

| **Service environment** | **Wrought alloys** | | **Cast alloys** | |
|---|---|---|---|---|
| | **μm** | **mils** | **μm** | **mils** |
| Interior | 13 | 0.5 | 19 | 0.75 |
| Mild exterior | 25 | 1.0 | 38 | 1.5 |
| Average exterior | 32 | 1.25 | 50 | 2.0 |

| | | | | |
|---|---|---|---|---|
| Severe exterior | 38 | 1.5 | 64 | 2.5 |

**Quality Control.** The most widely used methods for determining the quality of plated deposits on magnesium alloys are adhesion, relative-humidity, and salt-spray tests. Relative-humidity and salt-spray tests are considered standard acceptance tests where corrosion resistance is required.

Adhesion tests are conducted by either baking the plated parts at 175 to 260 °C (350 to 500 °F) for 1 h followed by air cooling or immersing the plated parts in an oil bath at about 260 °C (500 °F) for a sufficient time for the parts to reach the temperature of the bath followed by quenching in a room-temperature kerosene bath, and then inspecting the parts for evidence of blistering. The absence of blistering of the plate generally indicates that proper adhesion of the plate has been obtained. These heat tests are simple, effective, and inexpensive nondestructive methods for determining adhesion and are particularly convenient where 100% testing of parts is required.

**Stripping of Plated Deposits.** Plated deposits can be satisfactorily stripped from magnesium alloys with little if any attack of the base metal.

***Zinc immersion deposits*** can be stripped in a room-temperature bath containing 10 to 15 vol% of 70% hydrofluoric acid (HF). The standard acid activator as used prior to zinc immersion coating can also be used.

***Chromium*** can be stripped by reverse current in a hot alkaline solution, such as one containing 60 to 75 g/L (8 to 10 oz/gal) of sodium hydroxide (NaOH), or combinations of sodium hydroxide and sodium carbonate, in water.

***Copper*** can be stripped by immersion in hot alkaline polysulfide followed by a dip in cyanide, as in stripping copper from steel or die cast zinc.

***Nickel*** can be stripped in a bath containing 15 to 25% HF and 2% sodium nitrate ($NaNO_3$), using 4 to 6 V. Work to be stripped is made anodic; cathodes can be carbon, lead, or magnesium.

***Copper, nickel, tin, cadmium, and zinc*** can be stripped by immersion in the following solution, operated at room temperature: nitric acid (sp gr, 1.42), 1 part by volume; hydrofluoric acid, 70%, 2 parts; water, 2 parts. The tank for containing the solution should be made of polyethylene or some similar material.

***Gold, silver, copper, and nickel*** can be stripped by immersion in proprietary alkaline chemical strippers containing cyanide. Add 15 g/L (2 oz/gal) of sodium hydroxide (NaOH) per gallon of prepared solution to aid in preventing possible etching of the magnesium base metal. Operating temperature of the bath may range from 21 to 60 °C (70 to 140 °F). Low-carbon steel tanks and heating coils are used.

## Organic Finishing

Organic finishes are used on magnesium alloys to attain various effects in appearance and to provide durability. Organic finishing systems require careful adherence to manufacturers' recommendations on solvents, baking schedules, and compatibility of prime and finish coats to achieve desired film properties and adhesion.

A chemical conversion coating or anodizing treatment is required prior to application of organic coatings if the optimum in corrosion durability is desired. These treatments roughen and chemically modify the metal surface so that a good stable bond can be achieved with the paint coating applied. Surface treatments are not used for every application, however, as indicated in Table 1. Some commercial parts are coated with no more than mechanical cleaning. Oven drying should be used following spray or immersion surface treatment of castings to ensure that all moisture is driven from the porosity of the cast surfaces prior to applying bake-cured finishes. It has also been found that anodized components provide greatly improved corrosion durability, if the porosity, common to all, is sealed with a penetrating resin sealer prior to the application of primer and top coats (Ref 13).

Table 10 contains information on various appearance effects that are attainable with the mechanical or chemical pretreatment and organic finishing systems required for interior and exterior applications. Military finishing is controlled by specifications; Table 11 lists the various finishing steps involved and indicates the appropriate Government specifications.

## Table 10 Organic finishing systems for magnesium alloys

| **Appearance effect** | **Typical finishing system for** | |
|---|---|---|
| | **Interior service**[a] | **Exterior service**[b] |
| Bright metal | Buff + ferric nitrate bright pickle + clear epoxy or acrylic | Buff + ferric nitrate bright pickle + clear epoxy or acrylic |
| Satin finish | Wire brush + ferric nitrate bright pickle + clear epoxy or acrylic | Wire brush + ferric nitrate bright pickle + clear epoxy or acrylic |
| Tinted clear | Ferric nitrate bright pickle + tinted epoxy or acrylic | Not recommended |
| Dyed clear | Ferric nitrate bright pickle + clear epoxy or acrylic + dye dip | Not recommended |
| Metallic | Chrome pickle or dilute chromic acid + epoxy, acrylic, polyvinyl butyral or vinyl pigmented with metal powder or paste | Chrome pickle or dilute chromic acid + 1 coat polyvinyl butyral primer + epoxy or acrylic pigmented with metal powder[c] |
| Wrinkle | Chrome pickle or dilute chromic acid + standard wrinkle finish | Not generally used in outdoor service |
| High-gloss enameled | Chrome pickle or dilute chromic acid + epoxy, acrylic, polyurethane or alkyd enamel | Chrome pickle or dilute chromic acid + 1 coat polyvinyl butyral primer + acrylic, alkyd or polyurethane enamel |
| Leatherette (smooth or textured) | Chrome pickle or dilute chromic acid + vinyl cladding | Chrome pickle or dilute chromic acid + vinyl cladding |
| | Chrome pickle or dilute chromic acid + vinyl organosol | Chrome pickle or dilute chromic acid + polyvinyl butyral or vinyl primer + vinyl organosol |

(a) Suggested minimum total film thickness, 25 μm (1 mil).

(b) Suggested minimum total film thickness, 50 μm (2 mils); marine environments may require total film thickness of 75 μm (3 mils).

(c) Or metal paste

## Table 11 Military finishing systems for magnesium alloys

| **Operation** | **Appearance** | **Applicable specifications** |
|---|---|---|
| Cleaning | . . . | MIL-M-3171 |
| Chemical treatment | Varies with treatment | MIL-M-3171 or MIL-M-45202 |

| | | |
|---|---|---|
| Prime coat | Varies with protective pigment used | MIL-P-15930 or MIL-P-52192 |
| Second coat | Matte | TT-E-529 |
| | Semigloss | TT-E-485, TT-E-529, or MIL-L-52043 |
| | Gloss | TT-E-489 |
| Finish coat | Matte | TT-E-529, MIL-L-14486 |
| | Semigloss | TT-E-485, TT-E-529, or MIL-L-52043 |
| | Gloss | TT-E-489 |

**Selection of Paint.** Both air-drying and baking paints are currently in use. Baking paints are harder and more resistant to attack by solvents. Vinyl alkyds have been used for their resistance to alkali, acrylics for resistance to salt spray, alkyd enamels for exterior durability, and epoxies for good abrasion resistance. Vinyls can withstand temperatures up to about 150 °C (300 °F). Other finishes have increasing temperature resistance in this order: modified vinyls, epoxies, modified epoxies, epoxy-silicones, and silicones.

Primers for magnesium should be based on such alkali-resistant vehicles as polyvinyl butyral, acrylic, polyurethane, vinyl epoxy, and baked phenolic. Zinc chromate or titanium dioxide pigments are commonly used in these vehicles for corrosion inhibition. Finish coats are chosen to have:

- Compatibility with primer
- Adaptability to shop conditions and to finishing equipment available
- Ability to perform in service
- Economy consistent to compliance with service requirements

For a detailed discussion of types of paints and methods of application, see the article on painting in this Volume.

**Examples of problems** that might arise in productive painting of magnesium alloy products are given below, together with details of the methods used to solve them.

The first problem, masking multiple threaded inserts in castings before painting, was solved by this method:

1. A chemical-resistant finish was applied before drilling and tapping the castings for inserts.
2. Holes were then tapped and drilled.
3. Castings were reprocessed through the dichromate to treat threaded holes.
4. Inserts were set in zinc chromate sealer.

Another example involves bubbles and fisheyes appearing in the baked wrinkle-finish paint on dichromated magnesium alloy die castings. This condition was eliminated by lowering the paint-baking temperature from 150 °C (300 °F) to 120 °C (250 °F) and adding a baking cycle of 2 h at 175 °C (350 °F) after the dichromating treatment.

Die castings given a chrome pickle treatment followed by baked coats of primer and wrinkle-finish enamel present another example of problems that might arise. When the primer was applied and baked, small bubbles formed on the film surface; these would later break, leaving an unsightly ring on the surface and affecting uniformity and appearance of the wrinkle finish. Preheating the castings to drive out entrapped air and painting them after they had cooled, greatly reduced the number of bubbles but did not completely eliminate their formation. Painting the castings while they were still hot from the preheating solved the problem.

**Stripping of Paint.** The ability of magnesium alloys to withstand strong alkalis lessens the problem of paint removal. After painted parts are soaked in a hot, 82 °C (180 °F), solution containing 360 g/L (3 lb/gal) of sodium hydroxide in water, most paints dissolve or lose adhesion to the extent that they can be removed by flushing with water, hand brushing, or other mechanical means. Paint strippers with a phenol or methylene chloride base may be used, but extended soaking of more than 24 h causes slight etching of the magnesium alloy, which is undesirable for close-tolerance machined areas.

Stripping vinyl-based enamels from dichromate-treated magnesium is more difficult. One method entails softening the coating and weakening the bond by soaking in methylene chloride for $\frac{1}{2}$ to 1 h, then resetting the paint by soaking in hot alkalis for 5 to 30 min. The loose paint is then brushed off, and any remaining paint is removed by wet blasting with 150-mesh aluminum oxide. This stripping operation should be followed as soon as possible by a dichromate treatment.

Chrome pickle and dichromate coatings can usually be removed in hot sodium hydroxide. Old chromate coatings are usually more difficult to remove and work to be stripped of them may require soaking in sodium hydroxide solution followed by immersion in a chromic acid pickling solution.

Special baked primers and other finishes that are difficult to remove in a sodium hydroxide solution may be stripped by being immersed for 5 min or longer in the following solution, at 82 to 100 ° C (180 to 212 °F):

| | |
|---|---|
| Sodium hydroxide, vol% | 10-20 |
| Diethylene glycol, vol%<br>or ethylene glycol, vol% | 10<br>20 |
| Water | bal |

Coatings that are difficult to remove by the methods described above can be effectively stripped by mild abrasive blasting using plastic media. Plastic media blasting is widely used for stripping of aircraft and aerospace components with little or no damage to the substrate.

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## Health and Safety

Magnesium and magnesium oxide dusts are considered nontoxic. The usual precautions taken to prevent gross inhalation of dirt, dust, and other foreign matter are required. No unusual health hazard has been found associated with the handling, mechanical finishing, or pickling of magnesium alloys, including those containing thorium or beryllium.

Some of the chemical baths used contain chromate or fluorides. Because of the toxic nature of these materials, adequate ventilation is required when baths containing chromate or fluorides are used.

Although bulk magnesium is difficult to ignite unless temperatures are near the melting point, finer particles, such as chips, sawings, and especially sanding dust, are more easily ignited. Proper handling of these materials is required to prevent ignition.

**Polishing and Buffing.** Special precautions must be followed in the polishing and buffing of magnesium alloys. Magnesium dust or powder must not be allowed to accumulate because it will create extreme fire and explosion hazards. The fire hazards produced in buffing are somewhat less than those produced in polishing. Belt polishing is potentially more dangerous than wheel polishing because the resulting dust is more difficult to collect.

Under no circumstances should steel be polished in the same setup that is used for polishing magnesium, because the polishing of steel causes sparks that can ignite magnesium dust. Because of strong oxidizing properties, heavy chromate coatings also cause sparking when magnesium alloy parts to which they have been applied are being polished.

A system considered safe for the collection of magnesium grinding and polishing dust is one in which the dust is precipitated by a heavy spray of water or low-viscosity mineral oil to form a sludge with a great excess of liquid. The equipment must be designed so that the sludge does not accumulate and dry out and thus become flammable. Inspect the dust-collecting system periodically to ensure that the dust is kept moist.

The best collectors for grinding or polishing stands are small units that serve one or two stands and have the power supply for the grinder or polisher, water circulation, and air blower interconnected so that the grinder or polisher cannot operate unless the collector system is operating. Connect the grinding or polishing machine to the collector by short, straight ducts. Do not allow dry dust to accumulate in the ducts. Clean all polishing machines each day, dust collector and suction pipes at least once a week.

Hydrogen is formed in the reaction of magnesium with water. Ventilate sludge pits adequately to prevent the accumulation of hydrogen. The sludge that collects under the hood frequently must be removed and spread out in thin layers on a noncombustible surface in a safe, isolated area. The sludge may be burned in small quantities. Sludge from dust collectors may be rendered noncombustible by reacting it with a 5% solution of ferrous chloride ($FeCl_2 \cdot 2H_2O$) in an open container placed outdoors.

Central collecting systems in which the dust is passed through long dry ducts, or conventional dust collectors using dry filters, are definitely not recommended, because accident records have indicated dry systems of these types to be extremely dangerous.

**Wire Brushing.** The dust generated during wire brushing also must be trapped in a water-wash dust collector to minimize fire hazards and prevent the formation of explosive concentrations. This same method of collection has proved suitable for removing the dust during the wire brushing of sheet containing thorium (HK31A and HM21A) and preventing contamination of the air and work area with low-level radioactive dust.

# Surface Engineering of Titanium and Titanium Alloys

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## Introduction

TITANIUM AND ITS ALLOYS are characterized by low density relative to other structural metals and alloys, excellent corrosion resistance, and high specific proof strengths. Since titanium first became available in the mid-twentieth century, its major area of application has been in the aerospace industry, which makes up about 80% of its usage. Its level of use in chemical and petrochemical applications is also significant, and the combination of chemical and specific mechanical properties make titanium alloys ideal candidates for prosthetics in joint replacements. The desire to reduce moving mass in machinery is increasing interest in its use outside of these sectors (e.g., for use in general engineering applications, where titanium-base material is often a direct replacement for ferrous materials).

The first part of this article is concerned with cleaning and finishing operations that are used throughout titanium-related industry and are widely applied to semifabricated products (see Ref 1 and *Materials Properties Handbook: Titanium Alloys*, ASM International, 1994). The second part of the article describes surface engineering processes and their application to titanium-base materials, which are, in the main, applied to near-finished components. These processes are used either to improve the wear resistance of the titanium-base material or to improve its oxidation resistance:

- The poor wear resistance of titanium (Ref 2) is caused by its low c/a ratio as a hexagonal close-packed metal. The slip systems produce relatively low shear strengths and a high coefficient of friction. Lower tensile strengths allow relatively easy material transfer to conterfaces in adhesive wear. Low hardness allows damage by abrasive and related wear mechanisms.
- The oxidation (Ref 3) and general corrosion resistance of titanium and its alloys are excellent at relatively low temperatures, but for conventional alloys, at around 430 °C (800 °F) and above, depending on exposure time, oxygen is taken up by the substrate, which causes embrittlement. Titanium γ-aluminide alloys have useful mechanical properties up to ~900 °C (1650 °F), but their oxidation resistance is satisfactory to only ~815 °C (1500 °F).

Some of the processes described in this article, such as electroplating and thermal spraying, are widely used; others, such as ion implantation, are starting to find industrial applications; still other processes are as yet used only for prototyping or producing relatively small numbers of products, such as for use in racing cars.

The dominant engineering characteristics of the metal and its alloys are their ability to form a tenacious surface oxide film in air that dissolves in the titanium and the fact that titanium reacts with all but the most stable materials at some temperature.

## Acknowledgements

The authors wish to acknowledge the assistance of Metco UK, the assistance of Tecvac, Ltd., and their colleagues' contributions to their work in the area of surface engineering of titanium alloys.

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## Cleaning and Finishing

Cleaning and finishing processes for titanium and its alloys are similar to those for other metals. Proper selection of processes, methods, and cleaning solutions are of major importance to procure maximum use of the finished metal and to maintain safe procedure during the working of titanium materials.

Generally, a heavy oxide layer resulting from hot working of the metal is removed by grit blasting or other mechanical means, or by salt bath descaling. After removal of the scale, further mechanical or chemical treatment is applied to remove the hardened, oxygen-rich metallic case beneath the scale in order to avoid cracking during subsequent working operations. Heavy grease, oil, and black lubricant coatings resulting from cold working are removed by alkaline or caustic soaking, followed by acid pickling. To remove soil or light oil from a metal, cleaning by detergents, solvent washing, or vapor degreasing is generally applied.

### *Cleaning and Descaling Problems*

The metallurgical and chemical properties of titanium create a number of very special cleaning problems:

- Affinity of titanium to common gases
- Galvanic effects caused by discontinuities in scaled surfaces
- Metallurgical restrictions on the temperature of the descaling media

- Variety of scales encountered in titanium descaling
- Protective coatings used in titanium manufacturing

**Gas Absorption.** The property that causes the most difficulty is the capacity of titanium to absorb common gases, including oxygen, hydrogen, and nitrogen, all of which tend to embrittle the product. Because tightly packed hot-rolling scale acts as partial protection against additional gas absorption, some mills perform two or three heat treatments over the scale. Each additional heat treatment toughens the scale and compounds descaling difficulties. An additional problem is that heat-treating furnace atmospheres are maintained on the oxidizing side to prevent hydrogen pickup. A layer of oxygen-rich metal (Fig. 1) develops beneath the resulting scale formation, varying in thickness from 0.05 to 0.07 mm (0.002 to 0.003 in.) in the heat-treated condition to 0.15 to 0.20 mm (0.006 to 0.008 in.) in the hot-rolled condition. This brittle surface is usually removed by acid or electrolytic chemical pickling.

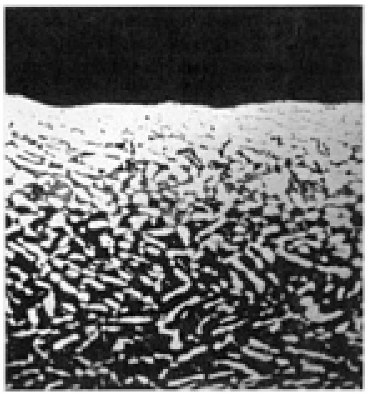

**Fig. 1 Ti-6Al-4V alpha case. 250×**

**Galvanic effects and discontinuities** in the surface scale are encountered in all types of metal descaling, but they appear to be more pronounced in titanium. Although the exact cause of small pits or cells formed in descaled material is debatable, possibilities include alloy or nonmetallic segregations, scale porosity, and surface contamination. A more severe galvanic attack problem is created by patch scale conditions on titanium surfaces when areas of heavy scale flake away from an apparently uniform surface. The same problem has been observed with superimposed oxides, even though the surface layer may be quite thin and powder-like. Surface contamination with oil, grease, or fingerprints can also create a patch scale condition. All of these factors promote severe localized attack when areas of the substrate metal are exposed selectively during descaling. Some producers have considered reoxidation of the product during processing as a possible solution.

**Metallurgical Restrictions on Descaling.** Solution-treated, age-hardenable titanium alloys are sensitive to time-temperature reactions and the temperatures of descaling media. The metastable or high-beta alloys, which are solution treated and aged at temperatures ranging from 370 to 540 °C (700 to 1000 °F) for $\frac{1}{2}$ h or more, may undergo a subsequent aging effect and cause a change in mechanical properties. This is particularly true in thin-gage sheet materials and may cause property changes of as much as 70 MPa (10 ksi) in tensile strength. These alloys normally should not be allowed to exceed 260 °C (500 °F).

**Variety of Scale.** Another factor that contributes appreciably to titanium descaling problems is the wide variety of scale encountered, including scale formed by annealing, forging, solution treating, stress relieving, extruding, rolling, aging, hot forming, or a combination of several of these operations. With processing temperatures ranging from 425 to 1150 °C (800 to 2100 °F), the scale spectrum for titanium is far broader than for most other difficult-to-descale materials.

**Protective coatings** are often used in titanium manufacturing operations. These coatings, which are an asset and a necessity in manufacturing operations, become a liability and a contaminant in cleaning operations. They are soluble and removable if the proper techniques are used. Protective coatings are applied to titanium surfaces during manufacturing operations to:

- Lubricate and aid in metal flow, good die contouring, and forming operations
- Act as barrier films, reducing gas contamination during high-temperature forming and heat-treating cycles
- Reduce surface flaws caused by nicking and scratching during manufacturing operations

The gas protective films are usually applied directly to the titanium surface. They are silicate-based materials that deposit uniform fusible films through solvent evaporation. These films form glassy barriers at treatment temperatures up to 815 °C (1500 °F) and are quite effective in reducing oxygen, hydrogen, and nitrogen contamination. Above 815 °C (1500 °F), most of these films are less effective, because speroidizing creates voids in the film. Lubricant films or abrasion-protective films are applied over a silica-based coating. This process has the advantage of providing double protection against scratching and scoring. During hot forming operations and metal surface stretching, some voiding and penetration occurs, creating a titanium oxide on the surface. The contaminant then consists of organic bond or residues, graphite, molybdenum disulfide, silicates, and titanium oxides.

### *Removal of Scale*

Scale is removed from titanium products by several mechanical methods. Abrasive methods, such as grinding and grit blasting, are preferred for removing heavy scale from large sections. Centerless grinding is used for finishing round bars, and wide-belt grinding is used for finishing sheet and strip. Grinding is usually most efficient when it is performed at low wheel and belt speeds.

Most alloy sheet materials with a high aluminum content, such as Ti-5Al-2.5Sn, are ground to eliminate pits and a rippled condition that develops in hot rolling as a result of discontinuous slip during plastic deformation. Grinding is frequently used to eliminate surface defects before cold rolling. Originally, strip was ground on standard strip grinders, using various oil lubricants; however, oils contributed to fire hazard and several grinding machines were partially or wholly destroyed when the oil ignited. When titanium was ground with aluminum oxide belts, a water lubricant was less effective than air. The water reacted with the aluminum oxide to form a weak hydroxide that proved ineffective as a grinding lubricant.

**Belt Grinding.** Dry belt grinding is dangerous because fine titanium powder can explode or ignite. Dry belt grinding is also uneconomical because of poor belt life. When stock is removed during dry grinding, small globules of molten metal and oxide roll along the sheet, causing a type of pitting by burning that is not removed by the grinding. Weld grit scratches and embedded grit result when titanium welds to the dry grit.

A 5% aqueous solution of potassium orthophosphate, $K_3PO_4$, is widely used as a grinding lubricant. It is applied as a flood at both the entrance and exit sides of the contact line. Water-soluble oils, particularly highly chlorinated and sulfochlorinated oils, have also been successful as lubricants. These compounds should be used with care because of the possibility of chloride residues remaining as an integral part of the surface. Both types of lubricants improve grinding efficiency when the belts are coated with aluminum oxide or silicon carbide.

Flooding the work with lubricant is recommended; however, machines built for flooding are equipped with a recirculating and filtering system and waterproof cloth belts, and they are expensive. An alternative is to spray a water-soluble wax fog through atomizing nozzles on the line of contact at both the entrance and exit sides of the belt. The solution should not be sprayed through an ejector that mixes it with air and increases the fire hazard; instead, it should be sprayed as an atomized liquid. Application of the spray can be controlled to volatilize the lubricant during grinding. This eliminates the need for waterproof belts. Care must be exercised to avoid a buildup of titanium chips that may cause a fire. Chips that would wash away in a flood are not removed by the spray.

Titanium should be ground at belt speeds not exceeding rates of 8 m/s (25 ft/s). Using a 5% solution of potassium orthophosphate as a lubricant, maximum efficiency is achieved at about 6 m/s (18 ft/s). Both billy roll and flat table grinding machines have been successful in grinding titanium. Sheet grinding machines, equipped with feed rolls, sometimes leave a ground line on the sheet where the feed rolls, on the exit side of the machine, and interrupt uniform travel when they grip the sheet. A high degree of grinding uniformity is obtained on machines equipped with a flat table and vacuum chuck. On these machines, the table holding the sheet usually oscillates. Traveling-head machines are available also.

The belt grinding sequence is usually begun with an 80-grit belt when it is necessary to remove more than 0.07 mm (0.003 in.) of stock from the surface of the sheet. Descaling and pickling the sheet before grinding prolongs belt life. Following the initial grit, each successive grit must remove enough stock to eliminate the scratches caused by the previous grit. The alpha alloys, such as Ti-5Al-2.5Sn, are less sensitive to surface condition than the alpha-beta alloys, such as Ti-6Al-4V. Surface pits on Ti-6Al-4V sheet, caused by weld grit scratches, seriously detract from bend ductility. A flow chart for the belt grinding of Ti-6Al-4V sheet is shown in Fig. 2.

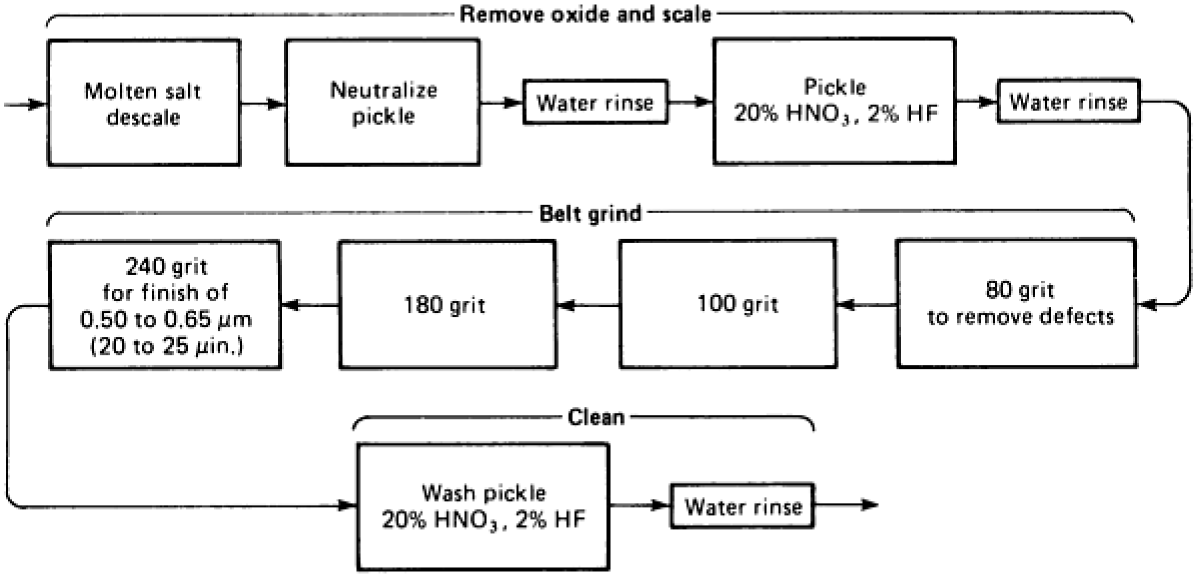

**Fig. 2 Cleaning and belt grinding sequences for Ti-6Al-4V sheet**

**Abrasive blast cleaning techniques,** either wet or dry, are convenient for removing scale from a variety of titanium products, ranging from massive ingots to small parts. Because it can be used at lower velocities and is less likely to be embedded in the surface, alumina sand is preferred to silica sand.

Sheet thicknesses to about 0.50 mm (0.020 in.) can be descaled without distortion if fine sand and low velocities are used. Mill scale on titanium products can be removed with coarse high-carbon steel shot or grit, whereas finished compressor blades can be cleaned with zircon sand of 150- to 200-grit. The type of product to be cleaned, the cleaning rate, and the cost of the abrasive must be balanced in the selection of a specific blast cleaning method.

Mineral abrasive particles, such as silica, zircon, or alumina sands, are used more commonly than metal abrasives for blasting finished or semifinished products. Although these abrasives are more expensive, they produce the finer finish that is required in final processing or service. Adequate safety precautions must be observed to avoid inhalation of fine sand particles. Air-circulating and dust-collecting systems must be cleaned frequently and equipped to cope with the fire hazard associated with titanium dust.

A fine dust remains on the titanium from the blasting operation, particularly when mineral abrasives have been used. This is not considered detrimental, although a washing or pickling cycle following the blast is desirable if the part is to be welded subsequently. The following describes a wet blasting procedure and a dry blasting procedure used for descaling titanium parts:

- *Wet blasting:* Parts are wet blast cleaned, using a slurry that consists of 400-grit aluminum oxide (40 vol%) and water. Air pressure of 655 kPa (95 psi) is used to pump the slurry in a steady stream with a pressure of about 34 kPa (5 psi). The descaling rate, normally about 50 min/m$^2$ (5 min/ft$^2$), depends on the complexity of the part. Distortion and the need for planishing are held to a minimum by placing the blast nozzle approximately 50 mm (2 in.) from the workpiece and by using a 60° angle of impingement.

- *Dry blasting:* Rocket motor case assemblies are dry blasted after final stress relieving at 480 to 540 °C (895 to 1005 °F). Blasting is accomplished with 100- to 150-grit zircon sand at an air pressure of 275 kPa (40 psi). Each assembly is rotated at 2.5 rpm and is passed at a speed of 65 mm/min (2.5 in./min) between two diametrically opposed fixed-position blasting nozzles. The nozzles blast the inside and outside surfaces simultaneously at the same wall location. To prevent distortion, each nozzle is placed at the same distance, 300 mm (12 in.), from the metal surface.

**Molten salt descaling baths** are primarily used for descaling, bar, sheet products, and tubing. With the most effective barrier films available today, some gas penetration of titanium surfaces can be expected at the elevated temperatures required for working and heat treatment. The alpha case or oxygen-enriched layer resulting from this gas reaction is extremely hard and brittle and must be removed. Bar products used for machining finished parts must have this hard scale and oxide removed because they are very abrasive and cause rapid tool wear. These scales must be removed before welding or forming, or poor and small welds will be made and forming (hot or cold) will be virtually impossible without surface rupture or failure of parts. Removal presents no serious problems, because chemical milling techniques have been perfected by the aircraft industry to effect weight savings. In the case of titanium, the purpose is to improve the structural soundness of metal, and the solvent materials applied are of a different chemical composition.

One specific problem encountered in alpha case removal is that the titanium oxide formed is substantially more insoluble in the nitric hydrofluoric etchant than the base metal. Residues of oxide on the surface develop areas resembling craters on the finished product. Figure 3 illustrates the effect of surface condition on etched metal surfaces.

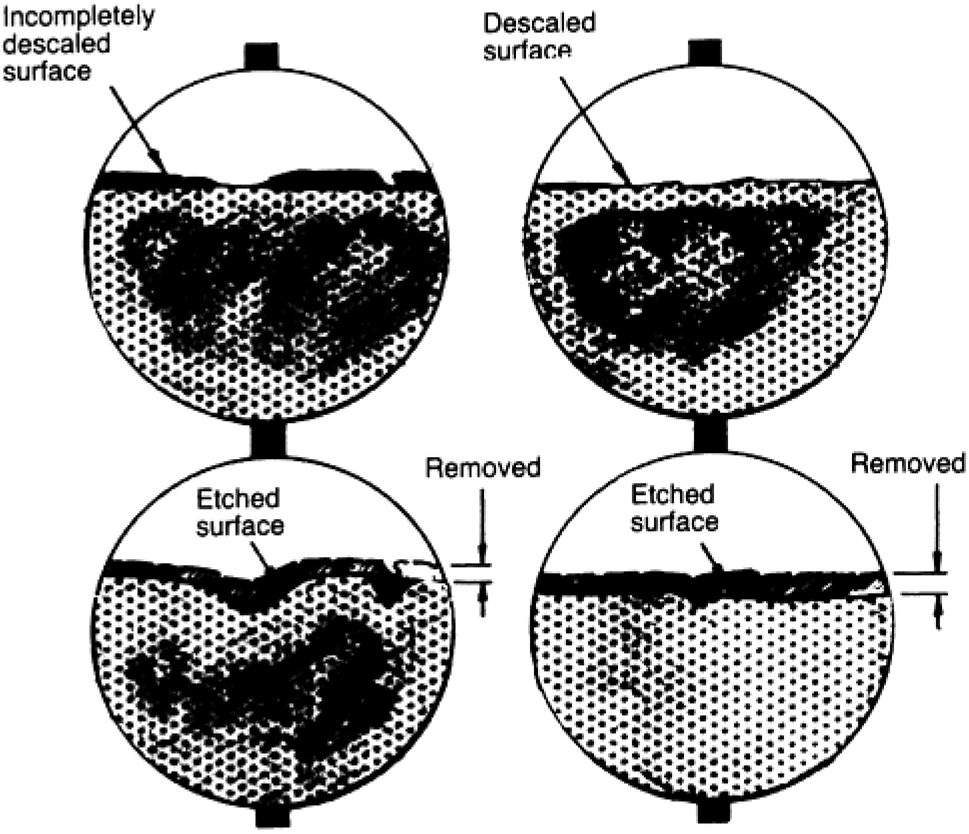

**Fig. 3 Effect of surface condition on etched metal surface**

Where alpha case removal is required, salt bath cleaning is specified, because proper cycling practically guarantees a chemically clean surface. Conditioning salt baths fall into two basic categories: high-temperature salt baths and low-temperature salt baths.

**High-temperature salt baths** may vary in chemical reaction and effectiveness, depending on composition. All types operate at a range of 370 to 480 °C (700 to 895 °F). The temperature range is sufficiently high to produce the most rapid reaction possible for soil and oxide films. High-temperature oxidizing salt baths are also capable of reacting chemically with organic films to destroy them. These baths are also excellent solvents for silicate barrier films. They do require special fixturing to reduce the strong galvanic effects present at these temperatures, and for this reason, they are used in cleaning primary forming operation products, such as forgings, extrusions, rolled plate, and sheet. The major advantage of high-temperature oxidizing or reducing salt baths for titanium descaling is their great speed in removing extremely tenacious scale. Although reducing baths have the inherent disadvantage of promoting hydrogen absorption, this can be overcome or minimized by chemical additions. Vacuum degassing is another solution.

A primary producer of titanium sheet uses an oxidizing salt bath for removing the hot-work scale in the following sequence of operations:

1. Immerse in oxidizing salt for 5 to 20 min at 400 to 480 °C (750 to 895 °F).
2. Quench with water 1 min.
3. Immerse in sulfuric acid, 10 to 40 vol%, for 2 to 5 min at 50 to 60 °C (120 to 140 °F).
4. Rinse with water 1 min.
5. Recycle if necessary.
6. Pickle in nitric-hydrofluoric acid solution, time and concentration as required.

The same producer also uses a sodium hydride reducing salt bath for descaling high-beta or metastable beta alloys. A typical cycle using this type of salt is:

1. Immerse in reducing salt for 1 to 3 min at 370 °C (700 °F).
2. Quench in water 1 min.
3. Immerse in sulfuric acid (10 to 40 vol%) for 2 to 5 min at 50 to 60 °C (120 to 140 °F).
4. Rinse in water.
5. Pickle in nitric-hydrofluoric acid solution, time and concentration as required.
6. Vacuum degas or decontaminate titanium beta alloys that absorb hydrogen in reducing baths.

These baths are used by one major aerospace contractor for cleaning titanium blades for jet engines. The blade materials are Ti-6Al-4V and Ti-8Al-1Mo-1V. The descaling cycles for removing oxides and proprietary glass-like compounds from these blades are:

1. Immerse in oxidizing salt for 15 min at 455 °C (850 °F).
2. Rinse in cold water.
3. Pickle in solution of 35% nitric acid and 3.5% hydrofluoric acid for 1 min max at 20 °C (70 °F).
4. Rinse in hot water.

**Low-Temperature Baths.** The temperature range used for cleaning fabricated parts is 200 to 220 °C (390 to 430 °F). Descaling systems based on salts in this temperature range eliminate some of the possible problems associated with higher-temperature baths, including:

- Age hardening
- Dissimilar metal reactions
- Chemical attack
- Metal distortion

- Hydrogen embrittlement

Salts in this range have a very limited composition because of the effect of various compounds on the melting point. Although they contain oxidizing agents, the effect of these materials is not as aggressive as it is in the high-temperature fused salts. Consequently, organic materials are not destroyed, but are saponified and absorbed. Silicate barrier films and molybdenum disulfide are soluble in these low-temperature salts. The temperature range permits cycling between salt and acid to reduce cleaning times and costs. Examples of salt bath and acid cycle times are given in Table 1.

**Table 1 Low-temperature salt bath and acid bath conditions for cleaning titanium alloys**

| **Sample composition** | **Scale formation temperature** | | **Salt bath immersion time(a), min** | **Acid cleaning bath time(b), min** | **Acid cleaning bath time(c), s** |
|---|---|---|---|---|---|
| | **°C** | **°F** | | | |
| Ti-6Al-4V | 650 | 1200 | 2 | 2 | 30 |
| Ti-8Al-1Mo-1V | 650 | 1200 | 2 | 2 | 30 |
| Ti-8Al-1Mo-1V | 820 | 1510 | 5 | 2 | 30 |
| Ti-6Al-4V(d) | 820 | 1510 | 5 | 5 | 30 |
| Ti-6Al-4V(e) | 950 | 1745 | 5 | 5 | 60 |
| Ti-8Al-1Mo-1V(f) | 950 | 1745 | 5 | 5 | 60 |

(a) Salt bath temperature 205 °C (400 °F).

(b) Bath composition, 30% sulfuric acid.

(c) Bath composition, 30% nitric acid, 3% hydrofluoric acid.

(d) Sample recycled in salt bath for 5 min, in sulfuric acid bath for 5 min, in nitric acid-hydrofluoric acid bath for 30 s.

(e) Sample recycled in salt bath for 5 min, in sulfuric acid bath for 5 min, in nitric acid-hydrofluoric acid bath for 60 s.

(f) Sample recycled in salt bath for 5 min, in sulfuric acid bath for 5 min, in nitric acid-hydrofluoric acid bath for 60 s

**Aqueous caustic descaling baths** have been developed to remove light scale and tarnish from titanium alloys. Aqueous caustic solutions containing 40 to 50% sodium hydroxide have been used successfully to descale many titanium alloys. One bath containing 40 to 43% sodium hydroxide operates at a temperature near its boiling point (125 °C, or 260 °F). Descaling normally requires from 5 to 30 min. Immersion time is not critical because little weight loss is encountered after the first 5 min. Caustic descaling conditions the scale so that it is removed readily during subsequent acid pickling.

A more effective aqueous solution contains either copper sulfate or sodium sulfate in addition to sodium hydroxide. This bath operates at lower temperature (105 °C, or 220 °F). A composition of this solution by weight is: 50% sodium hydroxide, 10% copper sulfate pentahydrate ($CuSO_45H_2O$), and 40% water. Using immersion times of 10 to 20 min, this bath has proved effective in descaling Ti-6Al-4V and Ti-2.5Al-16V alloys.

## *Pickling Procedures following Descaling*

All advantages gained through proper conditioning and handling of titanium parts during cleaning can be lost if the composition of the final pickling acid is not controlled. Cold spent acid solutions increase appreciably the time required for pickling and the possible quality problems experienced with hydrogen pickup. Highly concentrated hot acids can be overly aggressive, resulting in surface finish problems such as a rough and pitted surface caused by preferential acid attack. Sulfuric acid, 35 vol% at 65 °C (150 °F), is recommended for pickling immediately following salt bath conditioning and rinsing to remove molten salt and residual softened scales. An acid of this formula has very little effect on titanium metal. Metal salts in the original and additional acid solutions further minimize these base metal attacks. Table 2 gives conditions for corrosion of titanium in various sulfuric acid pickle baths.

**Table 2 Corrosion of titanium in sulfuric acid pickle baths**

A nitric-hydrofluoric acid solution, which is the final stage brightening in most alloy cleaning lines, should be maintained at a minimum ratio of 15 parts nitric acid to 1 part hydrofluoric acid to reduce hydrogen pickup effects. The concentration of hydrofluoric acid may vary from 1 to 5%, or even higher as long as the ratio is not exceeded. The activity of these pickle solutions is affected by titanium content, and the acids are frequently discarded at a level of 26 g/L (3 oz/gal). The solution used for final brightening can be used for the required alpha case removal also, with careful watch of titanium content.

| **Sulfuric acid concentration, %** | **Acid addition** | **Bath temperature** | | **Corrosion rate** | |
|---|---|---|---|---|---|
| | | **°C** | **°F** | **µm/yr** | **mils/yr** |
| 30 | 0.5% copper sulfate | 38 | 100 | 100 | 4.0 |
| 30 | 1% copper sulfate | 38 | 100 | 20 | 0.8 |
| 30 | 10% copper sulfate | 38 | 100 | 400 | 16.0 |
| 30 | 0.25% copper sulfate | 95 | 205 | 76 | 3.0 |
| 10 | 2% ferrous sulfate | Boiling point | Boiling point | 125 | 5.0 |
| 17 | 7-8% ferrous sulfate | 60 | 140 | 125 | 5.0 |

## *Removal of Tarnish Films*

Tarnish films are thin oxide films that form on titanium in air temperatures between 315 and 650 °C (600 and 1200 °F). After exposure at 315 °C (600 °F), the film is barely perceptible, but with increasing temperature and time at temperature, it becomes thicker and darker. The film acquires a distinct straw yellow color at about 370 °C (700 °F) and a blue color at 480 °C (900 °F). At about 650 °C (1200 °F), it assumes the dull gray appearance of a light scale. Alloying elements and surface contaminants also influence the color and characteristics.

Tarnish films are readily removed by abrasive methods, and all but the heaviest films can be removed by acid pickling. Prolonged exposures at temperatures above about 595 °C (1105 °F), in combination with surface contaminants, result in heavier surface films that are not removed satisfactorily by acid pickling and so require descaling treatments.

**Acid pickling** removes a light amount of metal, usually a few microns. It is used to remove smeared metal, which could affect penetrant inspection. Titanium and titanium alloys can be satisfactorily pickled by the following procedure:

1. Clean thoroughly in alkaline solution to remove all shop soils, soap drawing compounds, and identification inks. If coated with heavy oil, grease, or other petroleum-based compounds, parts may be degreased in trichloroethylene before alkaline cleaning. Degreasing will not be harmful to the part in subsequent processing.
2. Rinse thoroughly in clean running water after alkaline immersion cleaning.
3. Pickle for 1 to 5 min in an aqueous nitric-hydrofluoric acid solution containing 15 to 40% nitric acid and 1.0 to 2.0% hydrofluoric acid by weight, and operated at a temperature of 24 to 60 °C (75 to 140 °F). The preferred acid content of the pickling solution, particularly for alpha-beta and beta alloys, is usually near the middle of the above ranges. A solution of 33.2% nitric acid and 1.6% hydrofluoric acid has been found effective. When the buildup of titanium in the solution reaches 12 g/L (2 oz/gal), discard the solution.
4. Rinse the parts thoroughly in clean water.
5. High-pressure spray wash thoroughly with clean water at 55 ± 6 °C (130 ± 10 °F).
6. Rinse in hot water to aid in drying. Allow to dry.

To avoid excessive stock removal, the recommended immersion times for pickling solutions should not be exceeded. It is equally important to maintain the composition and operating temperature of the bath within the limits prescribed to prevent an excessive amount of hydrogen pickup. Gage loss from all acid pickling after descaling is estimated to be less than 0.025 mm/min (0.001 in./min), depending on the combination of variables used.

Hydrogen contamination is estimated to be 0 to 15 ppm per 0.025 mm (0.001 in.) of metal removed, depending on alloy composition and gage material pickled. Table 3 gives data on hydrogen pickup for an alpha, an alpha-beta, and a beta alloy pickled in a 15% nitric acid, 1% hydrofluoric acid bath at 49 to 60 °C (120 to 140 °F). Hydrogen contamination can be held to a minimum by maintaining an acid ratio of 10 to 1 or greater of nitric acid to hydrofluoric acid. Hydrogen diffuses more rapidly into the beta phase. Alpha-beta alloys that have α+ β microstructures, which have been heat treated to complete equilibrium, pick up less hydrogen than microstructures of transformed beta and/or simple mill-annealed structures.

### Table 3 Effect of titanium alloy composition on hydrogen pickup in acid pickling

Pickling bath is an aqueous solution containing 15% nitric acid and 1% hydrofluoric acid by weight; operating temperature is 49 to 60 °C (120 to 140 °F).

| **Alloy** | **Thickness** | | **Hydrogen pickup (gage removed), ppm/0.0250 mm (ppm/0.001 in.)** |
|---|---|---|---|
| | **mm** | **in.** | |
| **Alpha alloy** | | | |
| Ti-5Al-2.5Sn | 0.50 | 0.020 | 0-4 |
| Ti-5Al-2.5Sn | 1.00 | 0.040 | 0-3 |
| **Alpha-beta alloy** | | | |

| | | | |
|---|---|---|---|
| Ti-6Al-4V | 0.50 | 0.020 | 4-7 |
| Ti-6Al-4V | 1.00 | 0.040 | 3-5 |
| **Beta alloy** | | | |
| Ti-13V-11Cr-3Al | 0.50 | 0.020 | 10-15 |
| Ti-13V-11Cr-3Al | 1.00 | 0.040 | 5-8 |

**Mass Finishing (Barrel Finishing).** Oxide films formed by heating to temperatures as high as 650 °C (1200 °F) for 30 min have been effectively removed from Ti-8Mn alloy parts by wet mass finishing. At barrel speeds of 43,000 to 51,000 mm/min (1700 to 2000 in./min), parts have been cleaned satisfactorily in about 1 h. Complete barrel loading procedures for three barrels, ranging from 0.02 to 0.25 $m^3$ (0.75 to 8.85 $ft^3$) capacity, are given in Table 4.

**Table 4 Mass finishing conditions for titanium parts**

| **Barrel size** | | | | | | **Speed, rev/min** | **Part load** | | **Medium**[a] | | **Water** | | **Abrasive compound**[b] | | **Alkaline cleaner**[c] | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Capacity** | | **Diameter** | | **Width** | | | | | | | | | | | | |
| **$m^3$** | **$ft^3$** | **mm** | **in.** | **mm** | **in.** | | **kg** | **lb** | **kg** | **lb** | **L** | **qt** | **kg** | **lb** | **kg** | **lb** |
| 0.02 | 0.75 | 381 | 15 | 178 | 7 | 36 | 1-2 | 3-4 | 18 | 40 | 1.2 | 1.25 | 0.2 | 0.5 | 0.2 | 0.5 |
| 0.07 | 2.33 | 559 | 22 | 240 | 10 | 28 | 4-5 | 8-12 | 54 | 120 | 4 | 4 | 0.7 | 1.5 | 0.34 | 0.75 |
| 0.25 | 8.85 | 813 | 32 | 457 | 18 | 20 | 14-18 | 30-40 | 209 | 460 | 14 | 15 | 2.3 | 5 | 0.5 | 1 |

(a) Aluminum oxide nuggets 6.4 to 38 mm (0.25 to 1.5 in.) or preformed vitrified chips 4.8 by 9.5 to 7.9 by 28.6 mm ($\frac{3}{16}$ by $\frac{3}{8}$ to $\frac{5}{16}$ by $1\frac{1}{8}$ in.).

(b) Dry, mildly alkaline compound.

(c) Mild cleaner with high soap content

In mass finishing of titanium parts, the ratio of medium to parts should be between 10 and 15 to 1, depending on the size of the parts. Proportionately more medium is required as part size increases. Water is used to cover parts and medium. Surface finish is improved when more water is added, but cycle time required to obtain a given finish is increased. The rate of descaling increases directly with barrel speed but is limited by the fragility of the parts being processed. Parts are randomly loaded in the barrel and rotated at relatively low barrel speeds to minimize distortion and nicking. Conditions for mass finishing of titanium parts are also given in Table 4.

Aluminum oxide media are the most satisfactory. They do not contaminate the work and have a long useful life. For oxide removal, small well-worn media produce the highest finish. To avoid possible metallic contamination, the medium used for titanium should not be used in processing other metals. Strong acid-forming compounds should be avoided, principally because they are corrosive and contribute to hydrogen embrittlement. Because of the fire hazard created by fine, dry titanium particles, dry mass finishing of titanium parts is not recommended.

### *Polishing and Buffing*

The polishing and buffing of titanium is accomplished with the same equipment used for other metals. Polishing is frequently done wet, using mineral oil lubricants and coolants. Silicon carbide abrasive cloth belts have been effective. It is common to polish in two or more steps, using a coarser grit initially, such as 60 or 80, to remove gross surface roughness, followed by polishing with 120- or 150-grit to provide a smooth finish. Titanium tends to wear the sharp edges of the abrasive particles and load the belts more rapidly than steel. Frequent belt changes are required for effective cutting. A good flow of coolant improves polishing and extends the life of the abrasives.

Dry polishing is more appropriate than wet for some applications. For these operations, belts or cloth wheels with silicon carbide abrasive may be used. Soaps and proprietary compounds may be applied to the belts to improve polishing and to extend belt life. Abrasive belt materials that incorporate solid stearate lubricants offer improved results for dry polishing operations.

Fine polishing of titanium articles for extremely smooth finishes requires several progressive polishing steps with finer abrasives until pumice or rough types of abrasive are applied. With the softer grades of titanium, such as unalloyed material, fine polishing requires more time and care to prevent scratching. The harder alloy grades can be polished more readily to a surface of high reflectivity. If a matte finish is desired, wet blasting with a fine slurry may be used after initial polishing.

Titanium alloys can be buffed safely. The purpose of buffing is to improve the surface appearance of the metal and produce a smooth tight surface. Buffing is used as a final finishing operation and is particularly adaptable to finishing a localized area of a part. Parts such as joint prostheses, pacemakers, and heart valves require a highly buffed tight surface to prevent entrapment of particles. Close-fitting parts for equipment, such as guidance systems and electronics applications, require highly polished surfaces obtained by buffing. In addition, sheet sizes too large to be processed by other abrasive finishing methods, such as mass finishing or wet blasting, can be economically processed by buffing.

The principal limitations of buffing are distortion, caused by the inducement of localized stress; surface burning, resulting from prolonged dwell of the buff; an inability to process inner or restricted surfaces; and the feathering of holes and edges. Proper care of the buffing wheel is essential. Buffing with insufficient compound or a loaded wheel produces burning or distortion of the part. After buffing, no further cleaning of parts is required except degreasing to remove the buffing compound.

### *Wire Brushing*

Wire brushing of titanium alloys is not recommended when other finishing methods, such as buffing, can accomplish the objective. In one case, wire brushing resulted in serious defects. A stiff-bristled wire brush removed surface scratches and oxide films, but the surface was pitted by the wire tips. To avoid pitting, softer wire bristles were tried, and the surface of the titanium acquired a burnished appearance. When the surface layers were cold worked, the grinding scratches, instead of being removed, were filled with smeared metal. Wire brushing with a silicon carbide abrasive grease has been used successfully to remove burrs, break sharp edges from edge radii, and blend chamfers.

### *Removal of Grease and Other Soils*

Removal of grease, oil, and other shop soils from titanium parts is normally accomplished with the same type of equipment and the same cleaning procedures used for stainless steel and high-temperature alloy components.

**Vapor degreasing** normally employs either trichloroethylene or perchloroethylene. Under certain conditions, these solvents are known to be a cause of stress-corrosion cracking in titanium alloys. Methylethyl ketone is used as a cleaner in situations where chlorinated solutions are not desired. All titanium parts should be acid pickled after vapor degreasing.

**Other cleaning methods** use chemicals that, if they are left to dry on the part, may have a harmful effect on the properties of titanium. Among these are soda ash, borates, silicates, and wetting agents commonly used in alkaline cleaners; kerosine and other hydrocarbon solvents used in emulsion cleaners; and mineral spirits employed in hand wiping operations. Residues of all these cleaning agents must be completely removed by thorough rinsing. To ensure that a surface that is free of contaminants, rinsing is frequently followed by acid pickling.

## Surface Modification

### *Ion Implantation*

The ion implantation process involves the acceleration of ions to a sufficiently high velocity so that they are able to penetrate the surface of the substrate material being implanted. The mean depth of penetration depends on the energy, the atomic number, the atomic masses of the implanted and the target species, and the angle of incidence. A 1 mA beam takes approximately 16 s to achieve a dose of $1 \times 10^{17}$ ions over 1 $cm^2$, assuming perfect implantation. Industrial implanters are typically designed to accelerate the ions to energies of between 50 and 200 keV, resulting in implant layer thicknesses of up to several hundred nanometers. High ion current densities, 30 to 40 $\mu A/cm^{-2}$, reduce the time necessary to reach a required dose, but they significantly increase the workpiece temperature, which is also dependent on the thermal mass of the substrate, which may in turn be influenced by appropriate heat sinking.

**Wear resistance** of titanium and titanium alloys may be improved by ion implantation. This is the most commercially used aspect of the technology applied to titanium substrates. The most commonly implanted species are nitrogen and carbon, which may be noted from a review of the ion implantation of Ti-6Al-4V (Ref 4). This improvement in wear behavior is effected by the increase in surface hardness that is achieved by ion implantation offsetting a change in wear mechanism from mild oxidative to severe adhesive wear. The surface oxide layer formed on titanium and conventional titanium alloy substrates provides a useful low-friction surface, but when this oxide is removed, rapid adhesive wear occurs against many counterface materials. An increase in near-surface hardness allows the material to resist plastic deformation at higher stresses and hence support the oxide at higher stresses. A threefold increase in microhardness at loads of 1 to 2 g can be achieved in these alloys (Ref 5).

There are three mechanisms from which hardening of ion implanted titanium arises: ion-induced damage, solid solution hardening, and precipitation hardening. Ion-induced damage arises from the creation of a dense network of dislocations similar to that achieved during cold working or in shot peening: improvements in fatigue properties may be achieved through appropriate ion implantation. The strain fields associated with the dense dislocation network require that a higher-energy barrier be overcome to enable the atomic motion required for plastic deformation.

Solid solution hardening may be achieved by either substitutional or interstitial alloying elements. The strain field associated with an "impurity" atom increases the load required to permit dislocation movement.

Precipitation hardening is effected by dislocations being pinned by coherent or incoherent precipitates. For the maximum precipitation hardening effect, a fine distribution of coherent precipitates is required. For very low ion doses, ~$10^{15}$ to $10^{16}$ ions/$cm^2$, damage-induced hardening effects dominate; for intermediate doses, ~$10^{16}$ to $10^{17}$ ions/$cm^2$, solid solution hardening becomes dominant; for high doses, >$10^{17}$ ions/$cm^2$, precipitation hardening dominates. The boundaries obviously depend on the physical properties of the implanting and implanted species and the relevant phase equilibria.

The hardening effect achieved in implantation of nitrogen into Ti-6Al-4V is shown in Fig. 4, the maximum hardness increase being in excess of 170% at a depth of 50 nm below the surface. In this case, the microstructure of nitrogen-implanted Ti-6Al-4V consisted of a fine dispersion of TiN precipitates in a deformed nitrogen-rich matrix. This resulted in a hardening of the surface region and the presence of surface compressive residual stresses. A dose of $1 \times 10^{17}$ atoms N/$cm^2$ improved the wear resistance, but no TiN precipitation was observed. The survival of the implanted layer was extended by increasing the ion dose to $4 \times 10^{17}$ atoms N/$cm^2$, where the hardness increase levels off. The slower oxidative wear mode was obtained against both ruby and steel in ball-against-disc wear tests.

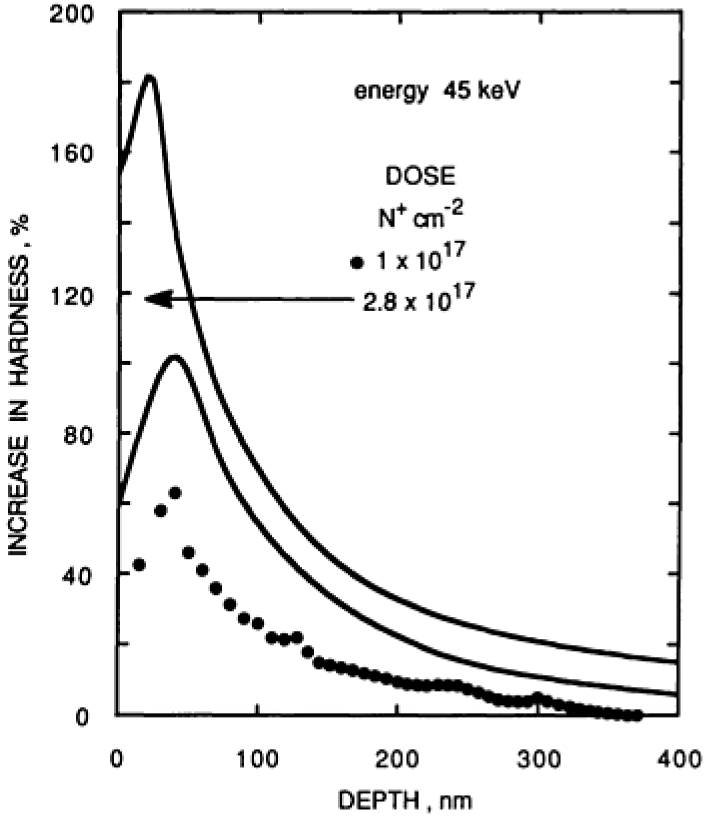

**Fig. 4 Percentage increase in hardness with depth into material for $N^+$ implanted Ti-6Al-4V. Source: Ref 6**

In addition to the simple hardening mechanism, ion implantation is thought to supply a reservoir of nitrogen to the oxide layer when it is removed, with the result that the reformed surface layer is possibly an oxynitride. Low wear rates have been maintained to depths two to three times the depth of the implanted layer, which can be explained in terms of physical displacement due to plowing during the wear process. The relative effects on hardness of nitrogen- and carbon-implanted Ti-6Al-4V are shown in Fig. 5. The very low solubility of carbon in α-Ti as compared to that of nitrogen in α-Ti limits the contribution of solid solution strengthening to the hardnesses measured.

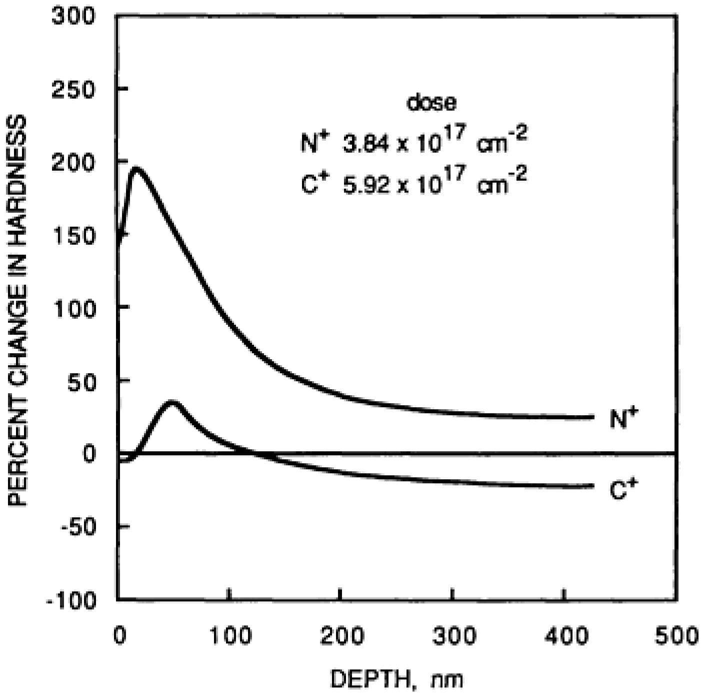

**Fig. 5 Percentage change in hardness with depth for $N^+$ and $C^+$ implanted Ti-6Al-4V. Source: Ref 7**

An example of the application of an ion-implanted titanium alloy is in total joint replacement, where the excellent biocompatibility combined with its specific mechanical properties make the use of Ti-6Al-4V desirable. The combination of this alloy and ultrahigh-molecular-weight polyethylene is unsatisfactory because of unacceptably high levels of wear in the joint. Ion implantation can improve this situation. In α+ β alloys such as Ti-6Al-4V, a hard α-case is produced at the surface because of the high levels of the α-stabilizing element, nitrogen, present. Although significant improvements in wear resistance for ion-implanted femoral heads have been noted in many investigations, wear does occur through a combination of oxidative wear, caused by the loss of the passivating oxide debris. The use of the process in the treatment of biomaterials has reached some degree of commercial maturity (Ref 5). Alloys used in hip, knee, and small quantities of wrist, shoulder, finger, and toe joint replacements are routinely ion implanted. Ion implantation of titanium and titanium alloys for improvements in wear is best summarized by noting that the very small depth to which hardening of the substrate alloy occurs allows these significant improvements to be effective only in moderately mild regimes of wear.

Other areas of application (Ref 5) are found in gas turbines, where discs and blades are implanted. Fretting wear is the problem, which can be significantly reduced by ion implantation. The best results using this process are obtained when one surface is treated with carbon and the other surface is implanted with a different species, such as nitrogen. Titanium gears for a variety of low-load aircraft applications are used because of weight savings, and problems of scuffing can be reduced by nitrogen implantation. Titanium components for use in hydraulic systems are often used because of the corrosion-resistant nature of the metal and its alloys. Ion implantation has been used to reduce galling against both steel and other titanium alloy counterface materials. Titanium ball valves articulating against PEEK valve seats suffer unacceptably high rates of wear, producing leaks after as few as ten open/close cycles. Ion-implanted balls withstand 100 operations with no sign of abrasion.

**High cycle fatigue** may be influenced by ion implantation with both nitrogen and carbon. Increases in fatigue strength have been measured in rotating beam fatigue tests (Ref 8). The endurance limits have been increased for both implanted species, the largest increase being 20% achieved with carbon implantation. The improvements are attributed to the creation of residual compressive stresses at the surface of the Ti-6Al-4V substrate, though the reasons for the greater improvement achieved with carbon implantation over that achieved with nitrogen implantation are not clear.

**Corrosion behavior** of titanium and titanium alloys can be modified by appropriate surface alloying using ion implantation. Implantation of molybdenum, tantalum, and molybdenum and tantalum together produces beneficial effects on passivation curves in a sulfuric acid solution (Ref 9). Other implanted species that produce beneficial effects include platinum and palladium. Palladium implantation also improves the resistance of titanium to crevice corrosion and hot chloride solutions (Ref 10).

**Oxidation resistance** of ion-implanted titanium alloys has been researched using a variety of alloying elements. Oxidation for 50 min in dry oxygen at 600 °C has been reduced by implantation to a level of $\sim 2 \cdot 10^{16}$ ions/cm$^2$ of species that have either oxides with high negative free energy of formation or large ionic radii for smaller heats of formation (Ref 11). Particularly beneficial effects were obtained from implanting barium, rubidium, cesium, strontium, calcium, ytterbium, and europium. The reduction in oxidation was thought to be caused by implanted impurities obstructing short-circuit diffusion paths or forming Ti + M (implant) mixed oxides. $BaTiO_3$ has been found after barium implantation and oxidation, which improved the fretting fatigue behavior of both titanium and Ti-6Al-4V. Implantation of various elements, including rubidium, cesium, strontium, and calcium, affected the oxidation resistance of titanium (Ref 12). This has been explained in terms of changes in oxidation rate laws, limited solubilities of the implanted elements in the titanium, and the tendency to form ternary oxides with titanium. Implantation of elements in excess of their equilibrium solubility may be necessary for a significant effect on oxidation behavior. Europium, which is one of the less soluble elements in titanium, was shown to produce significant inhibition to oxidation at 600 °C, where the presence of ternary oxides was a prerequisite for a strong inhibitive effect.

## *Laser and Electron Beam Treatment*

Energy beam surface treatment for materials encompasses a wide range of processes, ranging from laser ablation at very high power densities to the transformation hardening of steels and the annealing of metals and alloys at relatively low power densities. The only processes applied to titanium and titanium alloys to any significant extent are surface melting, surface cladding, and surface alloying techniques. These processes all involve the use of the energy beam to melt a surface layer in order to produce a conduction-limited melt profile, as opposed to melting in the "keyhole" regime, which is necessary for deep penetration welding. A conduction-limited melt profile may be close to hemispherical if the beam is a focused spot or something similar, or it may be flat-bottomed if some form of beam scanning across the direction of beam-workpiece relative movement is employed. This molten region may vary in size from <1 μm, where gas alloying is used to mark surfaces, up to >400 μm, where hard surface layers are created for load-bearing, wear-resistant applications. The maximum melt depth is dependent on the absorbed power of the beam by the workpiece, the traverse speed, and the maximum temperature reached in the melt pool before unacceptable surface disruption occurs.

**Surface melting** using energy beams can homogenize a surface by melting all the microstructural components of the workpiece and allowing the relatively rapid resolidification of the melted region, distributing the phases on a much refined scale, or allowing the phases to solidify as new, metastable phases. In the extreme case, surface melting can be used as a rapid solidification tool by employing very high power densities and very rapid traverse speeds, thus relying on the efficient heat extraction from the melted region by the unheated bulk of the workpiece. In simple terms, the cooling rate, $dT/dt$, through the solidification range is equal to the product of the temperature gradient, $dT/dx$, in the melt and the solidification rate, $dx/dt$, which is the speed of the solidifying interface where $T$ is temperature, $t$ is time, and $x$ is distance. The temperature gradient is related to the power density and the solidification rate is related to the traverse speed or pulse length.

Energy beam surface melting has been carried out using electron beams of powers similar to those commonly used for welding and a variety of lasers, the most useful of which is the carbon dioxide laser, which has output powers ranging from 500 W to multikilowatts. The depth of melting employed is normally between 0.1 and 1 mm, and the beams are usually moved across the workpiece surface at speeds between 5 and 100 mm/s. These parameters result in cooling rates through the solidification range of most alloys, between $10^2$ and $10^6$ K/s, with the heat being conducted away into the bulk of the workpiece. Mass transport in these melts results from thermal gradients and surface tension gradients.

No significant changes in the overall mechanical properties occur with either commercially pure titanium or Ti-6Al-4V after laser surface melting. For example, columnar beta grains formed upon solidification of Ti-6Al-4V transform to martensite on further cooling (Ref 13). Surface melting has been used to rapidly solidify dispersion-strengthened titanium alloys. For example, titanium plus erbium has been melted with the objective of improving the high-temperature strength of titanium alloys by forming thermally stable dispersoids (Ref 14). Supersaturated solutions containing erbium and oxygen were produced by laser surface melting of experimental alloys, which, after subsequent heat treatment, formed fine dispersions of rare earth oxides, partially coherent with the titanium matrix. Alloys with an excess of oxygen relative to the erbium content for the formation of $Er_2O_3$ were found to be the most resistant to coarsening of the precipitate.

**Energy beam surface alloying** is achieved by changing the chemical composition of the substrate material during surface melting. Of the many possible alloying additions, nitrogen is the most widely researched. The object of the process is to harden the surface of the titanium alloy to a depth of 0.1 to 0.5 mm in order to improve its wear resistance. It is usually carried out using a $CO_2$ laser and incorporates a gas jet blowing nitrogen or nitrogen and argon at the melt pool. By controlling the amount of nitrogen takeup by the melt pool, a range of solidification structures can be obtained that are usually described as predominantly TiN dendrites, nitrogen-rich α-Ti dendrites, or nitrogen-rich basket-weave. In fact, the microstructure most commonly contains TiN dendrites surrounded by nitrogen-rich α-Ti as a result of nonequilibrium solidification through the peritectic of the titanium-nitrogen phase equilibrium system. There is also a series of continuous layers across the surface of the laser-alloyed track that are responsible for the gold color of the surface after the process. The degree of alloying has a direct influence on the hardness of the alloyed volume, which can be simply controlled by changing the interaction time of the nitrogen with the melt pool (i.e., by altering the traverse speed) (Fig. 6) or changing the nitriding potential of the alloying gas (i.e., by diluting the nitrogen with an inert gas such as argon) (Fig. 7).

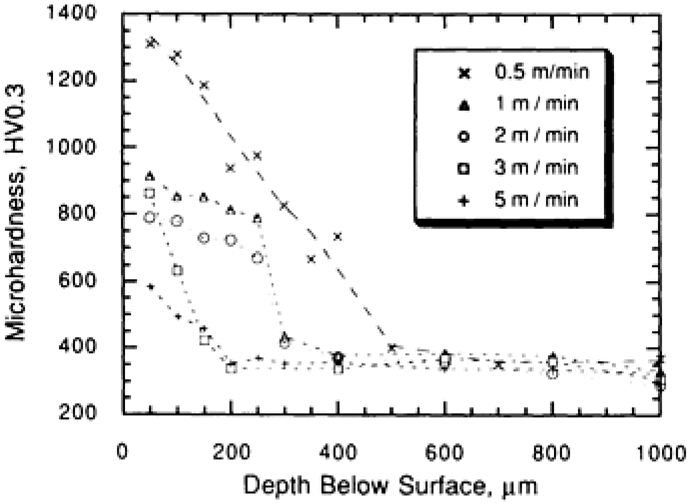

**Fig. 6 Influence of feed rate on hardness profile for laser gas nitrided Ti-6Al-4V, 6.6 × $10^4$ W/cm$^{-2}$, 40:60 N2:Ar, 75% track overlap. Source: Ref 15**

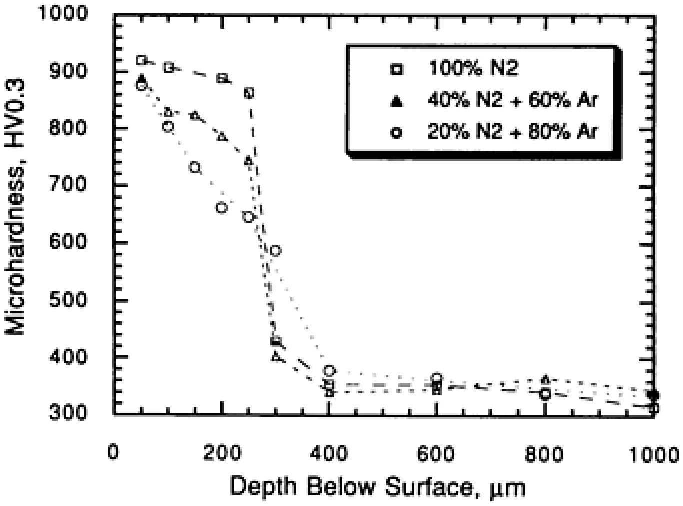

**Fig. 7 Influence of gas mixture on hardness profile for laser gas nitrided Ti-6Al-4V, 6.6 × $10^4$ W/cm$^{-2}$, 1 m/min$^{-1}$, 75% track overlap. Source: Ref 15**

The major concerns of this process, and of other energy beam melting processes of all materials, are to avoid cracking, porosity formation, and unacceptably rough surfaces. Cracking is the major problem associated with laser-gas-nitrided titanium; it results from thermal stresses acting on the hard, relatively brittle phases arising from the process. The problem is ameliorated by using a mixture of argon and nitrogen in the treatment gas to produce an alloyed region of less than maximum possible hardness (<650 HV) and by preheating the substrate. With typical processing parameters, if the preheating temperature exceeds 300 °C (570 °F), cracking can be completely eliminated (Ref 15, 16).

Laser gas nitriding has also been used on a much finer scale to produce marking on the surface of, for example, watch cases. Nitrogen is used to produce a gold color, and oxygen may be used to produce a gray color. Carbon dioxide or neodymium yttrium-aluminum-garnet lasers may be used for this process, where melts as shallow as 1 μm are created.

Other systems that have been investigated include carbon and boron alloying. These substances are usually added to titanium alloys by using preplaced graphite or boron powder, although laser gas carburizing of titanium alloys may be achieved using a carbon-bearing gas in a manner similar to that for laser gas nitriding. These two systems produce similar microstructures, which is a reflection of the similarity between the Ti-C and Ti-B equilibrium systems at the relevant compositions. At low alloying additions, a divorced eutectic solidification is predominant where Ti + TiC and Ti + TiB solidify in each system, respectively. At higher interstitial contents, primary TiC and TiB ($Ti_2B$) solidify as large dendrites, together with the eutectic solidification microstructure. The hardnesses measured in the alloyed regions have been found to be a reflection of the volume fraction of the compounds solidified, because negligible amounts of carbon and boron can be in solution in α- or β-Ti. Laser gas carburizing using methane diluted 1 to 4 with argon produces a maximum hardness of 650 HV for 100 μm, decreasing to the substrate value at a depth of 300 μm below the surface (Ref 17).

More recently, combinations of alloying elements have been used to produce hardness increases and wear performance improvements. The most successful of these is the simultaneous addition of carbon and silicon in the form of silicon carbide (Ref 16). Surface hardnesses of 650 to 750 HV without any cracking are achieved using electron beam surface alloying of a powder slurry of SiC powder and a polyvinyl alcohol binder. The microstructure comprises TiC dendrites surrounded by α-Ti dendrites, which contain some silicon and very fine precipitation of $Ti_5Si_3$, and a eutectic of α-Ti + $Ti_5Si_3$. The overall silicon content of the melt was ~6 wt% Si. The advantage of this system is that the α-Ti component of the microstructure is relatively tough compared to that solidified after laser gas nitriding. A typical hardness profile obtained from this process is shown in Fig. 8. Wear performance similar to that of hardened and tempered low-alloy steels, and superior to that of laser nitrided and untreated Ti-6Al-4V, has been measured in unlubricated sliding-rolling wear tests (30% sliding) at contact stresses of up to 750 MPa (applied load 120 kg/F) (Fig. 9).

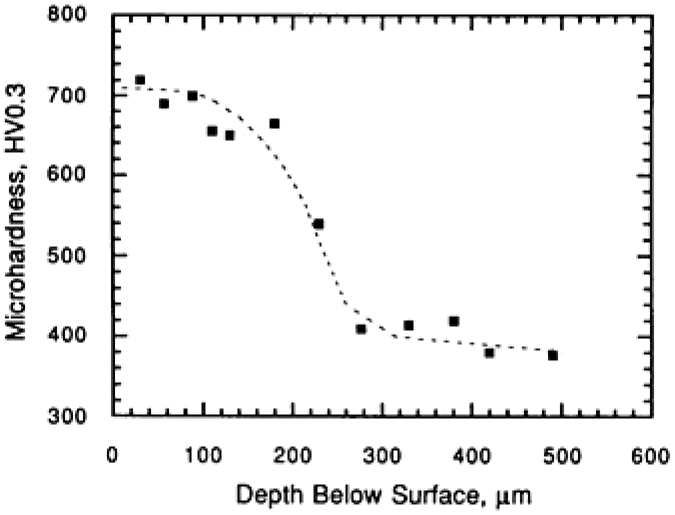

**Fig. 8 Hardness profile from electron beam SiC alloyed Ti-6Al-4V after surface grinding to remove rippling. Source: Ref 16**

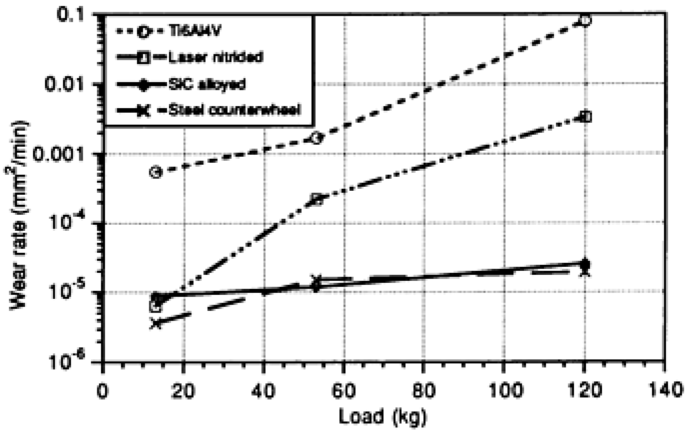

**Fig. 9 Wear rates from Amsler sliding-rolling wear tests for high-energy-beam beam surface alloyed Ti-6Al-4V. Source: Ref 16**

Other elements that have been electron beam surface alloyed into the surface region of titanium alloys include nickel, chromium, silicon, aluminum, and silicon and aluminum. Surface alloys containing silicon and aluminum (Ref 18) have been subjected to high-temperature oxidation tests, between 750 and 910 °C (1380 and 1670 °F) in air. Beneficial effects of the alloying were measured regarding both oxidation kinetics and the adherence of oxide scale.

Laser particle injection is an energy beam treatment that retains some solid phase during the thermal excursion. It involves the injection of hard particles into a shallow laser melt track. In a Ti-6Al-4V matrix, TiC particles ranging in size from +325-230 to +140-70 mesh have been injected (Ref 19). Partial dissolution of the carbides occurs, but they remain substantially in a particulate form, effectively creating a particulate-reinforced metal matrix composite. Maximum volume fractions of 0.6 included carbide have been created. Improvements in performance by a factor of four, independent of carbide volume fraction for $V_f > 25\%$, were measured for TiC-injected Ti-6Al-4V over untreated materials using dry sand/rubber wheel abrasive wear tests (Ref 20).

**Laser cladding** involves the addition of a sacrificial layer on the surface of the substrate material, ideally with minimum dilution of the cladding by the substrate but with good adhesion of the clad. A prerequisite for good bonding of the clad to the substrate is similar coefficients of thermal expansion. For erosion resistance in gas turbines, TiC in a β-Ti alloy matrix has been clad on a Ti-6Al-4V substrate, as has TiC in a maraging steel matrix for particularly arduous service (Ref 21).

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## Diffusion Treatments

Diffusion treatments, as the name suggests, require sufficient time at temperature to allow significant atomic mobility to occur. Because the process temperature usually affects the bulk of the component to be treated, the effects of the thermal cycle on the bulk properties of the material must be considered. If, for example, wrought Ti-6Al-4V bar has been annealed at 700 °C (1300 °F), it is highly likely that a thermal excursion to 800 °C (1470 °F) for 20 h will affect its mechanical properties to a significant degree. For this reason, it is desirable that a diffusion treatment be carried out at as low a temperature as possible if it is the final heat-treatment step for a material and if the workpiece is temperature sensitive.

### *Nonmetallic Elements*

**Oxidizing** of titanium and titanium alloys can be using to improve their tribological properties. Oxygen in solution in α-Ti produces significant strengthening of the material (Fig. 10).

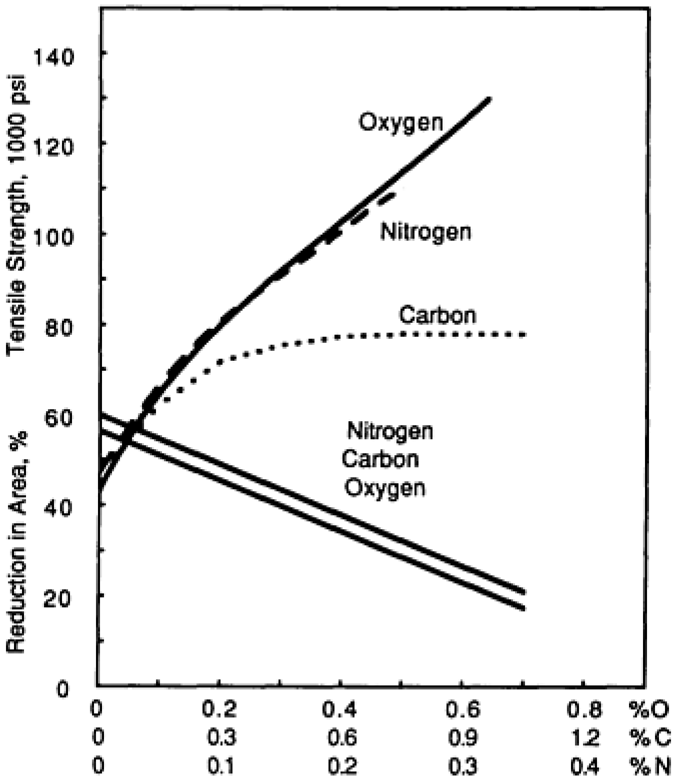

**Fig. 10 Effect of interstitial alloying elements on strength and reduction in area of iodide titanium. Source: Ref 22**

Over the past 40 years, a great deal of work has been devoted to the study of the oxidation of titanium and its alloys, as described above in this article. By contrast, little attention has been paid to deliberate oxidation as a tribological surface treatment of titanium alloys. Investigations are scattered over many journals over a long period of time. One observed that when chemically pure titanium was heated in the range 850 to 1000 °C (1560 to 1830 °F) in air at a pressure between $10^{-3}$ and $10^{-2}$mm Hg, the surface was effectively hardened (Ref 23). The process was commonly disregarded, however, because at a temperature high enough to achieve an appreciable hardening effect, a considerable amount of scale is also formed (Ref 24). Fatigue strength is also reduced. It was subsequently shown that the friction coefficient of commercial titanium markedly decreases when titanium is heated in air at 350 °C for 17 h (Ref 25) and that the coefficient of friction of the oxidized surface of titanium remains low after removal of the brittle compound layers (Ref 26). These early results led to a number of more detailed studies concerning the oxidizing treatment of titanium for improvements in wear behavior.

In view of the difficulties associated with the severe scaling of titanium alloys when heated in air, controlled oxidizing in molten salts has been attempted. When titanium specimens are heated in lithium carbonate salt baths at temperatures between 600 and 900 °C (1110 and 1650 °F) for 2 to 4 h, satisfactory layers are formed. The technique has been used for production batches of titanium pistons (Ref 27).

The Tifran process has been used to treat Ti-6Al-4V, and in one set of tests, even in the absence of lubricant, seizure was eliminated. Decreases in the wear rate and improvements in the behavior of the lubricating film were observed. The technique is based on diffusion in the gaseous phase, resulting in formation of a layer on the surface of the alloy, which has a titanium oxide base. The effect of Tifran treatment on the wear life and efficiency of annealed Ti-6Al-4V gears has been studied by vacuum testing. Compared with other surface treatments, Tifran-treated gears exhibit the best wear resistance and the lowest power losses (Ref 28).

Oxygen diffusion hardening (ODH) of Ti-6Al-7Nb alloys results in a surface with a gradation in hardness from the surface to a depth of 50 μm. The maximum hardness is 900 HV, compared with 360 HV for the untreated alloy. The corrosion resistance of the ODH-treated titanium alloy is equal to that of commercially pure titanium and untreated Ti-6Al-7Nb alloy (Ref 29).

A wear-resistant surface treatment, based on oxidizing of titanium alloys in air, is used to protect valve spring retainers made of Ti-22V-4Al β-Ti alloy (Ref 30). Better wear resistance was afforded to the component with the oxidation process treatment than with either ion nitriding or gas carburizing. The brittle oxide layer formed on the surface was removed before use. The wear resistance of oxidized (at 850 °C, or 1560 °F, for 30 min) valve spring retainers was better than that of steel retainers, and after shot peening, the fatigue strength of oxygen-surface-hardened Ti-22V-6Al exceeds that of the as-received alloy.

**Nitriding** of titanium and titanium alloys has been investigated for many years and is used effectively on a small scale for protection against wear. The wear resistance is imparted by a very favorable phase equilibrium relationship between the elements. Nitrogen has a high solid solubility in α-Ti, and the strength increase effected by the interstitial nitrogen is significant, as shown in Fig. 10. Reference to a titanium-nitrogen equilibrium phase diagram shows that above 12.7 wt% N, the compound $Ti_2N$ is formed at temperatures below 1100 °C (2010 °F); it has a tetragonal crystal structure and a hardness of ~1500 HV. At higher nitrogen contents, over a wide range of compositions, TiN with an NaCl-type crystal structure and a hardness of ~3000 HV is formed. Nitriding produces a thin compound layer of TiN at the surface, above a thicker compound layer of $Ti_2N$, which is above a diffusion zone of nitrogen-strengthened titanium. The surface differs from that achieved through oxidizing in that a useful, hard compound layer structure is created at the surface.

Nitriding cannot be achieved in air because of the tendency of titanium to form $TiO_2$ in preference to either of the nitrides, but it can be achieved in a nitrogen gas atmosphere. At 1 atm in nitrogen or ammonia, no technologically useful surface is created below 800 °C (1470 °F). However, treatment in ammonia at higher pressures, for example 1.2 MPa, yields thicker compound layers and diffusion zones. In order to remove the hydrogen from parts treated in ammonia, a tempering treatment at a temperature between 300 and 400 °C (570 and 750 °F) at a pressure of $10^{-2}$ mbar is included in this process. Components treated by this process include surgical instruments, watch cases, racing engine and racing car components, and precision machine parts. The high pressure used in the process allows treatment of narrow, deep, blind holes and intricate details such as fine threads (Ref 31).

It follows that nitriding of titanium alloys may be carried out in hot isostatic pressing equipment, where pressures of up to 100 MPa have been used (Ref 32).

An alternative medium for the introduction of nitrogen and its subsequent diffusion into the surface of titanium and titanium alloys is a plasma. Plasma, ion, or glow discharge nitriding has long been applied to ferrous alloys, but the direct current plasma process is equally applicable to titanium-base materials. Nitrogen, nitrogen-hydrogen, nitrogen-argon, or cracked ammonia may be used as the treatment gas. Nitriding may be achieved at temperatures down to 300 °C (570 °F), but the value of processing at these temperatures is doubtful because of the very thin (1 $\mu$m) hardened region produced. More usually, processing is carried out at temperatures in the range of 700 to 900 °C (1300 to 1650 °F). The plasma process uses and exhausts smaller volumes of gas than any gaseous treatment. However, experience is needed to monitor and control the temperature throughout the workpiece. Because all the heat input comes from the plasma, sections of component with significantly different surface area-to-volume ratios may differ in temperature. The thicknesses of compound layers found adjacent to corners also differ from layers on continuous surfaces of workpieces. This effect is attributed to variations in the sputtering rates at these different points. Successfully plasma-nitrided components include racing car steering racks, gears, and ball valves. Components are ready for use directly after treatment and have the characteristic gold color of TiN (Ref 16).

Significant improvements in wear resistance are gained after nitriding titanium-base materials, the sources of the benefits being twofold; the hard surface compound layers of TiN and $Ti_2N$ and the support given by the nitrogen-strengthened diffusion zone beneath them. A typical hardness profile from plasma nitrided Ti-Al-4V is shown in Fig. 11, in which the dashed line represents the hardnesses of the thin TiN and $Ti_2N$ compound layers. The processing conditions used were 850 °C (1560 °F) for 20 h in ammonia. A loss of about 10% of fatigue strength is associated with nitriding, but this can be mitigated against by appropriate design of a component.

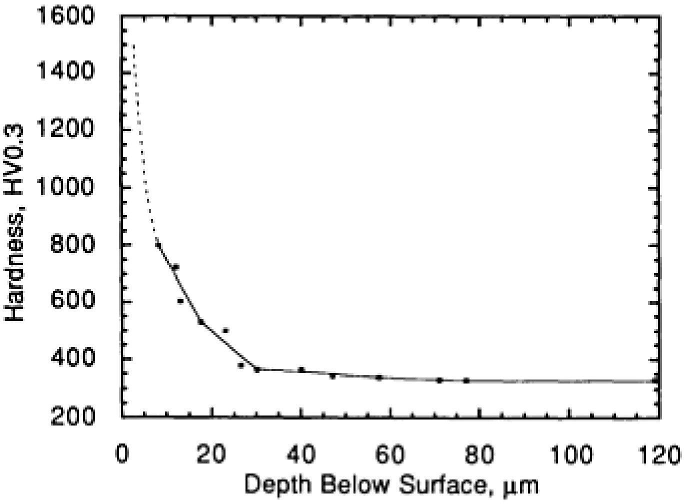

**Fig. 11 Hardness profile (Vickers, 0.3 kg load) from plasma-nitrided Ti-6Al-4V. Source: Ref 16**

A number of salt bath treatments have been developed for titanium, the oldest of which is probably the Tiduran process (Ref 33). In this process, the titanium component is immersed in a cyanide-based salt bath at 800 °C (1470 °F), usually for 2 h. Carbon and nitrogen, and sometimes small amounts of oxygen, diffuse into the surface to produce a hardened diffusion zone. The maximum hardness achieved in the process is in the range of 750 to 800 HV, falling progressively into the substrate, giving a case depth of about 50 μm. A uniform 10 μm is removed from the surface of the metal during the process. Components can usually be used in the as-coated condition, or they may be given a light pickle to remove the black surface.

Localized heat sources, such as a plasma torch combined with a nitrogen atmosphere, can be used to produce a superficial nitrogen-enriched surface region, but quality control is extremely difficult.

**Carburizing** of titanium and titanium alloys may be achieved in nonoxidizing, carburizing environments. The phase equilibrium system for Ti-C differs from those for Ti-O and Ti-N in that there is very little solid solubility for carbon in titanium. Hence, compound layer formation of TiC may result, but there is no significant diffusion zone beneath the TiC. Carburizing is accomplished in pack processes using carbonaceous media such as calcium carbonate, or following evacuation and heating to 1050 °C (1920 °F), a carburizing gas is introduced and is used for cooling. Carburizing has been used for the creation of wear-resistant surfaces on components such as engine valves.

**Boronizing** of titanium-base materials is similar to carburizing in that it results in the formation of an extremely hard compound layer with a negligible diffusion zone. $TiB_2$ is usually the outermost layer, although other borides are also formed. Wear resistance of boronized titanium has been studied (Ref 34), and in comparison with other surface treatments, it has performed very well in lightly loaded gear tests (Ref 35), compared to similar materials.

**Siliconizing** of titanium alloys can be achieved, for example, by using an atmosphere of 3 vol% silane in argon mixture at 1100 °C (2010 °F) for 2 h, which produces a 10 μm $Ti_3Si_5$ compound layer. The objective of this process is to improve oxidation resistance by changing the oxidation product. $TiO_2$ has been observed after oxidation in both air and oxygen at a range of temperatures. At low temperatures (<875 °C, or 1600 °F), the oxidation product was a dense mixture of $TiO_2$ and $SiO_2$, but at temperatures in excess of 900 °C (1650 °F), the outer layer consisted of pure $TiO_2$ (Ref 36). Titanium silicide surface layers have also been obtained using a pack process, the pack comprising of silicon with aluminum fluoride or sodium fluoride as the activator (Ref 37).

### *Metallic Elements*

**Aluminizing** has been carried out via pack processes or deposition and diffusion processes to improve the oxidation resistance of titanium alloys. In a pack process, the compound layers formed depend on the processing parameters. For example, at 760 °C (1400 °F) for 20 h, 50 μm of $TiAl_3$ is formed; 900 °C (1650 °F) for 16 h produces $TiAl_3$ at the surface and thinner layers of TiAl and $Ti_3Al$ form sequentially toward the substrate of $TiAl_2$. Cracks through the compound layers are often present, and Kirkendall porosity occurs in some cases. Diminution of the $TiAl_3$ layer by inward diffusion of aluminum at the oxidizing temperature is faster than the consumption of the coating by oxidation. Cracking of the aluminide coating, thought to occur on cooling after the aluminizing process, is a significant problem. Large, deep, open cracks form during the oxidation of pre-existing ruptures. Other pre-existing cracks that remain virtually closed are oxidized to a lesser degree. There are also closed cracks that seem to form during cooling from the oxidation temperature.

Nonetheless, at 900 °C (1650 °F) the weight gain of the aluminized coatings has been found to be 50 times less than for pure titanium, 30 times less than for Ti-6Al-4V, and 5 times less than for a silicide coating. After 10 h, assuming a linear rate, the oxidation of the aluminide coating was 300 times slower than for the pure titanium (Ref 38). Between 850 and 1000 °C (1560-1830 °F) and room temperature, cyclic oxidation of aluminized titanium also allowed the diffusion of aluminum to continue during the oxidation experiments (Ref 39), but at lower temperatures, the beginning of rapid oxidation was delayed. The $TiAl_3$ surface layers provided better oxidation resistance than the TiAl layer. Successful pack aluminizing of Ti-14Al-24Nb has been achieved (Ref 40). Similar pack-aluminized, intermetallic material has been subjected to cyclic oxidation, and excellent protection from cyclic oxidation resistance was measured to 1000 °C (1830 °F). Thicker coatings were found to offer limited resistance to oxidation because of cracking of the coatings after about five cycles; after more cycles, large growths were observed. Optimum coating thicknesses were found to be 40 to 70 μm (Ref 41).

Pack-aluminized layers are considered to be much thicker than is necessary for protection against oxidation. Thinner aluminized coating can be obtained by duplex routes, for example, by electron beam evaporation followed by a diffusion anneal (Ref 42).

**Nickel diffusion** treatments have been attempted for improvements in tribological behavior. In one case, an electrodeposition process was followed by a diffusion treatment in order to form the compound layers $Ti_2Ni$ (600 HV) and $TiNi_3$ (1000 HV), from which the excess nickel layer was subsequently removed by a chemical process (Ref 43). No particular attention was paid to the potential of the diffusion zone.

Electrodeposited nickel on a titanium alloy substrate that was subsequently diffusion heat treated produced nickel penetration to a depth of ~200 μm (20 h at 850 °C, or 1560 °F). The specimens were then solution treated at 900 °C (1650 °F) and water quenched. Aging at 500 °C (930 °F) for 2 h resulted in hardnesses of ~600 HV in the diffusion zone (Ref 44).

The fact that nickel diffusion into titanium readily occurs implies that the use of overlay coatings based on nickel (or iron or cobalt) are of limited use for oxidation resistance, both because of loss of the coating to the substrate and because some of the reaction products may degrade critical mechanical properties.

**Copper diffusion** has been achieved by both electroplating and ion plating copper onto the surface of titanium alloys, followed by a diffusion heat treatment. In one case a heat treatment of 800 °C (1470 °F) for 12 h followed by furnace cooling was used, which resulted in an outer compound layer of $Ti_2Cu$, beneath which there was a $Ti_3Cu$ layer and a diffusion zone. The $Ti_2Cu$ layer has been shown to perform well in wear testing, comparable with plasma-nitrided titanium and physical vapor deposited TiN. No optimization of the diffusion zone was carried out. The maximum diffusion zone hardness was 650 HV at 5 μm below the surface, dropping to a core hardness of 450 HV at 15 μm below the surface (Ref 45). Nickel and copper diffusion treatments involving electroplating followed by heat treatment are relatively low-cost surface engineering systems for wear resistance. The nickel diffusion treatment has been looked at as a possibility for a seal ring and a titanium alloy control rod couple in a nuclear power station; the surface treatment allows a reduction in friction and a longer component lifetime. Titanium alloy valves have been treated by nickel diffusion in the seat area in order to improve the cavitation erosion resistance of the components for use in chemical and power generation plants.

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## Coatings

### *Chemical Conversion Coatings*

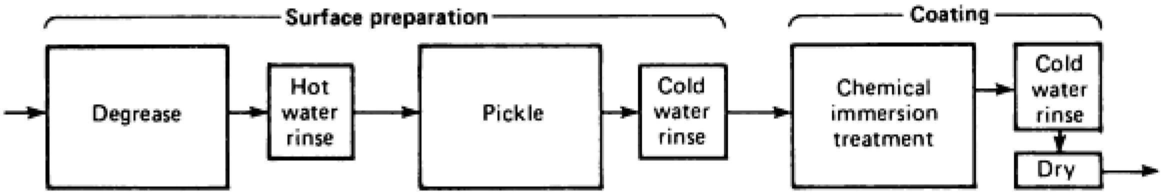
Chemical conversion coatings are used on titanium to improve lubricity by acting as a base for the retention of lubricants. Titanium has a severe tendency to gall, and lack of lubricity creates serious problems in applications involving the contact of moving parts in various forming operations (Ref 1).

Conversion coatings are applied by immersing the material in a tank containing the coating solution. Spraying and brushing are alternate methods of application. One coating bath consists of an aqueous solution of sodium orthophosphate, potassium fluoride, and hydrofluoric acid, which can be used with various constituent amounts, immersion times, and bath temperatures. The resultant coatings are composed primarily of titanium and potassium fluorides and phosphates. Several solutions are listed in Table 5. The flow chart in Fig. 12 indicates a processing sequence for the coating of titanium alloys.

**Table 5 Conversion coating solutions for titanium alloys**

| **Bath No.** | **Bath solution** | **Composition** | **Amount** | | **Temperature** | | **pH** | **Immersion time, min** |
|---|---|---|---|---|---|---|---|---|
| | | | **g/L** | **oz/gal** | **°C** | **°F** | | |
| 1 | Degreasing solution | $Na_3PO_4 \cdot 12H_2O$ | 50 | 6.5 | 85 | 185 | 5.1-5.2 | 10 |
| | | $KF \cdot 2H_2O$ | 20 | 2.6 | | | | |
| | | HF solution[(a)] | 11.5 | 1.5 | | | | |
| 2 | Pickling solution | $Na_3PO_4 \cdot 12H_2O$ | 50 | 6.5 | 27 | 81 | <1.0 | 1-2 |
| | | $KF \cdot 2H_2O$ | 20 | 2.6 | | | | |
| | | HF solution[(a)] | 26 | 3.4 | | | | |
| 3 | Chemical immersion solution | $Na_2B_4O_7 \cdot 10H_2O$ | 40 | 5.2 | 85 | 185 | 6.3-6.6 | 20 |
| | | $KF \cdot 2H_2O$ | 18 | 2.3 | | | | |

(a) Hydrofluoric acid, 50.3% by weight



| Type of solution | Composition | Operating temperature | | Cycle time, s |
|---|---|---|---|---|
| | | °C | °F | |
| Degreasing | Alkaline cleaner | Boiling point | | 60-120 |
| Pickling | 15% $HNO_3$, 1% HF in water | 23 | 75 | 10-60 |
| Chemical immersion | (a) | . . . | . . . | . . . |

(a) See Table 5.

**Fig. 12 Processing sequence used in the chemical coating of titanium alloys**

Cleanliness of the part before immersion is critical, and all preliminary cleaning and handling operations must be closely controlled for good results. Finger marks or residual grease on the surface of a part will interfere seriously with the coating process.

The appearance of the baths varies widely during the coating reaction, ranging from rapid bubbling to relative dormancy. Some coatings rub off when still wet; others are adherent. The various solutions produce coatings of approximately the same dark gray or black color.

The control of pH and immersion time is important. Dissolved titanium and the active fluoride ion make it impossible to use glass electrodes for pH measurements. Indicator paper and colorimetry are the most satisfactory methods for measuring in the degreasing and chemical immersion baths, which are held at 5 to 7 pH. The pickling bath is quite acid, and titrametric analysis offers the most practical method of control. When the bath is in the proper coating range, a 20 mL (0.70 fluid oz) sample in 100 mL (3.4 fluid oz) of water will neutralize 11.8 to 12.0 mL (0.4 to 0.41 fluid oz) of normal sodium hydroxide, using a phenolphthalein indicator.

Coating thickness depends on immersion time. In all three baths, a specific time is reached after which the coating weight remains essentially constant. In the fluoride-phosphate baths, a maximum coating weight is reached at some time before this equilibrium point. The maximum coating weight is obtained in about 2 min in the low-temperature bath and in about 10 min in the two other baths (Fig. 13).

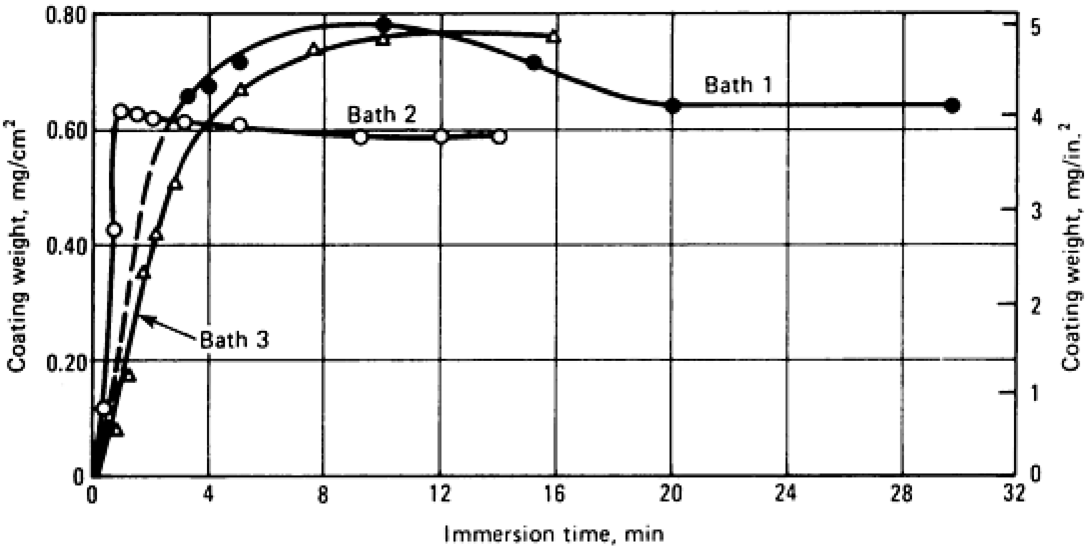


**Fig. 13 Weight of conversion coating as a function of immersion time. See Table 5.**

Results of extensive wire-drawing experiments (Table 6) illustrate the effectiveness of conversion coatings when used with various lubricants. Reciprocating wear tests showed that conversion coatings and oxidized surfaces provided some improvement in wear characteristics, but when conversion-coated samples were also oxidized, a marked improvement was noted. The conversion coating increases the oxidation rate of titanium at about 425 °C (800 °F) and may increase oxidation rates at temperatures up to 595 °C (1100 °F). The original coating is retained above the titanium oxide layers. High-speed rotary tests have indicated marked improvement in the wear characteristics of the metal after conversion coating and lubricating with one part of molybdenum disulfide and two parts of thermosetting eponphenolic resin.

**Table 6 Comparison of conversion coatings used with various lubricants in wiredrawing of titanium**

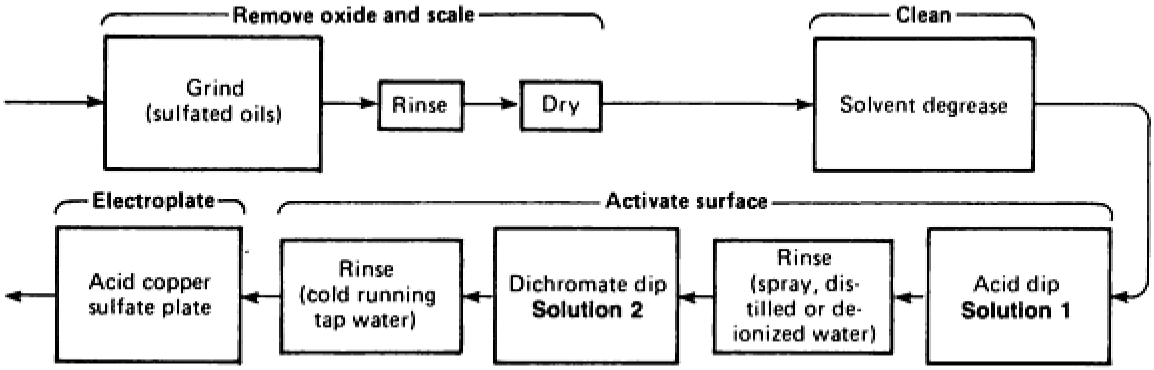
| **Coating** | **Drawing compound** | **Total reduction, %** | **No. of passes** | **No. of coats** | **Final condition** |
|---|---|---|---|---|---|
| Bare | Molybdenum disulfide with grease | . . . | 0 | . . . | Galled |
| Bare | Soapy wax | . . . | 0 | . . . | Galled |
| Degreasing bath | Molybdenum disulfide with grease | 85 | 8 | 2 | Smooth |
| Pickling bath | Molybdenum disulfide with grease | 94 | 17 | 7 | Smooth |
| Pickling bath | Soapy wax | 68 | 7 | 3 | Galled |
| Pickling bath[(a)] | Molybdenum disulfide with grease | 70 | 7 | 1 | Smooth |
| Chemical immersion bath | Lacquer molybdenum disulfide | 63 | 8 | 2 | Smooth |
| Chemical immersion bath | Molybdenum disulfide with grease | 63 | 8 | 3 | Smooth |

(a) Coating heated for 1 h at 425 °C (795 °F)

Conversion coatings are easily removable without excessive loss of metal by pickling in an aqueous solution containing 20% nitric acid and 2% hydrofluoric acid by weight.

## Plating

**Copper Plating.** The electrodeposition of copper on titanium and titanium alloys provides a basis for subsequent plating. A flow chart outlining the processing sequence for copper plating titanium is shown in Fig. 14. After cleaning and before plating, the surface of the titanium must be chemically activated by immersion in an acid dip and a dichromate dip to remove the passivating oxide film and obtain adequate adhesion of the plated coating. The compositions and operating temperatures of these activating solutions are shown in the table with Fig. 14.



| Solution No. | Type of solution(a) | Composition of solution |
|---|---|---|
| 1 | Acid dip | 60% HF, 1 vol, 69% $HNO_3$, 3 vol |
| 2 | Dichromate dip | $Na_2Cr_3O_7 \cdot 2H_2O$, 290 g/L (33 oz/gal), 60% HF, 55 g/L (6.2 oz/gal), $H_2O$, remainder(c) |

| Solution No. | Operating temperature | | Cycle time, s |
|---|---|---|---|
| | °C | °F | |
| 1 | Room temperature | | (b) |
| 2 | 82-100 | 180-212 | 20 |

(a) For preparation of Ti-6Al-4V and Ti-4Al-4Mn.

(b) Immerse to evolution of red fumes.

(c) Distilled or deionized water

**Fig. 14 Processing sequence for electroplating copper on titanium alloy parts**

Water purity is critical for the composition of activating solutions. Chemicals of technical grade are as effective as, and may be substituted for, chemically pure grades. In both the acid and dichromate baths, the hydrofluoric acid content is critical and must be carefully controlled.

After proper activation, titanium may be plated in a standard acid copper sulfate bath. The adhesion of the deposited copper is better than that of 60-40 solder to copper, and the deposit successfully withstands the heat of a soldering iron. The normal thickness of the plated deposit is about 25 μm (1 mil).

Copper-plated titanium wire is available commercially. The outstanding property of this material is the lubricity of its copper-plated surface. The wire can be drawn easily and can be threaded on rolls. Such wire has been used in applications that require electrical surface conductivity.

The titanium wire is plated continuously at a speed of about 60 m/min (200 ft/min) in a copper fluoborate acid bath at a current density of 7.5 to 12.5 $A/dm^2$ (75 to 125 $A/ft^2$). The final copper deposit is a thin flash coating. Higher current densities up to 150 $A/dm^2$ (1500 $A/ft^2$) have been tried, but if the copper coating is too thick, adhesion is poor.

**Platinum Plating.** Although titanium is not satisfactory as an anode material because an electrically resistant oxide film forms on its surface, application of a thin film of platinum to titanium results in a material with excellent electrochemical properties. Theoretically, the thinnest possible film is sufficient to give the highly desirable low overvoltage characteristics of platinum; furthermore, the film need not be continuous or free of defects to be effective.

The greatest immediate use for platinum-coated titanium is for anodes in the chlorine-caustic industry. Some horizontal-type chlorine cells use expanded metal anodes. From 1.3 to 2.5 μm (0.05 to 0.1 mil) of platinum is applied to the anode surface. Replating of the anodes may be required after about 2 years, depending on the operating conditions. The attrition rate for platinum appears to be about 0.6 g/tonne (0.5 g/ton) of chlorine.

Several platinum and electrode suppliers have developed reliable methods for platinum plating of titanium; most use proprietary solutions. A platinum diamino nitrite bath has been used successfully to apply platinum to titanium. In this and other procedures, certain precautionary steps are required to achieve adherent, uniform plates. The surface must be cleaned thoroughly and etched in hydrochloric or hydrofluoric acid to produce a roughened surface. Some procedures also involve a surface activating treatment just before plating. Immersion for 4 min in a solution of 895 mL (30 fluid oz) of glacial acetic acid containing 125 mL (4 fluid oz) of 52% hydrofluoric acid, followed by a prompt rinse, appears to be an effective activating treatment if performed immediately before plating. A postplating treatment, consisting of heating to 400 to 540 °C (750 to 1000 °F) for 10 to 60 min, stress relieves the plate and improves adhesion. This treatment can be done in an air atmosphere, and a light oxide film forms on unplated areas.

**Coatings for Emissivity.** Electrodeposits and sprayed coatings of gold on titanium are used to provide a heat-reflecting surface that reduces the temperature of the base metal. Gold-coated titanium has been used for jet engine components.

The gold coating is applied by spraying a gold-containing liquid on chemically clean titanium sheet. This is followed by a baking treatment. Normal coating thickness is about 25 μm (0.1 mil).

**Coatings for Wear Resistance.** Plating of hard chromium and electroless nickel are the most widely used on ferrous substrates for wear-resistant applications. However, in wear situations the thin oxide layer present on titanium alloys can make satisfactory adhesion of these coatings to titanium substrates difficult to achieve. Measures taken to overcome this problem include (Ref 46):

- In situ formation of alkali metal halogen complexes that protect from further oxidation and are later dissolved in acid plating solution
- Surface cleaning with an etchant, followed by rinsing in a water solution containing anions of cyanides, tartrate, citrate, and acetate complexing or chelating ions, followed by heat treatment
- Cathodic cleaning of the surface, activation in stannous chloride solution, coating in copper-reducing solution or gold chloride dip, electroplating copper, and copper striking from copper cyanide solution
- Chemical etching, immersion plating in a mixture of hydrofluoric acid, zinc sulfate, and sodium dichromate, followed by rinsing and conventional chromium plating
- Oxide removal in hydrofluoric acid/fluoboric acid solution, then transfer to a fluoborate plating solution to prevent reoxidation
- Immersion in nitric acid and sodium citrate solution; alkaline electroless nickel plate
- As above, abrade in hydrochloric acid, then Woods nickel strike, copper strike, chromium plate

These are some of the many procedures that have been attempted. An additional concern is that contact with acidic solutions allows hydrogen embrittlement of the titanium alloys.

Another approach to activation involves the dissolution of some microstructural constituents prior to plating. These are the aluminum-rich α-Ti phase and in Ti-6Al-4V, precipitated $Ti_2Cu$ in $Ti_2Cu$ and precipitated impurities at the grain boundaries of unalloyed titanium. Postplating heat treatment to 480 °C (895 °F) allows further improvements in adhesive strength, associated with diffusion of nickel into titanium and vice versa (Ref 47).

Heat treatment has been successfully used for enhancement of adhesion of hard chromium plating of titanium alloys. A 700 °C (1290 °F) temperature was used for the heat treatment, which resulted in a loss of hardness of the hard chromium, so a second chromium plating was applied to the initial, adherent, heat-treated chromium surface. Degradation in fatigue properties was ameliorated by the use of shot peening. Components treated using this procedure have included oil seal collars, racing car flywheels, bearing housings, and pistons (Ref 48).

### Physical Vapor Deposition

Physical vapor deposition (PVD) is a term that covers several processes (including evaporation, ion plating, and various forms of sputtering) to deposit metals, alloys, compounds, or metastable materials on a wide variety of substrates. The most successful engineering application is the coating of tool material substrates by reactive ion plating or reactive sputtering of TiN and related materials.

The PVD treatment of titanium alloy substrates has found limited application so far, but arc evaporation has been used to deposit 4.5 μm of TiN, and sputter deposition has been used to deposit 0.5 μm of TiN on gears for space mechanisms. The thinner coating suffered from problems of adhesion, whereas the thicker coating eventually failed through galling (Ref 31). Pin-on-disc wear tests have demonstrated reductions in coefficients of friction for TiN and TiC on titanium substrates against 440C stainless steel (Ref 49, 50). Electron beam source and arc source ion plating have been used to produce 1 to 2 μm of TiN on the surface of Ti-6Al-4V.

The failure of conventionally applied TiN coatings on titanium alloy substrates under load-bearing wear situations was evaluated and modifications were made to produce a better PVD TiN process. Initially, a coating produced using an electron beam evaporative source was found to perform significantly better than an arc source coating in lubricated Falex tests against steel jaws. The poor performance of the arc source coating was caused by removal of small splats of titanium from the coating and the introduction of titanium into the wear couple. This problem was negated by lightly polishing the arc source coating before testing. Survival of the electron beam source coating at higher contact stresses was achieved by an improved sputtering process at a higher-than-normal temperature (700 °C vs. 450 °C, or 1290 °F vs. 840 °F) before evaporation of the titanium component of the coating commenced (Ref 51, 52). This process is tradenamed Nitron and is provided by Tecvac UK, Ltd. The improvements in load-bearing wear situations of the modified process is demonstrated by the Falex wear test data shown in Fig. 15. Engineering components routinely coated with TiN include brake pistons and other components for racing cars, aerospace components for which titanium is used because of its strength-to-weight ratio, and pump parts and valve components for oil, chemical, and food industries for which titanium is used because of its corrosion resistance.

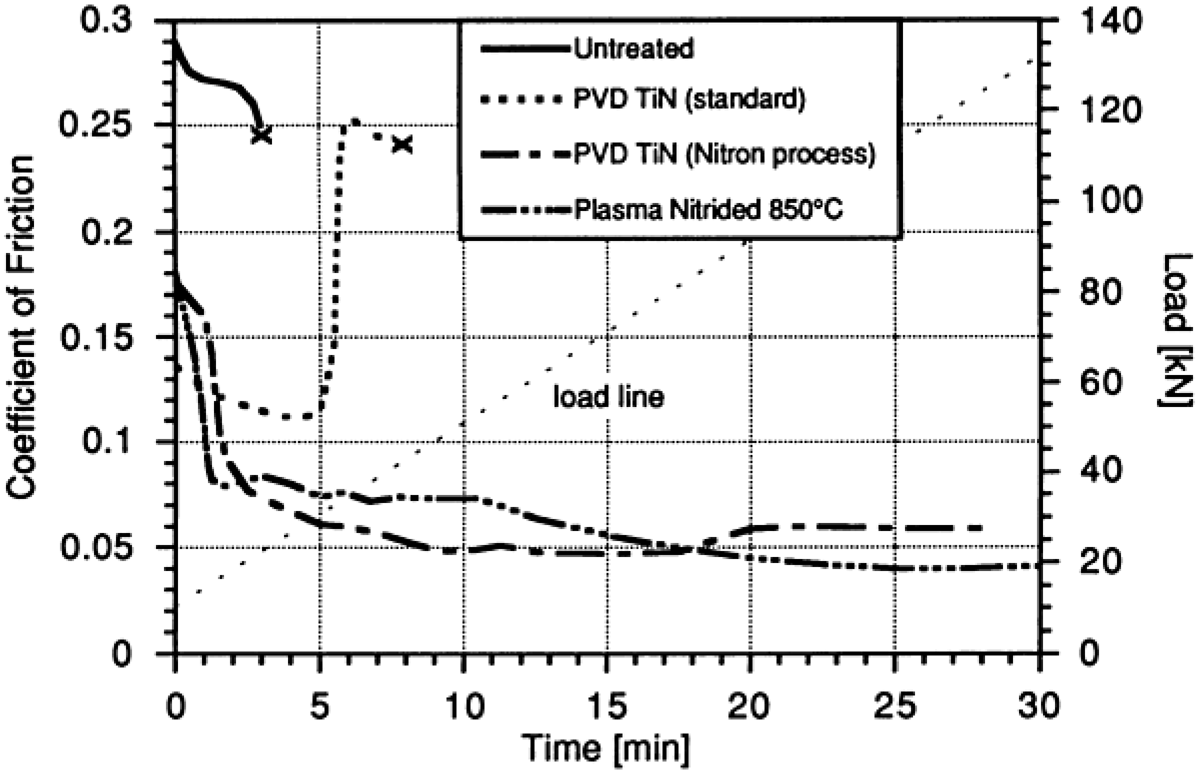


**Fig. 15 Results from lubricated Falex wear tests for untreated and plasma-processed Ti-6Al-4V; carbon steel jaws. Source: Ref 16**

One very active area of surface engineering research, mentioned above in the discussion of ion implantation, is in the area of surgical implants, where mechanical and chemical properties make titanium a useful material but its tribological properties require improvement. TiN deposition has been widely researched and is routinely employed by commercial coaters. Surface roughness of the component is a critical parameter in this type of wear couple, and polishing is usually required after TiN deposition (Ref 53).

In the same field of application (surface engineering of prosthetics), amorphous diamond-like carbon (DLC or ADLC) is stimulating interest. Optimization of the wide range of properties available from these coatings is essential, and, as in DLC coating of other substrates, adhesion problems must be overcome. The very low coefficients of friction and wear rates exhibited by these coatings are very promising, and the coatings have performed well in reciprocating abrasion wear tests against bone cement in Ringer's solution, as have TiN coating and zirconia (Ref 53) (Table 7).

**Table 7 Results of polymethyl methacrylate abrasion tests of various metals and ceramic coatings following $10^6$ wear cycles**

| **Material** | **Coating** | **Surface hardness, DPH** | **Initial $R_a$, µm** | **Final $R_a$, µm** | **Wear track depth, µm** |
|---|---|---|---|---|---|
| Ti-6Al-4V | . . . | 330 | 0.06 | 4.15 | 27.5 |
| Ti-6Al-4V | $N^+$ implantation | 700 | 0.05 | 3.30 | 30.5 |
| Co-Cr-Mo | . . . | 400 | 0.05 | 0.13 | 0.08 |

| | | | | | |
|---|---|---|---|---|---|
| 316L S.S. | . . . | 230 | 0.06 | 0.80 | 48.0 |
| Ti-6Al-4V | TiN | 1630 | 0.05 | 0.08 | 0.50 |
| Ti-6Al-4V | ADLC | 2850 | 0.02 | 0.16(a) | 0.3(a) |
| Zr | $ZrO_2$ | 1430 | 0.02 | 0.02(a) | 0(a) |
| $ZrO_2$ | . . . | 1430 | 0.02 | 0.02(a) | 0(a) |

Source: Ref 53

(a) $10^7$ abrasion cycles.

## *Sprayed Coatings*

Sprayed coatings may be applied to titanium alloy substrates as they are to many other materials; no special pretreatment is required for titanium-base materials. Sprayed coatings are mainly deposited using plasma spraying, but detonation gun, high-velocity oxyfuel (HVOF), and vacuum plasma spraying are also used. There is a vast range of materials that can be sprayed onto titanium substrates if so desired.

The main function of sprayed coatings on titanium is for wear protection in aerospace engines and other gas turbine applications. In the low-pressure compressor, titanium alloy midspan support faces are sprayed with tungsten carbide-cobalt for protection against fretting wear. Wear protection is also afforded to blade roots, location lugs and fan dampers by means of a "soft" coating (Cu-Ni-In) to protect the titanium components (Ref 54). The coating is very dense, has a very low oxide content, and resists fretting wear. The coating wears at a predetermined rate and the components can be removed and the coating resprayed after an establisher service period. The value of such a soft coating to combat fretting wear of titanium alloys has been demonstrated in laboratory tests in which a copper-base electroplated deposit outperformed many other surface treatments (Ref 55). In the intermediate-pressure compressor, abradable coatings are used for a variety of seals. These coatings, blends of aluminum-silicon and polyester powders, are worn away by, for example, blades. A good seal is maintained by partial wear of the coating and essentially no blade-tip wear occurs. Plasma-sprayed anti-fretting-wear coatings for titanium alloys, usually of tungsten carbide-cobalt, are also widely used.

Another major use of sprayed coatings is in repair of components. Some large, very expensive titanium components undergoing final machining operations are damaged, chiefly due to tool wear. Rather than scrap such components, plasma-sprayed coatings of Ni-Al-Mo are used to rebuild critical volumes. When titanium alloying processing vessels used in the production of dry-cell batteries undergo corrosion, they are repaired using plasma-sprayed tantalum.

Returning to the area of prosthetics, titanium implants are sprayed with hydroxyapatite (HAP). This compound is the ceramic constituent of bone, and when it is deposited with appropriate amounts of porosity and surface roughness, bone growth can occur and cementation between the bone and the HAP coating results. This material is commonly sprayed onto femoral stems, dental implants, knee implants, and acetabular caps (wherever a titanium prosthesis comes into contact with bone). The other widely used sprayed deposit in this area of application is titanium itself. Again, appropriate surface roughness and porosity are important because, although not a constituent of bone, titanium is biocompatible and does not discourage bone growth. Therefore, when a successful implant is carried out, the bone will grow, resulting in mechanical keying of the new bone and the porous titanium.

## *Other Coatings*

**Anodizing** of titanium and titanium alloys enhances the wear resistance of the material. It produces layers of $TiO_2$ less than 100 nm thick. Such coatings are unable to withstand more than relatively light loads, but they do produce significant improvements over untreated titanium. The process is frequently used on titanium fasteners and can be considered the basic minimum treatment for any titanium component subjected to a rubbing action. The range of interference colors produced by anodizing at different voltages is also used to obtain decorative effects on titanium jewelry and other items.

**Sol-gel coatings** on titanium alloys are being studied for use as oxidation protection surface treatments. A range of surface coatings on a $Ti_3Al$-Nb-based alloy, including sputtered oxides of magnesium, yttrium, zirconium, and hafnium, sputtered fluorides of calcium and yttrium, and 1 μm thick layers of silicon, aluminum, and boron oxides were applied both by sputtering and from sols, and calcium, sodium, and phosphorus oxides were also applied from sols (Ref 56). A reaction barrier undercoat expected to be stable with the titanium alloy was combined with oxidation barrier topcoats. Weight gains for various systems after 1 h at 982 °C (1800 °F) in air are shown in Fig. 16. The measured values for weight gain are indicative of the relative film integrity after exposure; sputtered coatings were often cracked. A sputtered yttria coating was improved by dipping in boric acid, which, during heating, forms boron oxide, which was believed to fill the cracks in the yttria layer, consequently improving the protection achieved.

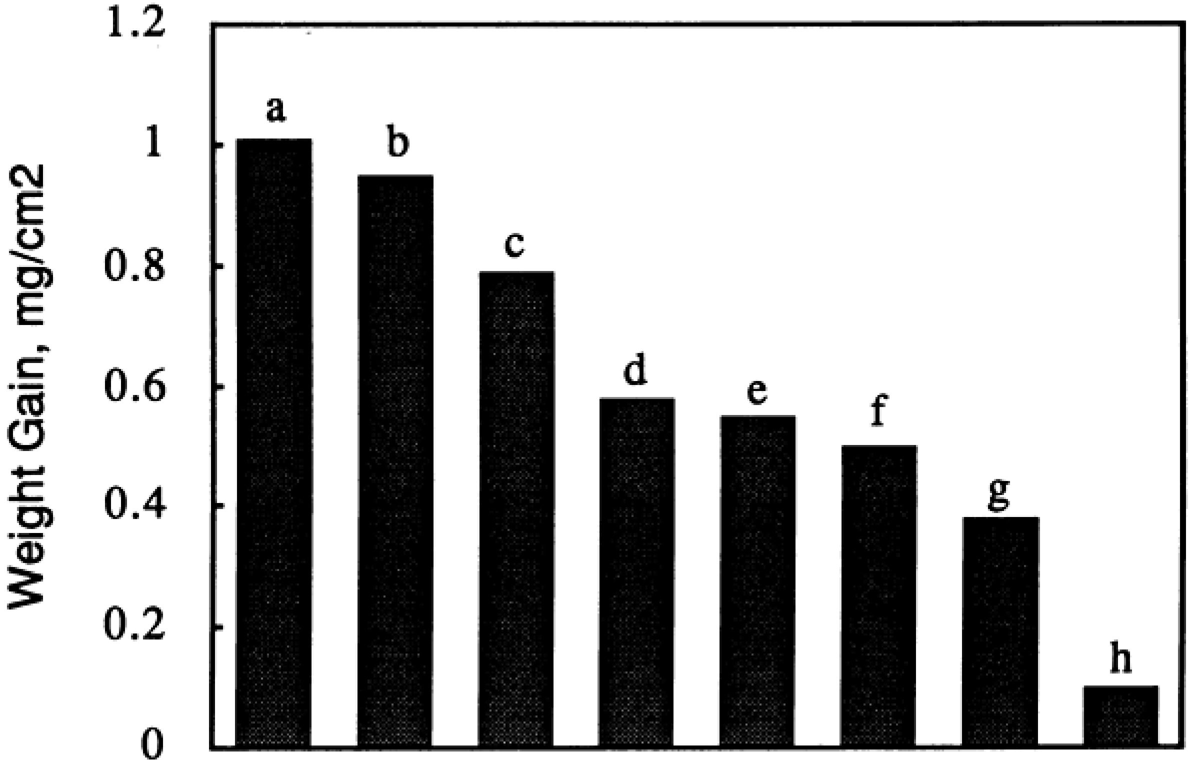


**Fig. 16 Weight gain for 1 h at 982 °C (1800 °F) in air for (a) uncoated alloy, (b) sputtered yttria, (c) boron oxide from solution, (d) sodium aluminum borophosphate from solution, (e) calcium phosphate from solution, (f) calcium aluminate from solution, (g) calcium aluminophosphate from solution, and (h) magnesium silicophosphate from sol-gel. Source: Ref 56**

A multilayered system involving 1 to 2 μm of reaction barrier coating is applied (either barium titanate or yttrium-stabilized zirconia), over which is a diffusion-barrier coating containing magnesium phosphate and silica glasses. In cyclic oxidation tests to 980 °C (1800 °F), the performance of this coating equaled and exceeded that of other, thicker reaction coatings (Ref 57).

**Chemical vapor deposition (CVD)** coatings are seldom applied to titanium-base substrates. However, some work has been done, again with the object of improving oxidation resistance (Ref 58). Sputtered silica and CVD silicate layers, both with and without aluminum base coats, have been tested for relatively low temperatures. The best results were obtained from the combined aluminum coating, which diffuses to form $TiAl_3$ and sputtered silica.

Another type of coating for γ-titanium aluminides is based on the Ti-Cr-Al system, within the composition range for which an alumina film is formed on the surface in elevated-temperature oxidation. Methods of application used are slurry fusion, low-pressure plasma spraying, HVOF spraying, and sputtering. Good oxidation behavior has been noted, but significant interdiffusion of the coating and the substrate occurs at the oxidation temperature (Ref 59).

## *Contemporary Developments*

**Plasma immersion ion implantation ($PI^3$)** has been developed at the Australian Nuclear Science and Technology Organisation. It is an innovative process that combines and exploits the advantages of the established techniques of both ion implantation and plasma nitriding to produce surface-modified components with optimum performance characteristics. As such, it offers the potential expansion of the surface engineering market to applications that are prohibitively expensive with current ion-beam technology (Ref 60).

Specifically, $PI^3$ involves surrounding the sample by the ion source, in the form of a radio-frequency generated plasma. This enables a steady-state sheath to form around the target. A series of short, high-voltage, negative pulses are then applied directly to the workpiece, causing ions to be accelerated from the plasma to bombard the target from all sides simultaneously at approximately normal incidence. Therefore the line-of-sight restriction of conventional ion implantation is eased and the sputtering effects are reduced, allowing uniform coverage to be achieved on complex shapes at a lower unit cost.

The technology results in a modified layer of much greater depth than in conventional ion implantation. As well as implanting ions into the first 0.2 μm to obtain a surface layer with unique tribological properties, there is the additional possibility at elevated temperatures of producing a strengthened diffusion-enhanced "tail" of up to 100 μm thickness that supports the implanted layer.

Work on the effects of $PI^3$ on titanium alloys has so far been limited to studies on the Ti-6Al-4V alloy. Samples have been treated in a nitrogen atmosphere at between 350 °C and 550 °C (660 and 1020 °F), for either 3 or 5 h. Preliminary investigations indicate that under these conditions, considerable increases in surface hardness can be achieved. At temperatures of 500 °C (930 °F) and above, the surface Knoop hardness of Ti-6Al-4V increases by 150 to 170% at 25 g load. Furthermore, samples treated at all temperatures in the range were hardened to some degree.

These findings were reflected in significant improvements in the wear resistance of the alloy. Pin-on-disc wear testing has been carried out at low loads (2 N) and in the presence of ethanol. Samples treated at 350 and 450 °C (660 and 840 °F) showed some decrease in wear volume, compared to the untreated material. However, the Ti-6Al-4V disc that had been treated at 500 °C (1020 °F) for 5 h exhibited no measurable wear after the test had been completed.

One drawback of $PI^3$ is its effect on the surface roughness of samples during treatment. Unlike conventional ion implantation, the $PI^3$ process results in significant increases in surface roughness that are greater as temperature and time of treatment are increased.

**Plasma source ion implantation (PSII)** was developed simultaneously at the University of Wisconsin. Whereas the $PI^3$ unit has a radio-frequency generated plasma, the PSII process employs a filament discharge (direct current source) that ionizes the gas.

Research using titanium alloy substrates has concentrated on implantation at ambient temperatures (i.e., not greater than 100 °C), with nitrogen implanted at 50 keV to a fluence of $3 \times 10^{17}$ atoms/cm$^2$, to produce a peak concentration of nitrogen of about 40 to 50% at the surface and a treated depth in the region of 2000 to 3000 Å.

Transmission electron microscopic analyses of the implanted layers show fine precipitates of TiN dispersed throughout the structure. However, in more recent work, comparing x-ray electron dispersive spectra for implanted and unimplanted Ti-6Al-4V, it has been concluded that this is more realistically represented by Ti(V)N, because the vanadium is thought to substitute for the titanium. Pin-on-disc wear testing has been carried out under extremely low loads (0.1 to 0.2 N) in both corrosive and lubricated conditions. Again, significant improvements in wear resistance have been exhibited by the surface-modified Ti-6Al-4V, comparable to those achieved by conventional ion implantation (Ref 61, 62).

**Duplex Treatments.** Plasma nitriding or modified PVD TiN coating provides a titanium surface with improved resistance to sliding contact under moderately high contact stresses. However, neither process is capable of providing a sufficiently deep case for use in bearings and gears. Deep hardened layers provided by laser or electron beam surface alloying are able to withstand the high stresses encountered in these applications but do not resist sliding motion.

Some work has been carried out to combine deep hardening with a subsequent surface treatment to enable the material to withstand the action of high load in mixed rolling/sliding and, in particular, to resist scuffing failure. Electron beam surface alloying of Ti-6Al-4V with silicon and carbon has been followed by surface grinding and then plasma nitriding.

Samples tested using a minidisc scuffing test with 54% slip (slide-roll ratio of 0.37) and a contact pressure of 1.3 GPa (Ref 16) demonstrated a dramatic improvement in scuffing resistance for the duplex-treated sample over and above that of the electron beam SiC-alloyed material alone. No visible signs of wear, other than a slightly polished appearance, resulted on the duplex-treated sample, whereas there was severe scoring on the surface-alloyed treated sample. The combination of a deep hardened case, able to resist high contact stresses, with a plasma-nitriding treatment to alter the chemical as well as physical and mechanical nature of the surface is capable of providing titanium alloys with a surface treatment of great potential value under severe wear conditions. The improvements to Ti-6Al-4V substrates produced by these surface engineering processes are summarized in Fig. 17.

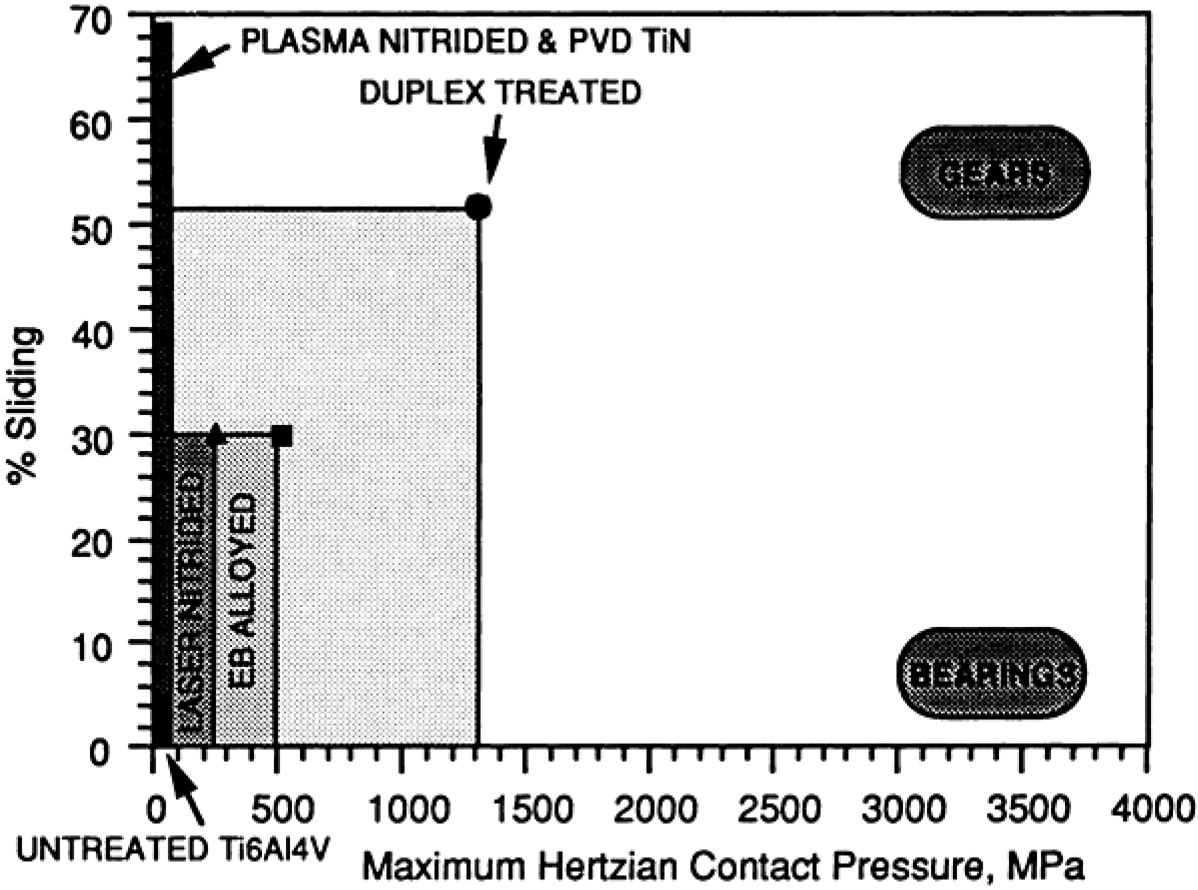


**Fig. 17 Survival of wear tests described by percentage sliding and contact stresses for surface-engineered Ti-6Al-4V. Source: Ref 16**

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# Surface Engineering of Zirconium and Hafnium

**Revised by R. Terrence Webster, Metallurgical Consultant**

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## Introduction

ZIRCONIUM AND HAFNIUM SURFACES may require cleaning and finishing for reasons such as preparation for joining, heat treatment, plating, forming, and producing final surface finishes. Special surface preparation and cleaning is generally not required for corrosion resistance because the naturally formed surface oxide protects the metal regardless of surface condition. They are difficult to electroplate via traditional methods, but plating can be accomplished using special alternative processes.

## Surface Soil Removal

Grease, oil, and lubricants used in machine forming and other fabricating operations may be removed by a number of techniques. Alkaline or emulsion cleaners used in simple soak tanks or with ultrasonic cleaning, acetone or trichloroethylene solvent washing, or vapor degreasing and detergents are all widely used. For light soil removal, hand wiping is done with solvents such as acetone, alcohol, trichloroethylene, or various alternatives to trichloroethylene (which is not environmentally attractive). Electrolytic alkaline cleaning is also used. In the electrolytic system, the work can be either anodic or cathodic polarity, provided the voltage and current can be controlled to avoid anodizing or spark discharge, and subsequent pitting. Removing these soils is essential before acid etching to provide uniform acid attack. The soils must be removed before heat treatment and joining to prevent contamination and consequent loss of ductility.

## Blast Cleaning

Mechanical descaling methods such as sandblasting, shot blasting, and vapor blasting are used to remove hot work scales and hard lubricants from zirconium and hafnium surfaces. Aluminum oxide, silicon carbide, silica sand, and steel grit are satisfactory media for mechanical descaling. Periodic replacement of used media may be required to avoid excessive working of the surfaces by dull particulates. Roughening of exposed surface areas occurs from grit or shot impingement, depending on the grit size used. Any abrasive or shot blast cleaning may induce residual compressive stresses and warpage in the surface of the material, particularly thin sheet. Warpage also may occur in sections that are subsequently chemical milled or contour machined.

Blast cleaning is not intended to eliminate pickling procedures. Abrasive blasting does not remove surface layers contaminated with interstitial elements such as carbon, oxygen, and nitrogen. Generally blast cleaning is followed by a pickling step to ensure complete removal of surface contamination and cold-worked layer and to produce a smooth, bright finish.

## Chemical Descaling

Some scale, as well as forming lubricants, can be removed by proprietary water solutions of strong caustic compounds, or by the use of molten alkaline-based salt baths. The salt baths operate at temperatures of 650 to 705 °C (1200 to 1300 °F) and must be used carefully according to manufacturer instructions. Salt bath descaling is accomplished by a series of cycles through the salt, a water rinse, and a sulfuric acid bath to remove scale before final pickling.

## Pickling or Etching

Metal removal by a chemical bath of nitric-hydrofluoric acid is used most commonly, although other baths have been used. The usual bath for zirconium, Zircaloys, and hafnium is composed of 25 to 50% nitric acid, 70 vol%; 2 to 5% hydrofluoric acid, 49 vol%; and the remainder water. The acid bath for zirconium-niobium alloys consists of 28 to 32% sulfuric acid, specific gravity 1.84; 28 to 32% nitric acid; 5 to 10% hydrofluoric acid; and the remainder water.

Bath temperatures should not exceed 65 °C (150 °F) during pickling, to help prevent excessive pickup of the hydrogen that forms during the pickling. Zirconium and hafnium are very sensitive to small amounts of hydrogen, which lowers their fracture toughness markedly.

To help prevent formation of insoluble fluoride surface stain, a stop bath consisting of 70% $HNO_3$, and 30% $H_2O$ can be used. The article is pickled in the nitric-hydrofluoric acid bath and is immediately dipped in the stop bath. Thorough rinsing in cold water follows the stop bath.

The hydrofluoric acid attacks the zirconium and hafnium, and the nitric acid oxidizes the hydrogen formed by the reaction and prevents its absorption by the metal. The ratio of nitric to hydrofluoric acid should not be less than 10 to 1 normality. Except for the zirconium-niobium alloys, the rate of metal removal is linear with hydrofluoric acid concentration and doubles as the bath temperature rises from 43 to 71 °C (110 to 160 °F).

Material etched in the nitric-hydrofluoric acid bath must be rinsed quickly and completely with flowing water, to prevent an insoluble fluoride surface stain from forming. This stain is extremely detrimental to corrosion resistance in hot water and steam environments of nuclear reactors. Extreme precautions to ensure a rapid and effective rinse are required for this service. A rapid temperature rise during the transfer to the rinse water can lead to redeposition of the etching product.

## Anodizing and Autoclaving

Zirconium and hafnium oxidize readily in air and aqueous solution, but the tenacious oxide layer generally protects the metal from further oxidation. Methods to produce a dense oxide layer to serve as a protective coating for zirconium and hafnium are anodizing and autoclaving. Before anodizing, the article should be cleaned in a 50% nitric acid/50% water solution and then in water with the assistance of ultrasonic vibration.

The anodizing solution used for zirconium and hafnium consists of:

- 45.4 vol% absolute ethanol
- 26.5 vol% water
- 15.2 vol% glycerine
- 7.6 vol% lactic acid, 85% concentration
- 3.8 vol% phosphoric acid, 85% concentration
- 1.5 vol% citric acid

Voltage during anodization is raised slowly from about 20 V to 200 to 300 V. A rapid rise in voltage may overload the amperage and/or power capabilities of the equipment. A wide variety of anodization films with different thicknesses and colors can be produced. Voltage governs the thickness of the oxide layer, which determines the color (first gold, then red, green, blue, and black with increasing thickness). This technique can be employed to decoratively color zirconium and hafnium alloys and to enhance metallographically prepared surfaces for light microscope observation. See P.E. Danielson's articles on color metallography and the metallography of zirconium, hafnium, and titanium in Volume 9 of the *ASM Handbook.*

Caution should be exercised during the anodizing process, especially when the high voltage is reached. Operators should wear rubber gloves. Rubber floor mats are also advisable.

Autoclaving is a standard test for zirconium and hafnium for the nuclear industry. Testing is conducted to determine proper processing history and/or surface cleanliness for critical applications. Specific (surface area basis) weight gain and/or visual standards are used to determine compliance. The test for zirconium and Zircaloys is carried out at 400 °C (750 °F) under a steam pressure of 10 MPa (1.5 ksi) for 1 to 14 days. The test for hafnium is carried out at 360 °C (680 °F) under a water pressure of 18.6 MPa (2.7 ksi).

Autoclaving procedure may be used to produce a dense oxide coating for zirconium and hafnium. The water used should have a pH value of 6 to 8, with a resistivity of $1 \times 10^4$ Ω· m ($1 \times 10^6$ Ω· cm) minimum when corrected to 22 °C (72 °F). The autoclave should be constructed of type 300 series stainless steel, and should be fitted with a pressure gage, pressure records, thermocouples, a safety blowout assembly, and a high-pressure venting valve. In preparation for anodizing, the article should be detergent cleaned, followed by solvent cleaning with reagent grade acetone, trichloroethylene, or perchloroethylene. The article should be cleaned further by acid pickling as described in a previous section. Upon completion of the designated pickling time, the article should be immediately and rapidly transferred to the first water rinse tank with a temperature maintained at 27 °C (81 °F) and a flow rate of at least two bath changes per minute. It should then be transferred to the second water rinse tank at the same temperature for at least 15 min. After this, the article should be transferred to the third rinse tank containing water at 80 °C (175 °F) minimum. All rinse water, especially in the third rinse tank, should have a pH of 7 (±1) and a resistivity of 5000 Ω· m (500,000 Ω· cm) minimum. After rinsing, the article should be dried by a method that prevents water marks, stains, or contamination on the surfaces of the article, by wiping with a clean, lint-free cloth, and blowing with dry air. Autoclaved zirconium and its alloys show a dense, shiny black coating of oxide, while hafnium shows a dense, iridescent coating of oxide, the color of which ranges from purple or blue to gold.

**Oxide Layer for Low Friction Surfaces.** A thick, dense, and adherent oxide layer can be produced on zirconium and hafnium by heat treatment. The resultant oxide layer will have low friction resistance and will resist galling and seizing, while retaining excellent corrosion resistance. For small precision-shaped components, compensation must be made for oxide buildup as well as stress-induced changes (see "Selected References" for citations on oxide growth).

The treatment consists of cleaning the surface, followed by heating for 4 to 6 h at 550 °C (1022 °F) in air. The resultant oxide layer will be approximately 5 μm (0.0002 in.). Thicker oxide films can be produced by heating in a controlled atmosphere of inert gas and oxygen in an air furnace, a fluidized bed furnace, or molten equimolar NaCl and KCl fused salts.

## Polishing and Buffing

The polishing and buffing of zirconium is accomplished with the same methods used for titanium. Polishing is frequently done wet, using mineral oil lubricants and coolants. Silicon carbide abrasive cloth belts have been effective. It is common to polish in two or more steps, using a coarser grit initially, such as 60 or 80, to remove gross surface roughness, followed by polishing with 120 or 150 grit to provide a smooth finish. Zirconium and titanium tend to wear the sharp edges of the abrasive particles and to load the belts more rapidly than steel. Frequent belt changes are required for effective cutting. A good flow of coolant improves polishing and extends the life of the abrasives.

Dry polishing is more appropriate than wet for some applications. For these operations, belts or cloth wheels with silicon carbide abrasive may be used. Soaps and proprietary compounds may be applied to the belts to improve polishing and to extend belt life. Abrasive belt materials that incorporate solid stearate lubricants offer improved results for dry polishing operations. *Caution: Accumulation of zirconium and titanium fines can be pyrophoric.*

Fine polishing of zirconium and titanium articles for extremely smooth finishes requires several progressive polishing steps with finer abrasives until pumice or rouge types of abrasive are applied. With the softer grades, such as unalloyed titanium or zirconium material, fine polishing requires more time and care to prevent scratching. Harder grades can be polished more readily to a surface of high reflectivity. If a matte finish is desired, wet blasting with a fine slurry may be used after initial polishing.

The purpose of buffing is to improve the surface appearance of the metal and to produce a smooth, tight surface. Buffing is used as a final finishing operation and is particularly adaptable to finishing a localized area of a part. Parts such as body prostheses, pacemakers, and heart valves require a highly buffed, tight surface to prevent entrapment of particles. Close-fitting parts for equipment, such as the modern guidance systems, and electronics applications require highly polished surfaces obtained by buffing. In addition, sheet sizes too large to be processed by other abrasive finishing methods, such as mass finishing or wet blasting, can be economically processed by buffing.

The principal limitations of buffing are distortion, caused by the inducement of localized stress; surface burning, resulting from prolonged dwell of the buff; an inability to process inner or restricted surfaces; and the feathering of holes and edges. Proper care of the buffing wheel is essential. Buffing with insufficient compound or a loaded wheel produces burning or distortion of the part. After buffing, no further cleaning of parts is required except degreasing to remove the buffing compound. Further information may be found in the Section "Finishing Methods" in this Volume.

## Vapor Phase Nitriding

Other surface modification techniques employ reactive gases such as nitrogen to form a surface layer that diffuses into the surface under temperature. The nitrogen must be extremely pure (less than 100 ppm oxygen with a dew point of -45 °C, or -50 °F). The part to be surface treated is heated in nitrogen, which forms a substoichiometric nitride layer on the surface. Depending on temperature and time, the nitride layer will form to a depth of several thousand angstroms. The coating thus produced is a light gold color for zirconium and its alloys. Typical temperatures are in the range of 850 to 1050 °C (1560 to 1920 °F) with times ranging from several minutes to 30 min at temperature. The operation may be performed in a vacuum furnace that is compatible with the introduction of nitrogen.

High-temperature vapor-phase synthesis (HVS) is used to form reactive layers of carbides, nitrides, and carbonitrides on the surface of zirconium, hafnium, tantalum, niobium, and their alloys. The ceramic surfaces of HVS-processed materials provide both wear and corrosion resistance, protecting the unreacted interior of the host material. The properties of the reacted material can be tailored to meet the requirements of a range of applications. In general, however, the materials have relatively high thermal conductivities and, unlike conventional oxide ceramics, are not particularly susceptible to thermal shock.

Metal-refining applications of HVS-processed materials are particularly promising. Most molten metals do not wet these ceramics, and they also resist both abrasion and corrosion. Other potential applications include transfer tubes for routing abrasive or reactive chemicals and gases, at high or low temperatures, and components of high-strength, high-stiffness structures. Property and performance testing are currently in progress.

## Electroplating

Hafnium, zirconium, and Zircaloys (zirconium-tin alloys), are difficult to coat with an adherent electroplate because they form a tenacious oxide film in air and aqueous solutions. There are alternative processes for plating nickel on zirconium.

In the first process, the zirconium article is etched in either an ammonium bifluoride sulfuric acid, 45 g/L (6 oz/gal) of ammonium bifluoride + 0.5 mL (0.02 fluid oz) of sulfuric acid aqueous solution for 1 min at 22 °C (72 °F), or an ammonium bifluoride solution, 45 g/L (6 oz/gal) of ammonium bifluoride aqueous solution for 3 min at 22 °C (72 °F). For nickel plating, the electrolyte consists of 81 g/L (11 oz/gal) of nickel as in $Ni(NH_2SO_3)_2$, 1.0 g/L (0.13 oz/gal) of nickel chloride, and 40 g/L (5.2 oz/gal) of boric acid in an aqueous solution, with an ideal surface tension of 0.038 N/m (0.003 lb/ft). The pH value should be kept at 3.8 to 4.0, with the current density of 2.15 $A/dm^2$ (21.5 $A/ft^2$), and the temperature at 50 °C (120 °F). Preheating is required to improve bond strength. Carry the treatment at 700 °C (1300 °F) in vacuum for 1 h with the plated article placed in a molybdenum alloy, TZM ring, or constrained case. Because the coefficient of thermal expansion for molybdenum is lower than that of zirconium and nickel, it provides a stress on the plating as the assembly is heated.

In the alternate process, the zirconium article is etched with an aged aqueous activating solution of 10 to 20 g/L (1.3 to 2.6 oz/gal) of ammonium bifluoride and 0.75 to 2.0 g/L (0.1 to 0.26 oz/gal) of sulfuric acid, for about 1 min at ambient temperature. The solution is aged by immersion of a piece of pickled zirconium for at least 10 min at ambient temperature. The next step is to remove any loosely adhering film or smut formed on the article in the activating step. This can be accomplished in one of the following methods:

- Using a chemical solution which is either an aqueous solution of 2 to 10 vol% fluoboric acid or a hydrofluosilic acid of a similar concentration. The solution is maintained at about 25 °C (77 °F), and the article is immersed in the solution for about 1 min
- Submerging the article in water and applying ultrasonic energy of 20,000 to 30,000 cycles/s for 1 to 2 min
- Swabbing the loosely adhering film from the article by rubbing the surface with cotton, paper, or a brush

An optional step of rinsing the article in water can be practiced by using deionized water to free the article of any residual traces of the material used in previous steps.

Preferred metals to be deposited on the article include copper, nickel, and chromium. The chemical compositions and conditions used for the different electrolytes are shown in Table 1. Similar procedures can be used for electroplating metals on hafnium, although information in this respect is sparse. Some work has been done on advanced surface treatments for the purpose of enhanced corrosion resistance, appearance, resistance to hydrogen uptake, texture control, and other features. (See, for example, selected references by Sabol and McDonald.)

**Table 1 Electrolyte compositions and conditions for plating on zirconium**

| **Electrolyte** | **Composition** | **Amount** | | **Temperature** | | **Current density** | | **Heat treatment**[(a)] | |
|---|---|---|---|---|---|---|---|---|---|
| | | **g/L** | **oz/gal** | **°C** | **°F** | **$A/dm^2$** | **$A/ft^2$** | **°C** | **°F** |
| Copper | $CuSO_4·5H_2O$ | 150-250 | 20-33 | 32-42 | 90-110 | 16-22 | 160-220 | 149-204[(b)] | 300-400[(b)] |
| | $H_2SO_4$ | 45-110 | 6-14 | . . . | . . . | . . . | . . . | . . . | . . . |
| | $NH_2·CS·NH_2O$ | 0.002-0.005 | 0.0003-0.0007 | . . . | . . . | . . . | . . . | . . . | . . . |
| | $H_2O$ | bal | bal | . . . | . . . | . . . | . . . | . . . | . . . |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Chromium | $CrO_3$ | 200-300 | 26-39 | 30-50 | 86-120 | 10-20 | 100-200 | . . . | . . . |
| | $H_2SO_4$ | 2-3 | 0.3-0.4 | . . . | . . . | . . . | . . . | . . . | . . . |
| | $H_2O$ | bal | bal | . . . | . . . | . . . | . . . | . . . | . . . |
| Nickel | $NiSO_4 \cdot 6H_2O$ | 320-340 | 42-44 | 45-65 | 115-150 | 2.1-10 | 21-100 | 700(c) | 1290(c) |
| | $NiCl_2 \cdot 6H_2O$ | 40-50 | 5-7 | . . . | . . . | . . . | . . . | . . . | . . . |
| | $H_3BO_3$ | 36-40 | 4.6-5.2 | . . . | . . . | . . . | . . . | . . . | . . . |
| | $H_2O$ | bal | bal | . . . | . . . | . . . | . . . | . . . | . . . |

(a) After plating.

(b) 3 h.

(c) 1 h

## Surface Engineering of Refractory Metals and Alloys

Revised by John A. Shields, Jr., Climax Specialty Metals

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### Introduction

THE REFRACTORY METALS include niobium (also known as columbium), tantalum, molybdenum, tungsten, and rhenium. With the exception of two of the platinum-group metals, osmium and iridium, they have the highest melting temperatures and lowest vapor pressures of all metals. The refractory metals are readily degraded by oxidizing environments at moderately low temperatures, a property that has restricted the applicability of the metals to low-temperature or nonoxidizing high-temperature environments. Protective coating systems have been developed, mostly for niobium alloys, to permit their use in high-temperature oxidizing aerospace applications.

Refractory metals at one time were limited to use in lamp filaments, electron tube grids, heating elements, and electrical contacts; however, they have since found widespread application in the aerospace electronics, nuclear and high-energy physics, and chemical process industries. Each of the refractory metals, with the exception of rhenium, is consumed in quantities exceeding 900 Mg (1000 tons) annually on a worldwide basis.

This article describes surface cleaning, finishing, and coating methods used with molybdenum, tungsten, tantalum, and niobium. Because of similarities in processes and applications, molybdenum and tungsten are discussed together, as are tantalum and niobium.

### Surface Engineering of Molybdenum and Tungsten

The surface engineering processes used for molybdenum and tungsten are largely similar to those used for steels and heat-resistant alloys (see the articles "Surface Engineering of Carbon and Low-Alloy Steels" and "Surface Engineering of

Heat-Resistant Alloys" in this Volume). This section describes exceptions, modifications, and special practices for treating molybdenum and tungsten surfaces.

## Mechanical Cleaning and Polishing of Molybdenum and Tungsten Surfaces

**Abrasive Blasting.** The oxides of tungsten and molybdenum become volatile at relatively low temperatures. Oxides formed on the metal surface during hot working are porous. To remove these oxides, abrasive blasting is not generally required. It can be useful, however, to remove surface oxides from large or bulky components such as forgings to prepare them for machining. Grit sizes ranging from 36 to 120 mesh are commonly used.

Caution should be exercised when using this technique for two reasons. It is easy for particles of the abrasive medium to become embedded in the surface of the material, and it is not always possible to remove them if they are ceramic. If "iron" grit is used, embedded particles may be removed with hydrochloric acid, or by the nitric-hydrofluoric acid cleaning process described later in this section. When thinner sections such as sheet or plate are subjected to abrasive blasting on one side for an extended length of time without being turned over, the thermal stress caused by the temperature difference across the thickness of the plate may result in cracking of the metal.

**Mechanical Grinding and Finishing.** Belt grinding is commonly used to produce uniform surface finishes on both flat and round mill products of molybdenum and tungsten. The choice of equipment and abrasive are dictated in part by the equipment available and in part by the finish required. Wet grinding is preferred to avoid overheating and subsequent cracking. The liquid medium (water or a water-soluble coolant) also serves to minimize airborne dust and to lubricate the cutting medium. Table 1 summarizes recommendations for grinding molybdenum (Ref 1). Grinding wheels and papers should employ aluminum oxide or silicon carbide media. Emery paper is ineffective in grinding molybdenum and tungsten.

**Table 1 Grinding recommendations for unalloyed molybdenum**

| | Surface grinding | | Cylindrical grinding | | Bench grinding | Cutoff | Snagging portable |
|---|---|---|---|---|---|---|---|
| | Surface grinding | Form grinding | Roughing | Finishing | | | |
| Wheel speed, m$^2$/min (ft$^2$/min) | 510-605 (5500-6500) | 510-605 (5500-6500) | 510-605 (5500-6500) | 510-605 (5500-6500) | 885 (9500) | 930 (10,000) | 605 (6500) |
| Table speed, m/s (ft/min) | 0.3 (50) | 0.3 (50) | 1/3[a] | 1/6[a] | . . . | . . . | . . . |
| Work speed, m$^2$/min (ft$^2$/min) | . . . | . . . | 6.5 (70) | 10 (120) | . . . | . . . | . . . |
| Crossfeed, mm (in.) | 0.813 (0.032) | . . . | . . . | . . . | . . . | . . . | . . . |
| Grinding fluid | Oil-water emulsion | Dry | Oil-water emulsion | Oil-water emulsion | Dry | Oil-water emulsion | Dry |
| Infeed/pass, mm (in.) | 0.51 (0.002) | 0.025 (0.001) | 0.025-0.051 (0.001-0.002) | 0.025 + sparkout (0.001) | . . . | . . . | . . . |
| Wheel dressing | Open | Open | Open | Fine | None | None | None |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Wheel grading grain | Dry-wet $Al_2O_3$ | $Al_2O_3$ | $Al_2O_3$ | $Al_2O_3$ | $Al_2O_3$ | $Al_2O_3$ | $Al_2O_3$ |
| Grit size[(b)] | 60 (F) | 60 (SF) 100 (F) | 465 (SF) | 80 (SF) | 203 (SF) | 60 (T) | 36 (T) |
| Grade[(b)] | H | J (SF) I (F) | K | K | R | N | L |
| Structure[(b)] | 8 | 8 (SF) 5 (F) | 6 | 6 | Normal | 6 | 6 |
| Bond | Vitrified | Vitrified | Vitrified | Vitrified | Resinoid | Rubber | Vitrified |
| Carborundum gradings | | | | | | | |
| Dry | AA60-H8-V40 | AA100-15-V40 | . . . | . . . | . . . | . . . | A36-L6-V30 |
| Wet | GA60-J8-V40 | . . . | DA465-K6-V11 | DA80-K6-V11 | TA203-R-B65 | A60-N6-RR | . . . |

Source: Ref 1

(a) Width of wheel per revolution of work.

(b) Grain type: F, friable; SF, semi-friable; T, tough.

## *Chemical Cleaning and Polishing of Molybdenum and Tungsten Surfaces*

**Molten Caustic Process.** To remove the heavy oxide scale from tungsten, molybdenum, and their alloys, the molten caustic process is used. The molten caustic bath can be sodium hydroxide ($NaOH$) containing 0.5 to 3% sodium nitrite ($NaNO_2$), or it can be molten potassium hydroxide ($KOH$) containing 10% $NaNO_2$. Individual plants may use slightly different formulations. The operating temperature ranges from 315 to 400 °C (600 to 750 °F), and the immersion time is from 5 to 20 min or until the bubbling reaction stops. Caution should be taken to avoid any water getting into the bath, or a violent reaction will occur. When the workpiece is removed from the caustic, it is rinsed immediately with a jet of hot water in order to blast off the dissolved material and attached salt.

In the molten salt bath room, a suction hood or other ventilation system should be installed. The operator should use a control in a separate room or be separated from the bath container by a partition. In the vicinity of the bath container, the operator should wear a respirator, a face shield, rubber gloves, and an apron. In case the skin or eyes come in contact with the salt, one should flush the eye or skin area with plenty of water for at least 15 min.

**Acid Cleaning and Pickling.** When tungsten and molybdenum are slightly oxidized on the surface or after the heavily oxidized workpiece is cleaned with molten caustic, acid cleaning is used. The acid solution consists of 50 to 70 vol% of concentrated $HNO_3$, 10 to 20% of concentrated HF, and the remainder water. The cleaning solution is best when maintained at temperatures of 50 to 65 °C (120 to 150 °F). The process of acid pickling is twofold. First the nitrogen dioxide generated by nitric acid oxidizes the metal surface. Then the oxide is dissolved in hydrofluoric acid. The nitric-hydrofluoric bath also dissolves iron-containing contaminants that may have become embedded or included in the metal surface during high-temperature processing.

In the pickling area, ventilation and drainage systems should be installed. For the pickling acid, a recycling system to remove the residues and to refresh the acid is recommended. In small operations without recycling, the acid solution should be disposed of in a manner consistent with environmental regulations.

The dangers of hydrofluoric acid cannot be overemphasized. Any personnel working with the material must be adequately protected with rubber gloves and garments. Emergency spill kits should be readily available to neutralize any acid spills and more importantly treat any acid burns. Hydrofluoric acid is a "calcium seeker" that can cause severe and permanent injury to bone, and even death if burns are not treated properly.

Tungsten normally receives no other acid cleaning treatments, but molybdenum is occasionally further acid cleaned in a nitric-sulfuric acid bath. Acid concentrations are normally 750 to 900 g/L (100 to 120 oz/gal) $HNO_3$ and 100 to 200 g/L (15 to 25 oz/gal) $H_2SO_4$. The bath is typically operated at ambient temperatures.

Thorough water rinses are necessary after all acid cleaning treatments to remove acid residues and dissolved species. The best approach is to employ clean water sprays; the effluent from all rinse operations must be handled carefully to conform with environmental and safety regulations.

**Solvent Cleaning.** To remove oil, grease, and other contaminants from the surface of tungsten or molybdenum, a common organic solvent such as trichloroethylene, acetone, or isopropanol may be used. Cleaning is usually performed at room temperature by immersing and soaking the part in the solvent. Ultrasonic vibration is sometimes used to loosen soils from deep recesses. For large parts, spraying or wiping with the solvent may serve the same cleaning purpose. A proper ventilation system should be installed in the room for solvent cleaning.

**Electrolytic Cleaning.** Two common methods for cleaning molybdenum and tungsten are acid electrolyte (aqueous solution of 5 to 50 vol% concentrated HF, using 5 V, 60 Hz alternating current) and alkaline electrolyte (aqueous solution of 2 to 10 wt% NaOH or KOH with a nickel cathode, using a current density of 230 A/dm$^2$, or 2300 A/ft$^2$).

## *Preparation of Molybdenum and Tungsten for Coating and Joining*

Plating is a coating technique that generally requires very clean surfaces, and a number of techniques have been developed to produce such surfaces. Table 2 summarizes operating information for several electrolytic cleaning techniques that have been applied to molybdenum. Table 3 lists nonelectrolytic techniques that are also in use.

**Table 2 Etching solutions and conditions for molybdenum**

| Solution composition | Amount | | Anodic current density | | Time, min | Temperature | |
|---|---|---|---|---|---|---|---|
| | g/L | oz/gal | A/dm$^2$ | A/ft$^2$ | | °C | °F |
| Sulfuric acid, $H_2SO_4$ | 880 | 1140 | 2-10 | 20-100 | 2-3 | 21-32 | 70-90 |
| Phosphoric acid, $H_3PO_4$ | 718 | 93 | | | | | |
| Chromate trioxide, $CrO_3$ | 100 | 153 | 38 | 380 | 2 | 21-32 | 70-90 |
| Sodium chromate, $Na_2CrO_4$ | 10 | 1 | | | | | |
| Sulfuric acid, $H_2SO_4$ | 1180 | 153 | 22 | 220 | $\frac{1}{2}$ | 21-32 | 70-90 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Chromate trioxide, $CrO_3$ | 250 | 33 | 15.5 | 155 | $\frac{1}{3}$ | 56 | 135 |
| Sulfuric acid, $H_2SO_4$ | 2.5 | 0.3 | | | | | |

### Table 3 Nonelectrolytic cleaning techniques for molybdenum

| **Solution** | **Temperature** | | **Immersion time, min** |
|---|---|---|---|
| | **°C** | **°F** | |
| **Satisfactory preparation for electroplating** | | | |
| Aqueous: 300 g/L (40 oz/gal) potassium ferricyanide | RT | RT | 1 |
| **"Ultra-clean" surfaces for electronic applications** | | | |
| Aqueous: 80% $H_2O_2$, 10% HCOOH | RT | RT | 5-10 |
| **Alternate "ultra-clean" surfaces for electronic applications** | | | |
| Concentrated $H_2SO_4$ and 3.5 vol% saturated $Na_2Cr_2O_7 \cdot 2H_2O$ | 90 | 195 | 1 |

Ion sputtering has been evaluated as a means for preparing molybdenum and tungsten for plating and has not been shown to have an advantage in producing adherent films. However, when sputter cleaning is combined with magnetron deposition of an underlayment coating, the strength of subsequently plated coatings is greatly improved (Ref 2, 3).

Cleaning is also critical to obtaining efficient joints in brazed or welded material. A two-step technique for cleaning molybdenum prior to brazing has been published by one brazing alloy manufacturer, as follows:

| **Bath No. 1 (wt%)** | |
|---|---|
| Potassium permanganate | 5 |
| Sodium hydroxide | 10 |
| Water | 85 |
| **Bath No. 2 (vol%)** | |

| | |
|---|---|
| Sulfuric acid (concentrated) | 15 |
| Hydrochloric acid (concentrated) | 15 |
| Aqueous solution of chromic acid (6-10 wt% $CrO_3$) | 70 |

Immerse the molybdenum in bath No. 1 for 5 to 10 min at 65 to 80 °C (150 to 180 °F), remove, and spray rinse. This will leave a black smut on the surface. Rinse with cold water, scrubbing off loose smut. Immerse the molybdenum in Bath No. 2 at room temperature for 5 to 10 min, remove, and spray rinse. This cleaning procedure will remove the oxides without attack of the base metal.

Several other processes have been developed for pre-welding cleaning of molybdenum:

### Alkaline-Acid Procedure

1. Degrease with acetone.
2. Immerse for 5 to 10 min at 65 to 80 °C (150 to 180 °F) in alkaline solution of 10 wt% NaOH, 5 wt% $KMnO_4$, and 85 wt% distilled water.
3. Rinse with cold water, scrubbing off the loose smut.
4. Immerse for 5 to 10 min at room temperature in a bath of 15 vol% concentrated $H_2SO_4$, 15 vol% concentrated HCl, 70 vol% distilled water plus 6 to 10 wt% $CrO_3$.
5. Rinse in flowing cold tap water and allow to drain dry.

The last step has been modified to use distilled water after the flowing tap water rinse and then dried with forced hot air.

### Dual-Acid Procedure

1. Degrease with acetone.
2. Immerse 2 to 3 min at room temperature in a solution of 15 vol% hydrochloric acid (37 to 38% HCl), 15 vol% sulfuric acid (95 to 97% $H_2SO_4$), 15 vol% nitric acid (90% $HNO_3$), and 55 vol% distilled water.
3. Rinse in flowing tap water.
4. Immerse for 3 to 5 min at room temperature in a solution of 15 vol% sulfuric acid (95 to 97% $H_2SO_4$) 15 vol% hydrochloric acid (37 to 38% HCl), 70 vol% distilled water, and 6 to 10 wt% chromium trioxide ($Cr_2O_3$).
5. Rinse in flowing tap water.
6. Rinse in distilled water.
7. Dry with forced hot air.

### Cleaning Procedure for Heavy Oxide Films

1. Vapor degrease in trichloroethylene.
2. Virgo (Virgo is a proprietary molten descaling process) descale; 5 to 15 s at 470 ± 15 °C (875 ± 25 °F).
3. Cold water rinse until all Virgo salt is removed.
4. Dry; repeat steps 2 and 3 if oxides are not removed.
5. Cold water rinse, until all Virgo salt is removed.
6. Nitric acid pickle; 20 to 25 vol% of 42 °Bé acid (63 ± 3 °C, or 145 ± 5 °F), until a uniform dark coating is formed.
7. Cold water rinse.
8. Dip in potassium ferricyanide-potassium hydroxide solution:

| | |
|---|---|
| Potassium ferricyanide, g/L(oz/gal) | 300 (40.2) |
| Potassium hydroxide, g/L (oz/gal) | 100 (13.4) |
| Temperature | Room |
| Time, s | 30-60 |

9. Cold water rinse.
10. Chromic acid dip; 187 g/L (25 oz/gal) $Cr_2O_3$, 30 to 45 s, room temperature.
11. Cold water rinse.
12. Alkaline cleaner (90 ± 6 °C, or 190 ± 10 °F), 6 s maximum.
13. Cold water rinse.
14. Hydrochloric acid pickle; 20 to 22 °Bé (63 ± 3 °C, or 145 ± 5 °F),10 s maximum.
15. Cold water rinse.
16. Deionized water rinse containing 0.01 wt% of a chelating material (Sequestrene NA4, NA2, or equivalent material; product of Geigy Chemical Corporation).
17. Repeat step 16 in a second solution.
18. Methyl alcohol--25 vol% acetone rinse.
19. Repeat step 18 in a second solution.
20. Drain dry.
21. Wrap in clean plastic sheeting.

### Cleaning Procedure for Nonvisible Oxide Films

1. Vapor degrease in trichloroethylene.
2. Alkaline soak clean:

| | |
|---|---|
| Sodium hydroxide, g/L (oz/gal) | 7.5 (1) |
| Sodium carbonate, g/L (oz/gal) | 30 (4) |
| Sodium phosphate ($Na_3PO_4$), g/L (oz/gal) | 15 (2) |
| Temperature, °C (°F) | 88±5 (190±10) |
| Time, min | 1-2 |

3. Cold water rinse.
4. HCl pickle; 20 to 22 °Bé (63 ± 3 °C, or 145 ± 5 °F), 10 to 15 s.

5. Cold water rinse.
6. Rinse in deionized water containing 0.01% by weight of chelating material (same as for above).
7. Repeat step 6 in a second solution.
8. Methyl alcohol--25% acetone rinse.
9. Repeat step 8 in a second solution.
10. Drain dry.
11. Wrap in clean plastic.

After cleaning, the parts are handled with clean, dry gloves until they are welded.

### Acid Cleaning Procedure

1. Solution: 95.0 parts $H_2SO_4$, 4.5 parts $HNO_3$, 0.05 parts HF, and 18.8 g/L (2.5 oz/gal) $Cr_2O_3$.
2. Temperature 60 °C (140 °F).
3. Immerse specimens for 30 s.
4. Rinse with hot water.

### Electropolishing Procedures for Cleaning Molybdenum Prior to Brazing

1. Solution: 2 parts concentrated $H_2SO_4$, one part water.
2. Solution temperature 55 °C (130 °F).
3. Current density, 62 to 78 A/dm$^2$ (4 to 5 A/in.$^2$).
4. Voltage: 10 to 11 V.
5. Polishing time: 2 min.

## *Plating and Coating of Molybdenum and Tungsten*

**Electroplating.** Molybdenum and tungsten are difficult to plate because the natural oxides formed on the surface of these metals interfere with the adherence of coatings. Chromium has been a favored strike coating because its thermal coefficient of expansion is similar to that of molybdenum. It has good as-plated adherence, and the two metals diffuse to form a solid solution at elevated temperatures. Nickel has also found extensive use as a strike plating because its adherence can be enhanced by a post-plating diffusion anneal. The anodic etching procedure for activation of molybdenum is as follows:

1. Chromium is deposited in a chromic-sulfuric acid bath, 250 g/L (33 oz/gal) $Cr_2O_3$ and 2.5 g/L (0.3 oz/gal) $H_2SO_4$, at 90 ± 5 °C ( 195 ± 9 °F), using a current density of 100 ± 20 A/dm$^2$ (1000 ± 200 A/ft$^2$).
2. Nickel is deposited in a Watts-type bath over an acid chloride Wood's nickel strike plate, 240 g/L (31 oz/gal) nickel chloride·hexahydrate, 80 g/L (10 oz/gal) HCl at room temperature, using a current density of 3 to 10 A/dm$^2$ (30 to 100 A/ft$^2$), on the chromium-plated molybdenum.
3. Molybdenum plated with 25μm (1 mil) of chromium and 175 μm (7 mils) of nickel is protected in air for 1200 h at 980 °C (1795 °F), and for 100 h at 1200 °C (2190 °F).
4. Chromium-strike plated tungsten is carried out in the same bath as for molybdenum at 50 °C (120 °F), for 1 min with a current density of 5 to 15 A/dm$^2$ (50 to 150 A/ft$^2$). Watts nickel can be deposited over an acid sulfate strike on chromium-plated tungsten. This is carried out in a bath containing 240 g/L (31 oz/gal) nickel sulfate·hexahydrate and 40g/L (5 oz/gal) $H_2SO_4$ at room temperature for 2 to 5 min with a current density of 5 to 10 A/dm$^2$ (50 to 100 A/ft$^2$).

Another process intended to produce a hydride film as a basis for nickel plating is as follows:

1. Tungsten is treated cathodically at 1 to 11 A/dm$^2$ (10 to 110 A/ft$^2$) in approximately 2% acid or alkali, by weight, for 5 to 15 s.

2. Tungsten is rinsed, and nickel plated for 2 min in a Watts nickel bath, pH 4.0, at 65 °C (150 °F), with a current density of 5 to 11 A/dm$^2$ (50 to 110 A/ft$^2$).
3. The nickel-coated tungsten, after heating under vacuum at 450 to 750 °C (840 to 1380 °F) until gas evolution ceases, is cleaned and activated by strike plating in a Wood's nickel bath and then plated as desired.

Recent development shows that gold can also be used as a preplate for the subsequent deposition of other metal coatings. A process for molybdenum is detailed as follows:

1. Alkaline ferricyanide etch for 10 s at room temperature in a solution of 200 to 250 g/L (26 to 33 oz/gal) ferricyanide and 75 to 85 g/L (10 to 11 oz/gal) KOH.
2. Water rinse.
3. Hydrochloric acid, 50 vol%, dip for 10 s at room temperature.
4. Water rinse.
5. Acid gold strike, alkaline gold-cyanide-tartrate bath, 1 to 3 min at 0.1 A/dm$^2$ (1 A/ft$^2$), deposit 0.12 to 0.72 mg/cm$^2$ (0.78 to 4.7 mg/in.$^2$), 0.06 to 0.37 μm (2.4 to 15 μin.).
6. Water rinse and dry.
7. Diffuse in dry hydrogen at 830 °C (1525 °F) for 30 min.
8. Acid gold strike 4 min at 0.1 to 0.2 A/dm$^2$ (1 to 2 A/ft$^2$) to deposit additional 0.2 to 0.5μm (8 to 20 μin.).
9. Water rinse and dry. Diffusion in dry hydrogen at 830 °C (1525 °F) for 30 min.
10. Acid gold strike for 45 to 75 s at 0.1 to 0.2 A/dm$^2$ (1 to 2 A/ft$^2$).
11. Water rinse.
12. Plate desired metal coating. A thermal treatment in dry hydrogen at 830 °C (1525 °F) reduces the natural oxide to form a metal-metal interface and a diffusion bond.

Tungsten is first plated with about 0.2 to 2.0 μm (8 to 80 μin.) gold, heated at 1200 to 1370 °C (2190 to 2500 °F) under vacuum for 5 min, and then plated with gold or other metals to the desired thickness.

The TZM (0.5% Ti, 0.08% Zr, balance Mo) alloy has good strength properties at high temperature, but is subject to galling in threaded fasteners. Rhodium plating on molybdenum tends to eliminate galling. The process is detailed as follows:

1. Solvent degrease.
2. Alkaline clean at 80 °C (175 °F) for 5 min.
3. Water rinse.
4. Alkaline ferricyanide etch with agitation for 30 s at room temperature.
5. Water rinse.
6. Sulfuric acid, 5 to 10 vol%, dip for 10 s.
7. Rhodium strike at 1 to 2 A/dm$^2$ (10 to 20 A/ft$^2$) at 50 °C (120 °F) to deposit a 0.06 to 0.10 mg/cm$^2$ (0.40 to 0.65 mg/in.$^2$) in an acid rhodium sulfate bath.
8. Water rinse and dry.
9. Diffusion heat treat at 1000 °C (1830 °F) for 30 min, $10^{-4}$ torr ($10^{-2}$ Pa) maximum, purge with helium.
10. Sulfuric acid dip for 30 s minimum at room temperature.
11. Rhodium plate at 1 to 2 A/dm$^2$ (10 to 20 A/ft$^2$) at 50 °C (120 °F) to thickness of 0.5 μm (2.0 μin.).
12. Water rinse and dry.

Application of the rhodium strike directly over the natural oxide to TZM is somewhat difficult to accomplish initially because of the usual high tensile stress in rhodium plate. Reducing this stress is more effective in achieving adherence of the rhodium strike than are efforts to reduce the thickness of the natural oxide on TZM.

Iridium coatings about 12 μm (475 μin.) thick, plated in a fused cyanide bath, over chromium on nickel over gold strike-coated molybdenum, offered oxidation protection for about $\frac{1}{2}$ h in air at 1000 °C (1830 °F).

A typical process for nickel plating is as follows:

1. Degrease.
2. Scrub in detergent.
3. Water rinse.
4. Etch 2 min in potassium ferricyanide.
5. Wipe smut with clean towel and detergent.
6. Cathodically clean in potassium cyanide solution (80 g/L KCN) at 4.65 A/dm$^2$ (0.30 A/in.$^2$).
7. Cold water rinse 1 $\frac{1}{2}$ min.
8. Strike plate in nickel sulfamate solution for 2 $\frac{1}{2}$ min at 0.78 A/dm$^2$ (0.05 A/in.$^2$):

| | |
|---|---|
| $Ni(NH_2SO_3)_2 \cdot H_2O$, g/L (oz/gal) | 335 (45) |
| $NiCl_2$, g/L (oz/gal) | 45 (6) |
| $H_3BO_3$, g/L (oz/gal) | 45 (6) |
| pH | 3.4 |

9. Water rinse.
10. Hydrogen anneal for 10 min at 875 °C (1605 °F).
11. Water rinse.
12. Repeat step 6.
13. Cold water rinse.
14. Plate in solution of step 8 at 2.3 A/dm$^2$ (0.15 A/in.$^2$) for 16 min.
15. Water rinse.
16. Repeat steps 12 to 15 until desired thickness is attained.

**Anodizing.** For the anodizing of tungsten and molybdenum, an acetic-based electrolyte for vanadium may be used. It consists of acetic acid, 0.02 *M* sodium tetraborate-decahydrate, and 1.0 *M* additional water. When the water content is less than 1.0 *M*, the conductivity is reduced to an inconvenient extent. When the content is more than 2*M*, the film formed on molybdenum becomes excessively unstable. In the process, a platinum cathode is preferred, and the temperature is maintained around 25 °C (77 °F), with the presence of air.

The anodic film formed on molybdenum is so unstable that it will change interference colors and eventually disappear when exposed to air. It can be stabilized either by dipping in glacial acetic acid, followed by drying with filter paper, or by using a jet of compressed air immediately after its withdrawal from the electrolyte. Once stabilized, it can be stored in a desiccator almost indefinitely.

**High-Temperature Oxidation-Resistant Coatings for Molybdenum.** Ductile metallic overlays are among the first materials investigated as coatings for molybdenum. The materials and processes used are summarized in Table 4. The electrodeposition processes have been discussed in the electroplating section. Chromium is the most promising of the metallic coatings for molybdenum. It offers excellent oxidation protection and is compatible with substrate; however, chromium is embrittled by nitrogen and will crack and spall on repeated thermal cycling. A nickel or nickel alloy overlay will protect chromium from nitriding. A duplex coating will give good service for molybdenum up to 1200 °C (2195 °F).

### Table 4 Metallic coatings for molybdenum

| Process type | Material | Thickness range | |
|---|---|---|---|
| | | µm | µin. |
| Electrodeposition | Chromium, nickel, gold, iridium, palladium, platinum, rhodium | 12.7-76.2 | 500-3002 |
| Flame sprayed | Nickel-chromium-boron, nickel-silicon-boron, nickel-chromium, nickel-molybdenum | 127-254 | 5004-10,007 |
| Clad or bonded | Platinum, nickel, nickel-chromium, platinum-rhodium | 50.8-508 | 2002-20,015 |
| Molten bath | Chromium | 12.7-25.4 | 500-1001 |

Noble metal coatings, such as platinum and iridium, can be used on molybdenum at temperatures to about 1425 °C (2595 °F). They provide a significantly longer useful life at all temperatures than the duplex chromium-nickel coatings.

Coatings based on compounds with aluminum, in initial attempts, were to develop molybdenum parts for aircraft gas turbines. Coatings of aluminum-chromium-silicon, aluminum-silicon, and aluminum-tin systems are indicated in Table 5. The aluminide coatings are applied as thick overlays, using a variety of spray or dip processes. The aluminide coatings provide good oxidation protection to molybdenum at temperatures up to 1540 °C (2805 °F). Life at higher temperatures is very short, less than 1 h, probably as a result of rapid interdiffusion.

### Table 5 Aluminide coatings for molybdenum

| Type | Compositions | Deposition process | Thickness range | |
|---|---|---|---|---|
| | | | µm | µin. |
| Aluminum-chromium | 20% Al + 80% (55Cr-40Si-3Fe-1Al) | Thermal spray | 178-254 | 7013-10,008 |
| Aluminum-silicon | 88% Al-12% Si | Thermal spray, hot dip | 12.7-178 | 500-7013 |
| Tin-aluminum | 90% (Sn-25Al)-10% $MoAl_3$ | Slurry dip or spray | 50.8-203 | 2002-7998 |

Interest in coatings for molybdenum shifted from an aluminide to a silicide base in the mid 1950s. A list of the basic silicide coatings is shown in Table 6. Most of the silicide coatings are deposited by pack-cementation diffusion processes. A major deficiency in the performance of silicide-base coatings appears when the system is used in low-pressure environments. As shown in Fig. 1, silicide coatings that protect TZM substrate for 4 h at 1650 to 1760 °C (3000 to 3200 °F) in air at 1 atm cannot be used above 1480 °C (2695 °F) in air at pressure of 0.1 to 1.0 torr (13 to 130 Pa).

### Table 6 Silicide coatings for molybdenum

| Type | Deposition process |
|---|---|
| Molybdenum silicide | Fluidized bed, pack cementation, slip pack, plasma spray, electrophoresis |
| Molybdenum silicide and chromium | Pack cementation |
| Molybdenum silicide and chromium, boron | Pack cementation |
| Molybdenum silicide and chromium, aluminum, boron | Slip pack |
| Molybdenum silicide and tin-aluminum | Cementation and impregnation |

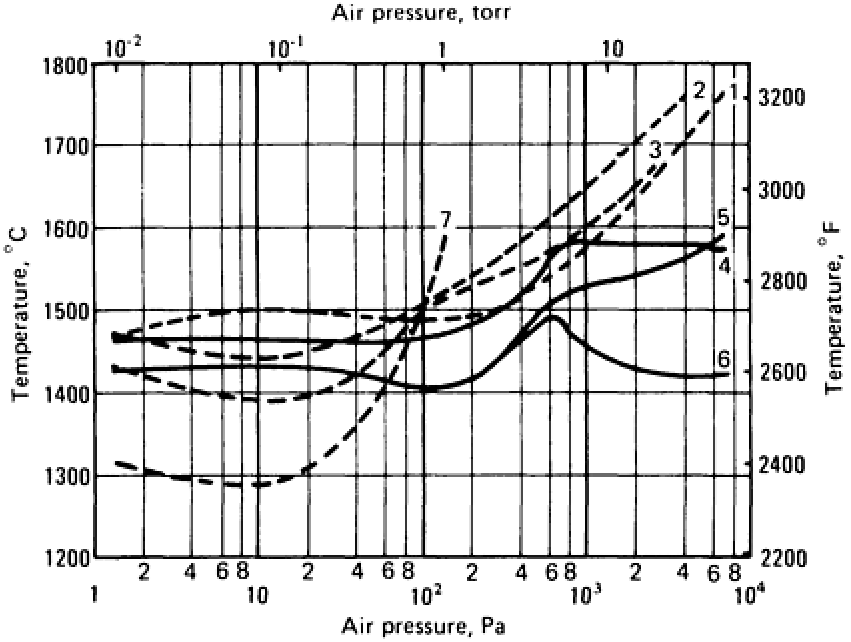

**Fig. 1 The effect of air pressure on the maximum temperature for a 4 h life of silicide-coated refractory materials. Alloy/coating: 1, TZM/PFR-6; 2, TZM/Disil; 3, TAM/Durak-B; 4, Cb-752/PFR-32; 5, Cb-752/CrTiSi; 6, B-66/CrTiSi; 7, Ta-10W/Sn-Al**

Refractory oxides or ceramics are the only materials suitable for the oxidation protection of molybdenum above 1650 °C (3000 °F) for any length of time. The types of oxide coatings that have been used on molybdenum are summarized in Table 7. Ceramic coatings suffer from one common problem. They crack on thermal cycling and tend to spall from the substrate. For only minutes, during single-cycle uses, such as for rocket motors, ceramic coatings provide useful protection from oxidation to 1930 °C (3505 °F) with $Al_2O_3$ and to 2200 °C (3990 °F) with $ZrO_2$.

**Table 7 Oxide coatings for molybdenum**

| Type | Deposition process | Thickness range | |
|---|---|---|---|
| | | µm | mils |

| | | | |
|---|---|---|---|
| Zirconium oxide-glass | Frit, enamel | 130-760 | 5-30 |
| Chromium-glass | Frit, enamel | 130-250 | 5-10 |
| Chromium-alumina oxide | Thermal spray over chromium plate | 200-380 | 8-15 |
| Alumina oxide | Thermal spray | 25-2500 | 1-100 |
| Zirconium oxide | Thermal spray | 25-2500 | 1-100 |
| Zirconium oxide | Troweling | 2500-7600 | 100-300 |

**High-Temperature Protective Coatings for Tungsten.** A more restrictive situation exists with tungsten. Silicide coatings are protective for a short time to 1925 °C (3500 °F). In the 1090 to 1650 °C (1995 to 3000 °F) range, lives of 10 to 50 h are attained.

Modifying the silicides with tungsten, zirconium, and titanium may be a more successful approach. A tungsten-modified silicide pack coating with $HfB_2$ additives is available commercially. A multi-element umbrella type, consisting of iridium electrodeposited from a fused salt bath, followed by a plasma-sprayed $ZrO_2$ layer prevents volatilization losses during very high-temperature oxidation. This may be serviceable at 1800 °C (3270 °F) for several hours. In the ceramic approach, a coating of $ThO_2$ over a tungsten wire mesh can be used at 2925 °C (5300 °F), and a coating of $HfO_2$ at 2700 °C (4890 °F).

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## Surface Engineering of Tantalum and Niobium

The processes and equipment for surface cleaning, finishing, and coating of tantalum and niobium, like those for molybdenum and tungsten, are similar to the processes and equipment used for steels and heat-resistant alloys. Important exceptions and special procedures are noted in this section.

### *Mechanical Cleaning and Polishing of Tantalum and Niobium Surfaces*

**Abrasive Blasting.** To remove intermediate thickness of the oxide scale of tantalum or niobium, abrasive blasting is applied. The abrasives to be used are usually silicon carbide of grit sizes ranging from 36 to 120 mesh. A good ventilation system is required in the abrasive blasting room, and the operator should wear a mask during working.

**Mechanical Grinding and Finishing.** Although commercially pure tantalum or niobium is worked at room temperature, their alloys are usually worked at elevated temperatures. Heavy oxide scale is formed. To remove such heavy oxide scale, mechanical grinding is the most effective method. For coarse grinding, a vitrified-bond grinding wheel having a 46 to 60 mesh of aluminum oxide is used. For finishing, a finer grit, vitrified or resinoid-bond grinding wheel 60 to 120 mesh of silicon carbide is used. For the cutting of tantalum or niobium, an abrasive wheel is also preferred. The grinding operation usually is performed dry, but the abrasive cutting is used with water cooling.

A good ventilation system should be installed in a grinding or polishing room. The operator should wear a face shield, mask, and gloves during working. Emery cloth and paper are ineffective for polishing tantalum and niobium. They are seldom used for finishing the product of these metals.

### *Cleaning and Polishing of Tantalum and Niobium*

**Alkaline Cleaning.** When oxide scale is combined with grease, graphite, molybdenum disulfide, and other lubricants on the workpieces of tantalum and niobium, an alkaline cleaning process is usually used. The starting product for the solution is a solid alkaline material that usually consists of 50 to 80% NaOH, with the remainder being sodium metasilicate and sodium carbonate. The solids are dissolved in water at a concentration of 0.6 to 1.2 kg/L (5 to 10 lb/gal), and the solution is kept at 65 to 80 °C (150 to 180 °F). The soaking time for the workpiece ranges from a few minutes to a few hours. After soaking, the workpiece should be immediately rinsed with a jet of water in order to blast off the loosened scale and attached salt. The operator should wear a face shield, rubber gloves, and an apron during working.

**Acid Cleaning and Pickling.** After mechanical grinding, abrasive blasting, or alkaline cleaning, tantalum and niobium are cleaned further with an acid solution. This consists of 40 to 60 vol% of concentrated $HNO_3$ to 10 to 30% of concentrated HF, and the remainder water. The cleaning solution is best when maintained at temperatures of 50 to 65 °C (120 to 150 °F). After acid pickling, the workpiece should be washed with water or rinsed thoroughly with a jet of water to remove any trace of acids.

Good ventilation and drainage systems should be installed in the acid pickling room. A recycling system to remove the residues and to refresh the acid is preferred both for economical and ecological reasons. For small operations without recycling, the acid solution should be disposed of in a manner consistent with environmental regulations.

The dangers of hydrofluoric acid cannot be overemphasized. Any personnel working with the material must be adequately protected with rubber gloves and garments. Emergency spill kits should be readily available to neutralize any acid spills and more importantly treat any acid burns. Hydrofluoric acid is a "calcium seeker" that can cause severe and permanent injury to bone, and even death if burns are not treated properly.

**Solvent Cleaning.** To remove oil, grease, and other contaminants from the surface of tantalum or niobium, a common organic solvent, such as trichloroethylene, acetone, or isopropanol can be used. Cleaning is performed at room temperature by immersing workpieces in solvent. Ultrasonic vibration is sometimes used to loosen soils from deep recesses. For large parts, spraying or wiping with the solvent may serve the same purpose. A proper ventilation system should be installed in the room for solvent cleaning.

**Electrolytic Cleaning.** Electrolytic etching may be used for the preparation and activation of tantalum and niobium before electroplating. The electrolytes usually used are as follows:

- For niobium, a concentrated hydrofluoric acid, 49% solution, with alternating current at 1 to 5 V and a current density of 22 to 108 A/dm$^2$ (220 to 1080 A/ft$^2$) for 1 to 3 min at room temperature is used.
- For tantalum, a solution consisting of 90% concentrated $H_2SO_4$ and 10% concentrated HF, used in the 25 to 40 °C (75 to 105 °F) range with a platinum cathode at a current density of 10 to 50 A/dm$^2$ (100 to 500 A/ft$^2$), gives excellent results.

### *Preparation of Tantalum and Niobium for Coating and Joining*

Before electroplating, the substrate to be plated should be electrolytically cleaned or activated. The electrolytic cleaning processes for niobium and tantalum have been mentioned in a previous section. After this, the article may be dipped in an aqueous solution of 50% concentrated $HNO_3$ and 2% concentrated HF, at 20 to 30 °C (68 to 86 °F).

### *Plating and Coating of Tantalum and Niobium*

**Electroplating.** Copper, chromium, gold, iron, nickel, and platinum are plated on niobium or tantalum. Conditions and solutions for these are given in Table 8.

**Table 8 Solutions for plating niobium or tantalum**

| **Solution** | **Constituent** | **Amount of constituent** | | **Current density** | | **Temperature** | |
|---|---|---|---|---|---|---|---|
| | | **g/L** | **oz/gal** | **A/dm$^2$** | **A/ft$^2$** | **°C** | **°F** |
| Copper | $CuSO_4 \cdot 5H_2O$ | 210 | 27 | 1.69 | 26.9 | 25 | 77 |
| | $H_2SO_4$ | 80 | 10 | | | | |
| | Molasses | 2.5 | 0.3 | | | | |
| Chromium | $CrO_3$ | 400 | 52 | 5.38 | 53.8 | 75 | 165 |
| | $H_2SO_4$ | 4 | 0.5 | | | | |
| Gold | $KAu(CN)_2$ | 44 | 5.7 | 2.15 | 21.5 | 54 | 130 |
| | $K_2C_4H_4O_5$ | 48 | 6.2 | | | | |
| | KOH | 3 | 0.9 | | | | |
| | $K_2CO_3$ | 10 | 1.3 | | | | |
| | KCN(a) | 30 | 4 | | | | |
| Iron | $Fe_2SO_4 \cdot 7H_2O$ | 300 | 39 | 3.23 | 32.3 | 60 | 140 |
| | $FeCl_2 \cdot 4H_2O$ | 42 | 5.5 | | | | |
| | $(NH_4)_2SO_4$ | 15 | 2 | | | | |
| | NaCOOH | 15 | 2 | | | | |
| | $H_3BO_3$ | 30 | 4 | | | | |
| | Wetting agent | 1 | 0.13 | | | | |
| Nickel | $NiSO_4 \cdot 7H_2O$ | 300 | 39 | 1(b) | 10 | 60 | 140 |
| | $NiCl_2 \cdot 6H_2O$ | 50 | 6.5 | | | | |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| | $H_3BO_3$ | 30 | 4 | | | | |
| | Wetting agent | 1 | 0.13 | | | | |
| Platinum | Bakers platinum solution No. 209 | (c) | (c) | 8.07 | 80.7 | 88 | 190 |

(a) pH, 12.1.

(b) 4.31 A/dm$^2$ (43.1 A/ft$^2$).

(c) Diluted to 4 g/L (0.52 oz/gal) of contained platinum made slightly ammoniacal

Iron and nickel deposits are fairly adherent. Other deposits easily peel off the niobium. The presence of a hydride layer between the plate and the niobium limits the strength of the bond, and heat treating is required to decompose the hydride. This involves heating in a vacuum for 1 h at 700 to 1100 °C (1290 to 2010 °F). Improved adhesion of the coating can also be obtained if the surface to be plated is first shot blasted and the flash coated with an undercoat of copper, deposited by chemical displacement from a specified electrolyte.

For plating gold on tantalum, heat treatment before and after the electrolytic plating will enhance the bonding. The temperature for preheating is 1955 °C (3550 °F), and the after-treatment is carried out at 1100 °C (2010 °F). Both treatments occur under vacuum.

For plating nickel, cathodic treatment at 2 A/dm$^2$ (20 A/ft$^2$) for 20 to 30 min in a solution of 2.5 vol% of 48% HF, 2.5 vol% of HCl, sp gr 1.16, and 95% absolute methanol at 40 to 50 °C (105 to 120 °F), gives a more uniform surface texture on tantalum. After this treatment, 0.3 μm (12 μin.) of nickel is deposited in a Watts bath, pH 4.0, vacuum heat treated at 500 to 600 °C (930 to 1110 °F), then nickel plated to 10 μm (390 μin.) thick, and again heat treated at 450 °C (840 °F).

Another procedure intended to produce a hydride film as a basis for electroplating with nickel on tantalum or niobium is as follows:

1. The metal is treated cathodically at 1 to 11 A/dm$^2$ (10 to 110 A/ft$^2$) in 2%, by weight, acid or alkali for 5 to 15 s.
2. The metal is then rinsed and nickel plated for 2 min in a Watts nickel bath, pH 4.0, at 65 °C (150 °F), with a current density of 5 to 11 A/dm$^2$ (50 to 110 A/ft$^2$).
3. After vacuum heating at 450 to 750 °C (840 to 1380 °F) until gas evolution ceases, the nickel-coated article is cleaned and activated by strike plating in Wood's nickel bath, and then plated as desired.

**Anodizing** is a process in which a current passes through an electrolyte from an inert cathode to the anode, on which a thin layer of the oxide forms during the process. The thin but dense oxide layer thus formed usually protects the metal from further oxidation in air and from abrasion. Anodic oxidation for tantalum and niobium is carried out at constant current density, about 1 to 15 A/dm$^2$ (10 to 150 A/ft$^2$), at room temperature either in 0.5 to 2 wt% ammonium citrate or in 0.5 wt% ammonium borate solution, with the pH kept at 9 by adding ammonium hydroxide.

**Oxidation-Resistant Coatings for Niobium.** The use of refractory metals at elevated temperatures is being pursued intensively by the aerospace industry. One of the major limitations to progress in this field is the need for coatings to protect the alloys from rapid oxidation and embrittlement at elevated temperatures. These coatings may be classified as intermetallic compounds, including silicides and aluminides that form compact or glassy oxide layers; alloys that form compact oxide layers; noble metals that resist oxidation; and stable oxides that provide a physical barrier to the penetration of oxygen.

Many techniques have been used to form protective coatings on niobium alloys. They are as described below.

***Pack Cementation.*** Immersion of the material to be coated in a pack consisting of inert filler, metal coating elements, and halide activator. Heat treatment is conducted in hydrogen or an inert atmosphere. Coating is formed by vapor transport and diffusion.

***Vacuum Pack.*** Immersion of material to be coated in an all-metal pack of coating elements plus halide activator. Heat treatment is performed in dynamic vacuum or under a partial atmosphere of inert gas. Coating is formed by vapor transport and diffusion.

***Slip Pack.*** Similar to the two processes above, substitution of thin disposable bisque for massive pack. Bisque is sprayed, dipped, or applied to the substrate surface in other ways.

***High-Pressure Pack Cementation.*** Similar to pack cementation and vacuum pack, with utilization of inert gas pressure in excess of 1 atm (100 kPa).

***Fused Slurry.*** Uniform application of a metal or alloy slurry to the substrate surface, followed by fusion of the slurry in an inert gas or vacuum environment. Coating forms by liquid-solid diffusion.

***Slurry-Sinter.*** Spray or dip application of metal particles plus binder to substrate surface, followed by solid- or liquid-phase sintering in vacuum or inert environment.

***Fused Salt.*** Electrolytic or nonelectrolytic deposition of metal ions from a fused metal salt solution, such as fluorides, chlorides, and bromides, on the substrate material. Pure or alloy coatings are formed.

***Electrophoresis.*** Deposition of charged metal particles from a liquid suspension onto a substrate surface of opposite electrical potential. Synthesis of particulate deposit generally involves isostatic compaction followed by vacuum or inert atmosphere sintering.

***Aqueous Electroplating.*** Electroplating of metal ions from aqeuous solution. Process can involve suspension of particulate materials in electrolyte and occlusion of these particles in metal deposit.

***Fugitive Vehicle.*** Involves spray or dip application of metal slurry onto the substrate surface, followed by vacuum heat treatment. Slurry contains coating elements and fugitive vehicle that is molten at the firing temperature. Fugitive vehicle has high solubility for coating elements and very low solubility for substrate. Coating forms by transfer of elements from the liquid solution to the substrate surface, with subsequent diffusion growth of the coating phase. Fugitive vehicle is eventually removed by evaporation.

***Fluidized Bed.*** Immersion of the material to be coated in a heated fluidized bed of coating elements, using as the fluidizing gases mixtures of reactive halogen gases and hydrogen or argon. Coating forms by disproportionation of gaseous metal halides on substrate surface, followed by diffusion alloying.

***Chemical Vapor Deposition (CVD).*** Entirely gaseous process. Metal halide gases, plus argon or hydrogen, pass over surface of metal to be coated. Coating forms by hydrogen reduction or thermal decomposition of metal halide at substrate surface, followed by diffusion-controlled coating growth.

***Vacuum Vapor Deposition.*** Evaporation of a metal or alloy from a filament, liquid bath, or other source, followed by condensation of the metal vapor onto a cold or hot substrate surface. Post diffusion treatment is optional.

***Hot Dipping.*** Immersion of material to be coated in a hot liquid bath of the molten coating elements. Coating forms by liquid-solid diffusion.

***Hydride and Oxide Reduction.*** Spray or dip application of metal hydrides or oxides on substrate surface, followed by vacuum or hydrogen reduction, respectively.

**Plasma Arc.** Spray deposition of particulate metal or oxide particles using conventional plasma arc facility.

**Detonation Gun.** Patented gun detonation metal spraying process.

**Gun Metallizing.** Utilization of conventional wire or powder metallizing equipment.

**Cladding.** Bonding of thin sheet metal cladding to substrate surface by diffusion bonding, forging, rolling, extrusion, and other methods.

Coating systems and processes for niobium are shown in Table 9.

**Table 9 Oxidation-resistant coating systems for niobium**

| **System concept** | **Composition** | **Process** |
|---|---|---|
| **Silicide coatings** | | |
| Complex silicide multilayered | Cr, Ti, Si | Vacuum pack and vacuum slip-pack, fused slurry and pack, fluidized bed, electrophoresis, chemical vapor deposition, electrolytic fused salt |
| Modified silicide | Si + V, Cr, Ti | Fluidized bed |
| Modified silicide | Si | Pack cementation, iodine |
| Modified silicide | Si-B-Cr | Pack cementation, multicycle |
| Modified silicide | Si-Cr-Al | Pack cementation, multicycle |
| Modified silicide | Si + additives | Pack cementation, single cycle |
| Modified silicide | Si + Cr, Al, B | Pack cementation, single cycle |
| Silicide | Si | Chemical vapor deposition |
| Molybdenum disilicide | Si + Mo | $MoO_3$ reduction and chemical vapor deposition |
| Modified silicide | Si + additives | Pack cementation, fluidized bed, fused salt, slurry dip |
| Modified silicide | Si + additives | Pack cementation, single cycle |
| Liquid phase-solid matrix | Se, Sn, Al | Porous silicide applied by pack or CVD-impregnated with Sn-Al |
| Multilayered complex silicide | 40Mo-40Si, 10CrB-10Al | Plasma spray-diffuse |

| | | |
|---|---|---|
| Modified silicide | Si + additives | Pack cementation |
| Complex silicide | Si-20Fe-20Cr | Fused silicides |
| Complex silicide | Si-20Cr-5Ti | Fusion of eutectic mixtures |
| Complex silicide | Si + (Cr, Ti, V, Al, Mo, W, B, Fe, Mn) | . . . |
| Complex silicide | V-Cr-Ti-Si | Vacuum and high-pressure pack |
| Complex silicide | Mo-Cr-Ti-Si, V-Cr-Ti-Si, V-Al-Cr-Ti-Si, Mo-Cr-Si | Multicycle vacuum pack |
| Glass-sealed silicide | Si + glass | Silicide by pack cementation or CVD + glass slip overcoat |
| Multilayered | Mo, Ti + Si and glass | Slurry sinter application of Mo + Ti powder, pack silicide, glass slurry seal |
| **Aluminide coatings** | | |
| Modified aluminide | Al + B | Pack cementation |
| Modified aluminide | 88Al-10Cr-2Si | Fused slurry |
| Modified aluminide | Al-Si-Cr | Fused slurry |
| Modified aluminide | Al-Si-Cr, Ag-Si-Al | Hot dip |
| Multilayered systems | Fe, Cr, Al, Ni, Mo, Si, $VSi_2$, $TiCr_2$, $CrSi_2$, B + Al | Powder metallize + aluminum hot dip |
| Simple aluminide | Al | Pack cementation |
| Multilayered systems | Cr, FeB, NiB, Si, $Al_2O_3$, $SiO_2$, $ThO_2$ + Al | Electroplate dispersions in Ni + Al hot dip |
| Modified aluminide | Al + (Si, Ag, Cr) | Silver plate + Al, Cr, Si hot dip |
| Multilayered systems | $Al_2O_3$ + Ti + Al | ($Al_2O_3$ + TiH), Spray-sinter + Al hot dip |
| Oxide-metal composite | $Al_2O_3$ + Al | Slurry fusion of $Al_2O_3$-Al mixture |

| | | |
|---|---|---|
| Aluminide | Al + additives | Fused slurry |
| Modified aluminide | Al + Sn | Hot dip |
| **Zinc coating** | | |
| Self-healing intermetallic | Zn and Zn + Al, Ti, Co, Cu, Cr, Fe, Zr, Cu, Si | Vacuum distillation and hot dip |
| **Oxide coating** | | |
| Glass-sealed oxide | $Al_2O_3$ + glass (baria, alumina, silica) | Flame spray $Al_2O_3$ + glass slurry |
| **Nickel-chromium coating** | | |
| Oxidation-resistant alloy | Ni-Cr | Flame spray, detonation gun, plasma arc |
| **Chromium carbide coating** | | |
| Carbide | Cr-C | Plasma spray |
| **Noble metal coatings** | | |
| Clad | Pt, Rh | Roll bonding and hermetic sealing |
| Barrier-layer-clad | Pt, Rh + Re, Be, $Al_2O_3$, W, $ZrO_2$, MgO, SiC, Hf | Noble metal clad over barrier layer-diffusion couple study |
| Pure metal | Ir | Fused-salt deposition |

**Oxidation-Resistant Coatings for Tantalum.** Much of the work on tantalum alloys is the outgrowth of approaches taken with niobium alloys. The development of coatings has come generally in the 1970s. Most of the emphasis is on the diffusional growth of intermetallic layers. A few commercial or semicommercial coatings are as follows:

- A series of tin-aluminum-molybdenum-base coatings are used by slurry process. These are limited primarily by poor resistance to reduced pressure and erosion at very high temperatures.
- Electrophoretical deposition of binary disilicides combined with a molybdenum-vanadium system shows no pest phenomenon during service. This process can be considered commercial for small parts.
- A fluidized-bed, three-step silicon-vanadium-silicon process may be used for niobium as well as Ta-10W.
- Complex titanium, molybdenum, tungsten, and vanadium modified silicide coatings can be applied by a two-step method: a slurry plus high-temperature sinter of an alloy layer followed by a straight silicide pack. Protection for hundreds of hours at 870 °C (1600 °F) and 1320 °C (2410 °F) in furnace tests has

been obtained.
- A fused-silicide coating system, particularly Si-20Ti-10Mo, appears practical for coating large, complex aerospace sheet metal components.
- A duplex coating consisting of a sintered hafnium boride-molybdenum silicide layer overlaid with a hafnium-tantalum slurry is serviceable at 1820 to 1870 °C (3310 to 3400 °F).

# Surface Engineering of Nickel and Nickel Alloys

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## Introduction

NICKEL is a versatile element and will alloy with most metals. Complete solid solubility exists between nickel and copper; wide solubility ranges between iron, chromium, and nickel make possible many alloy combinations. The face-centered cubic structure of the nickel matrix (γ) can be strengthened by solid-solution hardening, carbide precipitation, or precipitation hardening. Nickel alloys are used for a wide variety of applications, the majority of which are designed to take advantage of the corrosion resistance and/or heat resistance properties of these alloys. The classification, physical metallurgy, and applications of nickel and nickel alloys are described in Volume 2 of *ASM Handbook;* information on heat-resistant nickel alloys and stainless steels is provided in Volume 1 of *ASM Handbook.* This article describes cleaning and finishing of nickel alloys; additional and related information is available in the articles "Diffusion Coatings," "Surface Engineering of Heat-Resistant Alloys," and "Surface Engineering of Stainless Steels" in this Volume.

Nickel alloys do not require special techniques or precautions for the removal of shop soils such as soap, drawing compound, oil, grease, cutting fluid, and polishing compound. Oxide, scale, tarnish, or discoloration can be removed from nickel and nickel alloys by mechanical methods, such as grinding or abrasive blasting, or by chemical methods, such as pickling. Conventional methods of cleaning with alkaline compounds, emulsions, or solvents or vapor degreasing may be employed. These processes are described in the articles "Alkaline Cleaning," "Emulsion Cleaning," "Solvent Cold Cleaning and Vapor Degreasing," and "Mechanical Cleaning Systems" in this Volume.

## Pickling

Pickling is a standard method for producing bright, clean surfaces on nickel alloys, either as an intermediate step during fabrication or as a last step on finished parts. Procedures used for pickling nickel alloys are governed by both material composition and prior thermal treatment. The necessity of pickling can be avoided by using bright-heating practices, that is, the use of a protective inert and/or vacuum furnace atmosphere to prevent oxidation. Pickling should not be used to overhaul material by dissolving away appreciable amounts of metal. This practice can cause severe, irreversible damage such as pitting and intergranular attack. Significant material dimensional loss can readily occur if process parameters (e.g., continued maintenance of bath chemistry, temperatures, and immersion time) are ignored. Caution should be observed when pickling bimetallic items, weldments, and components with platings or coated surfaces, because selective, localized attack may occur, depending on system dynamics.

Oxidizing furnace atmospheres, high-sulfur-content fuels, and air leakage in furnaces during high-temperature operations can cause heavy scale to form on unprotected nickel alloys. Securely oxidized nickel alloys have a dull, spongy appearance. Hairline cracks are sometimes present, and patches of scale may break away from the surface. In such cases, the rough underlying metal will not allow an attractive finish to be attained by any pickling method. Table 1 provides selected formulas for pickling nickel alloys, and the table below will aid in preparing these formulas:

| Acid | °Bé | Specific gravity | Concentration, wt% |
|---|---|---|---|

|  |  |  |  |
|---|---|---|---|
| $HNO_3$ | 42 | 1.41 | 67 |
| $H_2SO_4$ | 66 | 1.84 | 93 |
| HCl | 20 | 1.16 | 32 |
| HF | 30 | 1.26 | 70 |

**Table 1 Formulas for pickling nickel alloys**

| Formula No. | Reagents | Weight, % | Amount |  | Temperature |  |
|---|---|---|---|---|---|---|
|  |  |  | mL | oz | °C | °F |
| 1 | Nitric acid ($HNO_3$) 1.41 sp gr | 20 | 300 | 10 | 70 | 160 |
|  | Water |  | 1000 | 34 |  |  |
| 2[a] | Nitric acid ($HNO_3$) 1.41 sp gr | 10 | 133 | 4 | 75 | 170 |
|  | Sodium chloride (NaCl) | 5 | 63 g | 2 |  |  |
|  | Water |  | 1000 | 34 |  |  |
| 3 | Nitric acid ($HNO_3$) 1.41 sp gr | 20 | 315 | 11 | 50 | 125 |
|  | Hydrofluoric acid (HF) 1.26 sp gr | 2 | 34 | 1 |  |  |
|  | Water |  | 1000 | 34 |  |  |
| 4 | Sulfuric acid ($H_2SO_4$) 1.84 sp gr | 25 | 200 | 8 | 80 | 180 |
|  | Water |  | 1000 | 34 |  |  |
| 5 | Sulfuric acid ($H_2SO_4$) 1.84 sp gr | 15 | 111 | 4 | 80 | 180 |
|  | Sodium chloride (NaCl) | 5 | 63 | 2 |  |  |
|  | Water |  | 1000 | 34 |  |  |
| 6 | Sulfuric acid ($H_2SO_4$) 1.84 sp gr | 15 | 119 | 4 | 20-40 | 70-100 |

| | | | | | | |
|---|---|---|---|---|---|---|
| | Sodium dichromate ($Na_2Cr_2O_7$) | 10 | 135 g | 5 | | |
| | Water | | 1000 | 34 | | |
| 7 | Sulfuric acid ($H_2SO_4$) 1.84 sp gr | 12 | 82 | 3 | Ambient | |
| | Sodium fluoride (NaF) | 2 | 23 g | 1 | | |
| | Water | | 1000 | 34 | | |
| 8 | Sulfuric acid ($H_2SO_4$) 1.84 sp gr | 20 | 171 | 6 | 80 | 180 |
| | Sodium chloride (NaCl) | 5 | 73 g | 3 | | |
| | Sodium nitrate ($NaNO_3$) | 5 | 73 g | 3 | | |
| | Water | | 1000 | 34 | | |
| 9 | Sulfuric acid ($H_2SO_4$) 1.84 sp gr | 35 | 1200 | 41 | 20-40 | 70-100 |
| | Nitric acid ($HNO_3$) 1.41 sp gr | 30 | 1860 | 63 | | |
| | Sodium chloride (NaCl) | 0.5 | 30 g | 1 | | |
| | Water | | 1000 | 34 | | |
| 10 | Hydrochloric acid (HCl) 1.16 sp gr | 6 | 200 | 7 | 60 | 140 |
| | Water | | 1000 | 34 | | |
| 11 | Hydrochloric acid (HCl) 1.16 sp gr | 12 | 535 | 18 | 80 | 180 |
| | Cupric chloride ($CuCl_2$) | 2 | 33 g | 1 | | |
| | Water | | 1000 | 34 | | |
| 12 | Hydrochloric acid (HCl) 1.16 sp gr | 1 | 30 | 1 | Ambient | |
| | Ferric chloride ($FeCl_3$) | 1 | 11 g | 0.3 | | |
| | Water | | 1000 | 34 | | |

|  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|
| 13 | Sodium hydroxide (NaOH) | 15 | 188 g | 7 | 80 | 180 |
|  | Potassium permanganate ($KMnO_4$) | 5 | 63 g | 2 |  |  |
|  | Water |  | 1000 | 34 |  |  |
| 14 | Ammonium hydroxide ($NH_4OH$) | 2(b) | 20 | 0.5 | Ambient |  |
|  | Water |  | 1000 | 34 |  |  |
| 15 | Alkaline cleaner |  | 60-75 g/L | 7-9 oz/gal | 80 | 180 |
|  | Water |  | 1000 | 34 |  |  |
| 16 | Agar-agar | 1 | 10 g | 0.3 | 20-65 | 70-150 |
|  | Potassium ferricyanide ($K_3Fe(CN)_6$) | 0.1 | 1 g | 0.03 |  |  |
|  | Sodium chloride (NaCl) | 0.1 | 1 g | 0.03 |  |  |
|  | Water |  | 1000 | 34 |  |  |

(a) An addition of at least 40 g of nickel per liter to Formula 2 will prevent overpickling of chromium-bearing alloys.

(b) Volume %

The best methods for removing heavy scale are mechanical removal techniques such as abrasive blasting or grinding, usually with aluminum oxide or silicon carbide, followed by flash pickling. Abrasive blasting requires a relatively low capital investment compared to pickling, considering the extensive equipment needed for pickling and the cost of complying with environmental regulations. Abrasive blasting also eliminates the need to use and dispose of acids and the need to treat the rinse water. However, the removed scale and spent media may be considered a solid waste for disposal purposes. An alternative method is to soak the oxidized material in hydrochloric acid pickle (Formula 11, Table 1), followed by flash pickling if brightening is required.

**Precautions** must be taken in handling pickling solutions, because noxious and sometimes toxic fumes are liberated. Positive ventilation, either the use of a ventilating hood over the bath or provision of a controlled draft, is required to remove the fumes. Pickling acids must be handled with care, particularly hydrofluoric acid. Protective clothing, face shields, and rubber gloves must be used at all times. When solutions are prepared, acid should always be added to the water. This is especially important when sulfuric acid is diluted. In preparing the solutions shown in Table 1, the ingredients should be added to the water in the order listed.

**Bath Life.** Pickling baths should be analyzed regularly to determine acidity. Only total acidity can be determined in baths composed of more than one acid; it is impossible to distinguish acidity contributed by one acid source from that contributed by another. However, when the acidity of a bath is being maintained, the ingredients should be added in the proportions used for the original solution. Bath analysis should be performed by a qualified individual, by either wet chemistry or another acceptable means, on an established schedule. Subsequent additions should be made to maintain the bath at the initial acidity level.

With the exception of flash pickling solutions, bath solution should be disposed of when the total metallic content reaches 150 g/L (20 oz/gal). If the bath is used for only one type of alloy, only one element needs to be determined in the analysis. The remaining metallic elements can be determined from the percentage of each in the composition of the alloy. For example, in analyzing baths used for pickling nickel-chromium alloys, the nickel content determines whether the total metallic content is within the 150 g/L limitation.

Flash pickling solutions continue to perform satisfactorily even when nearly saturated with metal salts. Fresh solution should be made up only when salts begin to crystallize on the side of the bath container.

### *Alloy Groups*

For the purpose of discussing pickling procedures, the nickel alloys can be divided into four groups:

- *High-nickel alloys* such as Nickel 200, Nickel 201, Nickel 270, and Duranickel alloy 301
- *Nickel-copper alloys* such as Monel alloys 400 and K-500
- *Nickel-chromium alloys* such as Inconel alloys 600, 625, 718, and X-750
- *Nickel-iron-chromium alloys* such as Incoloy alloys 800 and 825

All alloys within any one group have virtually the same pickling characteristics. However, the pickling procedures for alloys within a group must be varied to suit the surface condition of the metal.

### *Surface Conditions*

Alloys within each composition group that have similar surface conditions are pickled in the same solutions using the same procedures. Three different surface conditions are generally encountered, primarily depending on the method of prior heating:

- *Bright annealed white surface* requiring removal of tarnish by flash pickling
- *Bright annealed oxidized surface* requiring removal of a layer of reduced oxide, sometimes followed by a flash pickle to brighten
- *Black or dark-colored surface* requiring removal of adherent oxide film or scale

**Tarnish** and dullness from bright annealed metal can be removed by flash pickling or bright dipping. Bright annealed white surfaces are generally found on drawn and spun shapes, cold-headed rivets, cold-drawn wire, and other cold-worked products. The white surface is a result of annealing in a reducing, sulfur-free atmosphere and cooling either out of contact with oxygen or by quenching in a 2 vol% alcohol solution.

Flash pickling solutions act rapidly, and care must be exercised to prevent overpickling and etching. These solutions are used at room temperature. If the bath is cold, it should be warmed slightly to prevent unduly slow action. Best results with flash pickling are obtained by warming the parts by dipping them in hot water, placing them in the acid for a few seconds, and rinsing them again with hot water. A second dip in acid may be used if necessary. Badly tarnished metal may require a total of 3 min in acid, but the material should be withdrawn frequently from the bath and inspected to prevent overpickling.

**Reduced-oxide surfaces** occur when hot-worked products, such as forged and hot-rolled material, are heated after hot working in a reducing, sulfur-free atmosphere and are cooled out of contact with air or quenched in an alcohol solution. On such products, pickling produces a clean surface for further processing by cold forming, or it produces the finished surface necessary for items such as rivets.

At annealing temperatures in reducing atmospheres, oxides formed on the high-nickel alloys, except those containing chromium, are readily converted to a spongy, tightly adherent layer. On nickel alloys, the layer consists of metallic nickel.

On Monel alloys the layer is a mixture of metallic nickel and copper. The oxide film formed on nickel-chromium alloys and nickel-iron-chromium alloys does not undergo complete reduction in reducing atmospheres, which makes pickling more difficult. The oxide on these alloys is selectively reduced to a mixture of metallic nickel and chromic oxide. The surface color ranges from the characteristic chrome green of chromic oxide to dark brown.

**Oxidized or scaled surfaces** are present on all hot-worked products and heat-treated material cooled in air. This type of surface also occurs on the nickel-chromium and nickel-iron-chromium alloys in all conditions except bright heated. The oxide film forms on properly heated nickel and nickel-copper alloys during contact with air after the work is withdrawn from the furnace. The nickel-chromium and nickel-iron-chromium alloys form oxide films even when heated and cooled in atmospheres that keep other alloys bright. Thus, the usual pickling procedure for Inconel and Incoloy alloys is designed to remove oxide and scale.

## *Nickel-Copper Alloys*

Depending on the methods of prior heating and cooling, nickel-copper alloys can have any of the surface conditions discussed previously. Accordingly, the appropriate pickling procedure depends on the surface condition of the material.

**Tarnish** is best removed from bright annealed nickel-copper alloys by pickling in two solutions in sequence. First, the metal should be pickled thoroughly in Formula 2 (Table 1) in brief exposures and rinsed in water at 80 °C (180 °F). After rinsing, the metal should be dipped in Formula 1. The second dip should be followed by rapid rinsing of the workpiece and neutralization in a 1 to 2 vol% solution of ammonia (Formula 14). To dry, small workpieces should be dipped in boiling water and rubbed in sawdust or with a clean, dry cloth.

**Reduced-Oxide Surfaces.** Formula 8 is recommended for reduced-oxide surfaces on nickel-copper alloys if pickling is done on a large scale. This acid mixture is more destructive to tanks and racks than solutions used for steel or copper. Steel tanks lined with 4.8 mm ($\frac{3}{16}$ in.) thick natural rubber and a double layer of yellow acid bricks have proven to be the best and most economical containers for this corrosive solution. After pickling in Formula 8, the metal should be rinsed in hot water and neutralized in a 1 to 2 vol% ammonia solution. The Formula 8 pickling solution works best after a short period of use. Therefore, when new solutions are prepared, about 2 vol% of spent solution should be added to the fresh mixture to improve its action.

When a pickling room is not regularly operated, the time required for complete pickling of small lots in Formula 8 is usually a disadvantage. Adequate results in most cases can be obtained by using flash pickling solutions (Formulas 1 and 2). However, Formula 8 may be used for occasional small jobs if ceramic vessels or wooden barrels are used as containers. The solution can be heated and agitated by injecting live steam, either through a rubber hose or through a carbon pipe that has a perforated carbon-block end.

**Oxidized or Scaled Surfaces.** Oxidized nickel-copper alloys having a thin to moderately thick oxide are pickled by immersion in Formula 11, followed by brightening in Formula 6. After treatment in the first bath, the work should be rinsed in hot water before it is transferred to the brightening dip. The second dip in Formula 6 should be followed by rinsing the work in cold water and neutralizing it in a 1 to 2 vol% ammonia solution (Formula 14).

## *High-Nickel Alloys*

Nickel 200, Nickel 201, Nickel 270, Duranickel alloy 301, and similar alloys can have any of the three types of surface conditions. With the exception of flash pickling, high-nickel alloys are pickled in the same solutions used for Monel alloys. However, maintaining separate baths for the two groups of alloys is usually advisable.

**Tarnish.** Only one dip, Formula 9, is required to remove tarnish from bright annealed high-nickel alloys. The metal should first be dipped in hot water to warm it. Immersion in the acid bath for 5 to 20 s is usually sufficient to produce bright, clean surfaces. After the metal is removed from the pickling solution, it should be rinsed in hot or cold water and neutralized in a dilute ammonia solution.

The pickling action of Formula 9 can be retarded, if necessary, by decreasing the amount of acid to as little as one-third the volume that is added to the standard formula [e.g., as low as 400 mL (13.5 oz) of sulfuric acid or 620 mL (21 oz) of nitric acid]. Normally, however, the formula gives the best results in the proportions given in Table 1.

**Reduced-Oxide Surface.** The solution used to pickle reduced-oxide surfaces on nickel-copper alloys, Formula 8, is also used for high-nickel alloys. The procedure is the same as the procedure for reduced-oxide surfaces, described in the section "Nickel-Copper Alloys" in this article. If both groups of alloys are being pickled, separate baths should be maintained. Formula 8 may be used for occasional small lots, but suitable results can usually be obtained in less time by flash pickling in Formula 9.

**Oxidized or scaled surfaces** on high-nickel alloys can be pickled with the hydrochloric acid/cupric chloride solution (Formula 11) used for nickel-copper alloys. A longer time is required, however. Immersion from 1 to 2 h is necessary to obtain a good pickle on high-nickel alloys. After removal from the pickling bath, the work should be rinsed with hot water and dipped for a few seconds in Formula 9, if brightening is required. The brightening dip should be followed with a cold-water rinse and neutralization in a dilute ammonia solution.

### *Nickel-Chromium and Nickel-Iron-Chromium Alloys*

Tarnished or reduced-oxide surfaces are usually not encountered on nickel-chromium or nickel-iron-chromium alloys. These alloys can only be bright annealed in very dry hydrogen or in a vacuum. Oxides formed on their surfaces in other atmospheres do not undergo complete reduction. Oxide or scale is the usual surface pickled on nickel-chromium and nickel-iron-chromium alloys.

Pretreating in a fused-salt bath is strongly recommended to facilitate pickling of oxidized or scaled surfaces. However, if the metal has been properly heated and cooled, it will usually have a surface suitable for direct pickling in Formula 3. If a fused-salt bath is used for pretreating, the following procedure should be used for pickling nickel-chromium and nickel-iron-chromium alloys:

1. Treat in fused-salt bath.
2. Quench in and spray with water.
3. Immerse in Formula 4.
4. Withdraw from bath and rinse with water.
5. Immerse in Formula 1.
6. Withdraw from bath and rinse with water.
7. Pickle in Formula 3 as required.

As with the nickel-copper alloys and high-nickel alloys, an alternative procedure employing a salt bath and Formula 8, with 10 g/L (1 oz/gal) of ferric chloride added to the formula, effectively removes oxide from hot-rolled or annealed Inconel alloys 601 and 671, and from Incoloy alloys 804 and 903. The procedure for the use of a salt bath is described in the section "Nickel-Copper Alloys" in this article.

If the oxide film cannot be readily removed by pickling directly in Formula 3, or if a fused-salt bath is not available, Formula 13 is a useful pretreatment. The work should be soaked for 1 to 2 h in Formula 13, removed, rinsed to remove all of the caustic solution, and pickled in Formula 3. On highly refractory oxides, it is sometimes necessary to repeat the cycle. Adding 7 to 10 g/L (0.9 to 1 oz/gal) of iron to Formula 3 decreases the danger of overpickling. This can be done conveniently by adding the proper weight of scrap iron to the bath when it is prepared.

The nitric acid/hydrofluoric acid bath (Formula 3) must be used with care. Nickel-chromium and nickel-iron-chromium alloys are subject to intergranular attack in this solution if they have been sensitized by heating in, or slowly cooling through, the 540 to 760 °C (1000 to 1400 °F) temperature range. Time in the bath should be kept to a minimum, and bath temperature must not exceed 50 °C (125 °F). Stress-relieved and age-hardened material can also be sensitive to intergranular attack if the heat treatment involved exposure to sensitizing temperatures.

### *Salt Baths*

Pretreatment baths of fused salts aid in the pickling of many alloys. They are particularly effective in pickling nickel-chromium and nickel-iron-chromium alloys. Several proprietary baths are commercially available; information on their use can be obtained from manufacturers.

**Precautions** must be taken in handling salt baths. Protective clothing, face shields, and suitable gloves should be used. Room-temperature solution, or powder residue, may cause severe chemical burns. Extreme temperatures of working salt baths exacerbate the need for constant vigilance. Operators should avoid mixing salt bath constituents with those of pickling baths. Typically, rinse water should be used after salt bath processing and prior to pickling. Tank carryout should be minimized by sufficient draining. *Caution: Operators should not dispose of salt bath and pickling bath materials in the same container without approval from a qualified supervisor.*

**Bath Life.** Salt baths are basically alkaline and not acid in constitution. Bath maintenance should be in accordance with the supplier's instructions. Bath monitoring and control will be similar to that described in the section "Pickling" in this article.

Salt baths are of three types: reducing, oxidizing, and electrolytic. Oxidizing baths are usually the least expensive to operate and the easiest to control, whereas reducing baths are no longer in common use. Electrolytic baths, although more expensive to install and operate, are quite effective for nickel alloys.

***Oxidizing salt baths*** have a base of either sodium hydroxide or potassium hydroxide. Other salts, such as sodium nitrate and sodium chloride, are added to provide controlled oxidizing properties. The sodium hydroxide bath is operated at temperatures of 425 to 540 °C (800 to 1000 °F); a temperature of 480 °C (900 °F) is preferred for descaling nickel alloys. The potassium hydroxide bath operates at lower temperatures, usually 200 to 260 °C (400 to 500 °F). Treatment time in oxidizing baths is usually 5 to 20 min. In the operation of continuous strand pickling lines, the time may be as short as 15 to 60 s.

The salt bath oxidizes the lower oxides on the surface of the work to form soluble salts and water. Quenching after treatment removes part of the scale and loosens the remainder so that it is easily removed by appropriate acid dips. Oxidizing salt baths are also effective cleaners. They remove oil, grease, organic materials, and some inorganic substances from metal surfaces.

***Electrolytic salt baths*** have a sodium hydroxide base and contain other salts, such as sodium chloride and sodium carbonate, that form reducing agents at the cathode and oxidizing agents at the anode when electrically activated. Baths are usually operated at about 480 °C (900 °F), and although electrolytic salt baths can be used as a batch process, they are more suitable for continuous operations such as descaling of strip. Two tanks are normally used for continuous processes. The work is made anodic in the first tank and cathodic in the second.

## *Specialized Pickling Operations*

Although pickling is most often used to remove the oxide or scale formed during heating, it is also used to remove foreign metals and other substances. Several procedures specifically designed for such purposes are applicable to nickel alloys.

**Removal of Lead and Zinc.** Lead and zinc embrittle high-nickel alloys at elevated temperatures. Consequently, when the alloys are formed in dies made of materials containing lead and zinc, all traces of the die material picked up during forming should be removed. When parts will be given intermediate anneals for processing, or when they will be exposed to high temperatures during service, removal of lead and zinc becomes especially important.

Formula 10 is used to remove lead and zinc from nickel and nickel-copper alloys. For nickel-chromium and nickel-iron-chromium alloys, a bath of nitric acid similar to Formula 1 (but with the concentration of nitric acid increased to 30%) is used. After being immersed in the appropriate bath for 15 min, the work is removed, rinsed in water, and dried.

**Detection and Removal of Embedded Iron.** During mechanical operations such as rolling to shape or hot pressing, small particles of iron may become so firmly embedded in the surfaces of nickel alloys that they cannot be removed by the cleaning methods normally used for dissolving grease or cutting compounds. Under certain corrosive conditions, such iron particles can initiate local attack. For that reason, it is often necessary to test for iron traces and remove them.

For large-scale testing, a solution of about 1% sodium chloride is effective. A chemically pure grade of salt should be used to prevent false results from iron that might be present in less pure grades. When compressed air is available, it is usually less expensive to keep the tank full of salt spray with an atomizer than to fill it with the solution. After 12 to 24 h in the dilute salt solution, any iron particles in the nickel alloy will appear as rust deposits.

The ferroxyl test works well for small-scale testing. A potassium ferricyanide solution, made up in approximately the proportions shown in Formula 16, is applied to the surface of the material. The ingredients are mixed in earthenware, glass, or ceramic vessels and then boiled until all of the agar-agar is dissolved and a clear liquor is formed. Chemically pure sodium chloride should be used to prevent iron contamination of the test solution. The warm solution is applied to the surface to be tested and allowed to remain for at least 1 h. The solution gels as it cools, and the presence of iron on the metal surface is indicated by blue spots in the gel.

The ferroxyl test is sensitive enough that minute particles of iron that collect on the surface in the form of shop dust will appear as small blue spots in the gel. Because the iron dust will be washed off with the gel, the small spots should be distinguished from the larger ones caused by embedded iron. If spots of relatively major proportions develop, large iron particles are probably present.

A solution of hydrochloric acid and ferric chloride, Formula 12, is used to remove embedded iron. This solution should be used cold and should remain in contact with the metal for only the minimum time required for iron removal, not exceeding 1 h. After the work is removed from the solution, it should be rinsed thoroughly in cold water, then rinsed again in warm water. The detection tests should be repeated to verify the removal of the iron.

**Prevention and Removal of Copper Flash.** Copper flash sometimes forms on the surface of nickel alloys during pickling. For copper deposits to form, copper ions in the solution must be in the cuprous state, or they must pass from the cupric to the cuprous state during the cementing process. Consequently, any agents in the pickling bath that tend to maintain the cupric state will help prevent coppering.

Oxidizing agents such as nitric acid and sodium nitrate promote the action of pickling solutions but become depleted with use. As the pickling bath ages, the concentration of copper ions increases while the concentration of oxidizing agents decreases. Thus, aging the bath facilitates coppering on areas where the reducing effect of the metal exceeds the oxidizing power of the bath.

When coppering occurs on Monel alloy 400 and other high-nickel alloys containing an appreciable amount of copper, the bath can be restored by adding small amounts of nitric acid or sodium nitrate. Nickel has greater reducing capacity than Monel alloy 400 and requires a greater concentration of oxidizing agents to prevent coppering in solutions containing copper salts. For this reason, Nickel 200 and similar alloys must not be pickled in solutions that have been used for nickel-copper alloys.

Patches of copper will plate out on nickel-copper alloys if steel contacts the alloys while they are wet with acid. Steel tongs or other devices used to handle the work are the usual sources of kippered areas. Coppering is prevented by using handling devices made of Nickel 200 or Monel alloy 400.

Copper flash is readily removed by immersing the alloy in an aerated, 4 to 5% ammonia solution at room temperature. The solution composition should be approximately 125 mL of ammonia to 1 L of water, or 1 pint of commercial aqua ammonia to 1 gal of water. The work should be immersed for about 1 min only, then rinsed in water.

**Electrolytic Pickling.** Light oxide films on any of the nickel alloys can be removed by electrolytic pickling in Formula 7. The work should be made anodic by using a current density of 5.4 to 10.75 A/dm$^2$ (50 to 100 A/ft$^2$). Electrolytic pickling is also useful for etching ground material to obtain a surface suitable for inspection.

**Electropolishing** of high-nickel alloys smooths the surface by removing metal through a controlled electrochemical process that is similar to, but essentially the reverse of, electroplating. When the alloy is immersed into an electrolyte and maintained anodic, metal is electrochemically removed ion by ion. This simultaneously deburrs the alloy, maximizes tarnish protection, and reduces surface fouling while producing a uniformly bright and smooth surface luster. Properly electropolished surfaces are microscopically featureless, non-contaminating, non-particulating, and effectively stress relieved. Such high-performance and high-purity metal surface finish properties are unattainable by more traditional mechanical finishing techniques.

High-quality electropolishing of the high-nickel alloys produces brilliant lustered reflectivity. Best results are obtained from metals with fine grain boundaries that are free of nonmetallic inclusions and seams. Electropolished surfaces should not exhibit frosting, shadows, streaks, stains, pitted areas, or an "orange peel" or pebbly appearance.

Important factors in final finish quality are proper electrolyte selection, bath temperature, and bath maintenance (specific gravity, acid concentration, and metals content) and direct current from a ripple-free source applied at optimum voltage and current density. More complex configurations require adequate cathode design for effective polishing in inaccessible areas, inside corners, and in other areas of low current density. Agitation of either the electrolyte or the metal may be necessary to prevent gas entrapment, gassing streaks, flow marks, or similar undesirable markings.

**Cleaning of Springs.** In general, cleaning of springs made of a high-nickel alloy is not recommended after heat treating. The oxide on heat-treated springs usually aids in resisting corrosion at high temperatures. When the oxide is removed, resistance to relaxation is often lowered. If cleaning is necessary for inspection of the springs, they should be treated in a salt bath, quenched in water, and rinsed to produce a good surface. Table 2 shows the effect of the cleaning method on resistance to relaxation of Inconel alloy X-750 springs that were age hardened at 730 °C (1350 °F) for 16 h.

**Table 2 Effect of cleaning method on relaxation of Inconel alloy X-750 springs(a)**

| Cleaning method | Relaxation(b), % |
|---|---|
| No cleaning, as age hardened | 10.0 |
| Oxidizing salt bath plus Formula 3 | 11.5 |
| Tumbling in sand and oil | 12.8 |
| Abrasive blasting (120 grit with water) | 13.3 |
| Shot peening | 13.5 |
| Abrasive blasting (standard sand, dry) | 14.6 |

(a) Cold drawn (No. 1 temper) and age hardened at 730 °C (1350 °F) for 16 h.

(b) Relaxation after 250 h at 415 MPa (60 ksi) and 540 °C (1000 °F)

**Cleaning for Welding.** Before maintenance welding is done on high-nickel alloys that have been in service, products of corrosion and other foreign materials must be removed from the area to be welded. Clean, bright base metal should extend 50 to 75 mm (2 to 3 in.) from the joint on both sides of the material to prevent the corrosion products from embrittling at welding temperatures.

Cleaning can be done mechanically (by grinding with a fine wheel or disk) or chemically (by pickling). Mechanical cleaning methods usually use an abrasive medium containing either aluminum oxide or silicon carbide grit. Care must be taken to avoid embedding abrasive grit into the weldment surface. Sometimes wire brushing with an austenitic stainless steel brush and/or local macroetching with a Schantz etch, or similar flash pickling, is an appropriate procedure immediately prior to welding.

Flash pickling solutions are effective in cleaning before welding. The solutions can be applied by swabbing, brushing, or dipping, if the parts are easily handled. A single dip in Formula 2 is adequate for the nickel-copper alloys. Formula 1 is used for nickel alloys, and Formula 3 is useful for nickel-chromium and nickel-iron-chromium alloys.

## Reactive Gas Ion Thermal Processing

Reactive gas ion thermal processing is high-temperature processing that introduces certain extremely reactive gases disassociated into ions, specifically hydrogen and fluorine. It has been shown to be effective in reducing tenacious oxides of aluminum and titanium and scale found on high-nickel alloy surfaces.

Although hydrogen, considered an industrial gas, is generally readily available, the source of the fluoride ion is a commercially available system: chromous fluoride ($CrF_2$,) polytetrafluoroethylene (PTFE), or hydrogen fluoride gas (HF). The process uses a heated reaction vessel, generally a retort, and the work and its holding fixtures are placed inside. Reaction temperatures for high-nickel alloys are typically around 1100 °C (2000 °F), although times and temperatures will depend on specific processing requirements. Forethought must be given to safety and environmental concerns.

### Example: Repair of Gas Turbine Engine.

For acceptable repair of an aircraft gas turbine engine that had some high-nickel alloy components, it was necessary to use high-purity, dry hydrogen gas, introduced into a retort during an elevated-temperature run, to reduce most surface oxides. Subsequent establishment of next-generation braze repair technologies was possible on these alloys only after successful incorporation of fluoride ion processing. The significantly more reactive fluoride ion and its innate, aggressive reduction of oxides achieved surface, and even subsurface, cleaning with complete subsurface oxide/scale conversions in cracks as fine as 0.013 mm (0.0005 in.).

**Results.** Process parameter definition ensures repeatable oxide reduction without unacceptable substrate damage. Positive results are removal of surface oxide from exposed internal/external surfaces; effective cleaning prior to coating, welding, or brazing; removal of mill scale; and stripping of aluminide coating. Negative results are slight alloy depletion, typically of aluminum, molybdenum, and titanium constituents, on exposed surfaces; and slight intergranular attack on exposed surfaces.

## Finishing

Nickel alloys can be ground, polished, buffed, or brushed by all methods commonly used for other metals. For high-nickel alloys, a series of operations is required to produce a satisfactory finish. The number and type of operations required depend on the initial finish of the material, the desired final finish, and the type of equipment used. The pressures and speeds of the finishing equipment must be closely controlled. The high-nickel alloys, particularly nickel-chromium and nickel-iron-chromium alloys, do not conduct heat away as rapidly as copper and aluminum. Excessive heat will destroy the true color of the metal and may warp flat, thin articles.

Some general recommendations for finishing operations are given in Table 3. Table 4 lists spindle speeds and corresponding surface speeds for various wheel diameters.

**Table 3 Recommended finishing procedures**

| Operation | Wheel | Grit No. | Compound | Speed | |
|---|---|---|---|---|---|
| | | | | m/s | sfm |
| Grinding | Rubber bond | 24 or 36 | None | 40-45 | 8000-9000 |
| | Vitrified bond | 24 or 36 | None | 25-30 | 5000-6000 |
| Roughing | Cotton fabric, sewn sections | 60 or 80 | None | 30-40 | 6000-7500 |
| Dry fining | Cotton fabric, sewn sections | 100 or | None | 30- | 6000- |

| | | | | | |
|---|---|---|---|---|---|
| | | 120 | | 40 | 7500 |
| Greasing | 64-68 unbleached sheeting, spirally sewn sections | 150 or 180 | Polishing tallow or No. 180 emergy grease cake | 30-40 | 6000-7500 |
| Grease coloring | 88-88 unbleached sheeting, spirally sewn or loose disk; or quilted sheepskin | 200 or 220 | Polishing tallow or "F" emery grease cake | 30-40 | 6000-7500 |
| Bobbing and sanding | Leather wheel for two bobbing operations, second with medium-density felt wheel | . . . | Grout | 25 | 5000 |
| Cutting down | 88 unbleached sheeting, loose spirally sewn sections or loose-disk wheel | . . . | Tripoli | 40-45 | 8000-9000 |
| Coloring | | | | | |
| Bright finish | 88-88 unbleached sheeting, loose spirally sewn sections or loose-disk wheel | . . . | White aluminum oxide | 50 | 10,000 |
| Mirror finish | Loose-disk, 88-88 unbleached sheeting or Canton flannel | . . . | Green chromium oxide | 50 | 10,000 |
| Brushing | Tampico | . . . | "F" emery grease cake or grout | 5-15 | 1200-3000 |

## Table 4 Spindle speed for various surface speeds and wheel diameters

| **Surface speed** | | **Spindle speed, rev/min, for indicated wheel diameter** | | | | | | |
|---|---|---|---|---|---|---|---|---|
| **m/s** | **sfm** | **150 mm (6 in.)** | **200 mm (8 in.)** | **250 mm (10 in.)** | **300 mm (12 in.)** | **360 mm (14 in.)** | **410 mm (16 in.)** | **460 mm (18 in.)** |
| 15 | 3,000 | 1930 | 1450 | 1150 | 950 | 820 | 710 | 640 |
| 20 | 4,000 | 2550 | 1900 | 1500 | 1300 | 1100 | 950 | 850 |
| 25 | 5,000 | 3200 | 2400 | 1900 | 1600 | 1375 | 1200 | 1050 |
| 28 | 5,500 | 3500 | 2600 | 2100 | 1750 | 1500 | 1300 | 1175 |
| 30 | 6,000 | 3800 | 2850 | 2300 | 1900 | 1650 | 1425 | 1275 |
| 38 | 7,500 | 4800 | 3550 | 2850 | 2400 | 2100 | 1800 | 1600 |
| 40 | 8,000 | 5100 | 3800 | 3100 | 2550 | 2200 | 1900 | 1700 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 45 | 9,000 | 5750 | 4300 | 3450 | 2850 | 2450 | 2150 | 1900 |
| 50 | 10,000 | 6400 | 4750 | 3800 | 3200 | 2750 | 2400 | 2100 |

**Grinding,** often the first operation in a finishing sequence, is used to remove large surface imperfections and to rough-down welds prior to polishing and buffing. Rubber-bond grinding wheels are used for nickel and Monel nickel-copper alloys for their cutting effectiveness and for their relative softness, which reduces the heat generated. Rubber-bond wheels should be operated at a surface speed of 40 to 45 m/s (8000 to 9000 sfm). Vitrified-bond wheels are preferred for grinding harder alloys such as the Inconel and Incoloy alloys. These wheels should be operated at a surface speed of 25 to 30 m/s (5000 to 6000 sfm). Light welds can be ground efficiently with a No. 36 grit wheel, whereas a No. 24 grit is more practical for heavy welds.

**Polishing.** The first polishing operation should be done with very fine grit to remove all surface defects and give a base upon which to build the final finish. Wheels of No. 60 to 80 grit are usually required to remove heavy oxide or deep defects.

The first operation should be done dry. After the initial roughing, tallow should be used on all roll-head wheels of No. 150 grit or finer. Tallow clogs the wheel, giving a smoother finish and reducing the amount of heat generated.

When flat work is polished, each subsequent operation should be done with a grit 30 to 40 numbers finer than the previous one, until the surface is ready for the brushing or bobbing operations needed to prepare for buffing.

When possible, the scratches produced by the abrasive should cross the scratches left by the preceding operation. When polishing is done in only one direction, the finer abrasive will follow in the grooves made by the coarser abrasive, and the efficiency of the polishing wheels will be impaired.

Wheels for roughing and dry finishing should be made of tightly woven, unbleached cotton fabric. To prevent chattering, the wheels should be perfectly balanced and should have a soft or cushioned face. Fine grit wheels require more cushions than coarse wheels.

A more resilient and flexible wheel should be used for greasing operations. Greasing wheels should be made of 64- to 68-count unbleached sheeting and should have more cushion than the wheels used for coarser polishing. Grease coloring may be done on a full-disk, quilted sheepskin wheel or on a spirally sewn wheel made of fine-count (88-88) heavy sheeting. Compounds of artificial abrasives are preferred for roughing and dry finishing. Turkish emery is usually used for greasing and grease coloring.

Bobbing done with emery grout is more like burnishing than polishing, and if it is performed in one operation, it is best done with leather wheels. If it is done in two operations, the second should be done with a medium-density felt wheel, because felt wheels require less pressure. The best results are obtained from emery roll-head wheels at surface speeds of 33 to 38 m/s (6500 to 7500 sfm). The metal drags at slower speeds, and at excessive speeds, the wheel tends to pull up the surface of the metal.

**Buffing.** For good results in buffing, a high-quality wheel of the proper construction and material is essential. Wheels should be of sturdy, closely woven, high-count sheeting. The close weave gives good cutting, and the heavy threads provide good coloring.

Buffing is usually done in two operations. The first, the cutting-down operation, is done with a sewn buffing wheel operating at a surface speed of 40 to 45 m/s (8000 to 9000 sfm). The second, the coloring operation, is done with a loose-disk wheel operating at a surface speed of approximately 50 m/s (10,000 sfm). A loose disk, Canton-flannel wheel is best for buffing to a mirror finish. The high speeds used in buffing create a high heat. Consequently, less pressure is necessary than for polishing.

The cutting-down operation is normally performed with tripoli compound, which leaves a haze on high-nickel alloys. Buffing compound with less grease should be used to promote deep color. White aluminum oxide and green chromium oxide compounds can be used for the final coloring. Chromium oxide compounds produce less friction and give a truer color.

**Brushing.** A tampico or wire wheel produces a brushed finish on the high-nickel alloys. Tampico wheels usually produce a better finish and higher luster, and because of their flexibility, they are better for irregular shapes. A tampico wheel is used with emery paste or grout to produce a satin finish, or with pumice and water or pumice and oil to produce a better finish. For wet brushing, tampico wheels should have wooden hubs.

Wire brushes can be used to produce a satin finish on sheet metal articles. Brushes should have a wire diameter of 0.10 to 0.20 mm (0.004 to 0.008 in.). They should not be made of steel or brass wire, because small particles from the brush are always embedded in the metal during the process. Steel particles rust, and brass particles discolor the nickel alloys.

Brushing is done at slower speeds than those used for polishing. Brushing speeds are normally 5 to 15 m/s (1200 to 3000 sfm), depending on the final finish desired. Higher speeds, 20 to 30 m/s (4000 to 6000 sfm), are required to produce a bright wire brush finish. Wire brushes operated at too slow a speed produce coarse, undesirable scratches.

**Blasting.** Abrasive media blasting has the ability to produce a cosmetically appealing, uniform, matte gray appearance that varies from dull to a high-sheen luster. The appearance depends on the medium chosen (aluminum oxide, silicon carbide, glass bead, steel shot, crushed plastic, etc.); particle size (No. 24 grit for rough finishes vs. No. 220 for smooth finishes); and particle shape (angular grit or cut shot for a dull appearance vs. crushed plastic, round glass beads, or cast steel shot for luster and sheen).

### *Nondestructive Inspection*

Care must be taken in finishing high-nickel alloys when subsequent inspection will be performed with an ultrahigh-sensitivity, fluorescent penetrant nondestructive method. Under certain conditions, finishing operations using plastics, such as plastic blasting media, plastic brushes, or buffing pads with embedded grit, leave a residue of thin, smeared plastic on the surface that introduces high background fluorescence during fluorescent penetrant inspection. Similarly, coarse abrasive blasting may hamper the detection of surface flaws by penetrant methods. On the other hand, fine grit blasting (No. 60 or finer) has been successfully used to enhance detection of surface flaws, such as investment casting defects.

# Surface Engineering of Zinc Alloys

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## Introduction

THE PRIMARY PRODUCT FORMS of zinc and zinc alloys requiring surface engineering prior to coating or use are die castings, wrought zinc alloys, and zinc-coated steels. The vast majority of die castings are nominally Zn-4Al alloys covered by ASTM B 86 (Ref 1). These alloys are known commonly as alloys 3, 5, and 7. However, during the 1980s, applications increased for zinc die castings containing higher aluminum contents, nominally 8, 12, or 27% (Ref 2). In addition to the increased use of electrogalvanized zinc-coated steel by the automotive industry, there has been a significant increase in other applications that use painted or powder-coated galvanized steel, particularly in the appliance industry (Ref 3, 4).

Because of their inherent corrosion resistance, zinc and zinc alloys can be used satisfactorily in many applications without subsequent finishing. However, a variety of finishes are used for improved corrosion protection or appearance: conversion coatings, such as chromate, phosphate, and anodize; organic paint of various types; and metallic coatings, including electroplating, electroless plating, and vacuum metallizing. The normal sequence of preparation steps prior to painting or electroplating of zinc alloy die castings includes:

- Mechanical finishing to smooth parting lines and rough or defective surfaces, plus buffing, if necessary
- Solvent degreasing or aqueous-based solution degreasing followed by rinsing
- Soak alkaline cleaning and/or alkaline electrocleaning followed by rinsing
- Acid dipping followed by rinsing

Guidelines for preparing zinc die castings for electroplating are contained in ASTM B 252 (Ref 5). If die cast parts are to be painted, they are often given a chromate or phosphate conversion coating treatment following alkaline cleaning to improve corrosion resistance and coating adherence. Wash primers also are used for those purposes.

Wrought zinc products are subjected to solvent cleaning, soak alkaline cleaning, and electrolytic alkaline cleaning prior to electroplating (Ref 6). Zinc-coated steel products (hot dip or electrogalvanized) typically are solvent cleaned to remove stamping and forming lubricants and general handling soils, then are alkaline cleaned and are given either a phosphate or chromate treatment prior to coating, to improve corrosion resistance and coating adherence.

Surface preparation and cleaning prior to plating or painting is considered by many to be the most important aspect of the finishing process. If surfaces are not properly prepared, defects in the base metal will show through the finished coating, and if the parts are not properly cleaned, coating adherence will be reduced and premature corrosion often results.

For die castings, proper runner and gating design and proper control of the die casting process, particularly die temperature control, can produce castings in which surface defects are minimized. Thus, preplating or prepainting surface preparation processes can be reduced with substantial savings in finishing costs. Similarly, proper trim die design and maintenance can reduce the amount of effort spent smoothing parting lines.

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## Mechanical Finishing

**Finishing of Parting Lines.** Of the various product forms of zinc alloys, die castings require the most extensive mechanical finishing prior to electroplating or painting. This situation results because the castings must be trimmed to remove gates and runners, overflows, vents, and flash. Grinding and polishing of the parting lines is the first step after the castings have been trimmed. Finishing of the parting lines is done on set-up wheels or abrasive belts, by tumbling with abrasive media, or by vibratory finishing. Wheels or belts with coarse grit (60- to 120-mesh) are used for heavy metal removal, if necessary (Ref 2). The parting line regions typically are finished with 220- to 300-grit abrasive wheels or belts (Ref 5, 6). A lubricant, such as paraffin, may be used to produce a finer finish. Set-up wheels are typically operated at peripheral speeds ranging from 1800 to 2400 m/min (6000 to 8000 ft/min). Abrasive belts should not be operated at speeds greater than 2100 m/min (7000 ft/min); speeds ranging from 1080 to 1200 m/min (3500 to 4000 ft/min) often are used (Ref 5, 6).

Tumbling in barrels loaded with abrasive media such as limestone, preformed and fused alumina, ceramic shapes, or abrasive-loaded plastic chips can be used to remove parting line burrs. A lubricant such as soap or detergent solution (alkaline cleaner) often is used during barrel tumbling. Tumbling cycle times to remove parting line burrs range from 4 to 12 h.

Vibratory finishing also is used to finish the parting line regions (Ref 7, 8, 9, 10, 11). Abrasive-loaded plastic chips usually are used for zinc die castings because they do not mar the casting surface. Ceramic media and steel media can be used, but these media, because they have greater densities than plastic media, will indent the casting surface, leaving an "orange peel" type of surface. Coarse grit abrasives (80-grit) can remove burrs in minutes during vibratory finishing.

Resin-bonded abrasive chips remove burrs in times ranging from 1 to 4 h. The speed of finishing in vibratory finishing is controlled by the frequency and amplitude of vibration. Frequencies from 700 to 2100 vibrations/min and amplitudes from 0.8 to 6.4 mm ($\frac{1}{32}$ to $\frac{1}{4}$ in.) are used to deburr zinc die castings. Traditionally, neutral to alkaline cleaners (lubricants) have been used during vibratory finishing of zinc die castings. Acidic solutions with pH from 2.5 to 4.5 also have been used to increase the speed of metal removal and thus shorten the process cycle time (Ref 7). If tumbling or vibratory deburring is used without a cleaner, the media must be cleaned periodically to remove contamination (Ref 9). If not maintained properly, the media will contaminate, rather than clean, the castings.

**Surface Polishing.** Many die castings have sufficiently smooth surfaces that require only buffing prior to the chemical treatments used in preparation for electroplating or painting. However, others may require spot or overall polishing to remove surface defects or roughness. Spot or surface polishing is done with set-up wheels or abrasive belts with 220-mesh or finer abrasive, run at the same speeds as those used for preparing the parting lines. The abrasive surface should be lubricated. The surface finish produced by abrasive wheels or belts typically ranges from 0.2 to 0.4 μm (8 to 16 μin.).

Polishing of the casting surfaces also can be accomplished by tumbling or vibratory finishing under the conditions described previously. Generally, vibratory finishing concentrates the finishing action on the casting corners and edges, although all surfaces receive some finishing action (Ref 8). Abrasive-loaded plastic media are used for die cast zinc because they do not mar the surface. Ceramic media, which are heavier than plastic media, also are used for surface finishing; however, they may produce a slight orange peel texture. Steel media, which are significantly heavier, result in burnishing of the surface to a high luster, but they are suitable for applications for which the surface finish is secondary (Ref 8). To produce a fine, smooth finish, abrasives with 400-mesh are used with commensurate increases in finishing time. The sizes of the media vary significantly, ranging from 1.5 to 50 mm (0.06 to 2 in.) in diameter (Ref 10). Generally, the larger the diameter of the media, the rougher the surface. With proper control of the media, vibratory finishing parameters, and cycle times, buffing prior to plating with a leveling electroplate often can be eliminated. Because of its higher hardness, Alloy 27 may require a longer vibratory finishing time to receive a finish comparable to those on the lower-aluminum-content alloys (Ref 2).

The surfaces of zinc die castings can be polished smooth in centrifugal barrel finishing equipment (Ref 5, 6, 8). The drums are rotated with a peripheral speed of about 600 m/min (1970 ft/min) in an abrasive material such as ground corn cobs or nut shells mixed with a lubricant. Finishing times typically range from 5 to 10 min, and the resulting surface finish is 0.1 to 0.2 μm (4 to 8 μin.), depending on the abrasive used (Ref 6).

**Brushing** with wheel-mounted filament or fiber strands, run dry or lubricated, also is used to polish casting surfaces, particularly functional castings (Ref 7). Brushing removes sharp edges and burrs and generates fine radii. It does not result in the heavy stock removal, as does abrasive belt polishing, because it does not abrade the surface; however, it reaches internal recesses to deburr, descale, and clean.

**Controlled shot peening** can be used to smooth rough or defective castings and to remove fins, burrs, and flash from the surface (Ref 5). This process plastically deforms and densifies the casting surface and near-surface layers. That action can seal surface pores, which can create problems in subsequent electroplating and conversion coating. The shot-peening process is described in MIL-S-13165C (Ref 12), which should be consulted for selection of the peening media, shot size, peening intensity, and coverage. Those selections are based on the casting configuration, the smallest-size radii and wall thickness, and the required surface finish and contamination limits, as detailed in the specification.

**Buffing** of zinc die castings is used to smooth rough areas, eliminate polishing scratches, and produce a mirror-like finish prior to plating with conventional solutions when good leveling plating solutions are not available. If the castings have good surface finish or can be uniformly polished to a finish of 0.25 μm (10 μin.), buffing can be omitted if solutions with good leveling power are used for plating copper and nickel (Ref 5, 6).

Buffing is accomplished on cloth wheels rotated at peripheral speeds up to 2150 m/min (7000 ft/min). Slower speeds, from 1000 to 1600 m/min (3500 to 5000 ft/min), are used for smaller die castings (Ref 4, 5). Buffing wheels (buffs) usually are made of cloth (muslin or canvas) with 34 to 37 threads/cm (86 to 93 threads/in.) (Ref 5, 6). The buffs should be sewn to provide a mushing action from 6.4 to 13 mm (0.25 to 0.5 in.) while remaining rigid through the remaining depth of the buff (Ref 7, 13). The typical buffing compound used for zinc is tripoli (amorphous silica) or lime mixed with 25 to 30 wt% tallow or stearic acid to form a bar. The lubricant used should be readily saponified or emulsified to aid in removal during subsequent cleaning. In addition, only as much lubricant as is necessary should be used to facilitate subsequent cleaning. The compound is applied manually or automatically to the buffing wheels. With automated buffing systems, water slurries of fine abrasive particles and lubricants are applied to the wheels by dripping through controlled-flow tubes or by spraying. With these automated systems the castings advance through a series of buffs with varying diameters and widths, which smooth different areas of the casting surface. After buffing, the casting surfaces should be cleaned by passing them over a relatively clean, dry buffing wheel. Buffing produces surface finishes ranging from 0.025 to 0.05 μm (1 to 2 μin.) (Ref 5, 6, 14).

Buffed castings are more difficult to clean than vibratory-finished parts, especially when the buffing compounds packed in holes, grooves, and other recesses are not removed within a few hours of buffing. It is strongly recommended that the initial removal of the buffing compound and other soils in a precleaning operation be done as soon as possible after polishing and buffing. Most buffing compounds become substantially more difficult to remove after aging several days (Ref 5).

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## Solvent Cleaning

Following the mechanical finishing of die castings or the forming of wrought zinc or zinc-coated steel, the parts are cleaned to remove finishing compounds, forming lubricants, and general shop and handling soils. Traditionally, the first step in the cleaning process is solvent degreasing, vapor degreasing, or emulsion cleaning. Solvent degreasing typically is done in chlorinated hydrocarbons, such as methylene chloride, 1,1,1-trichloroethane, trichloroethylene, and perchloroethylene. Many of the commonly used solvents are being banned from use, and exposure to their vapors is being strictly regulated for health, safety, and environmental reasons (Ref 5, 15, 16). Thus, before the solvent degreasing process is considered, federal, state, and local safety and environmental laws and regulations should be consulted. In addition, current safe exposure levels for various solvents should be determined prior to their use.

Cold solvents, such as mineral spirits, methylene chloride, trichloroethylene, perchloroethylene, and 1,1,1-trichloroethane, are used with brushing to loosen packed buffing compounds. Simple dipping in cold solvents often is ineffective in removing soil; consequently, vapor degreasing with trichloroethylene or perchloroethylene is still widely practiced. Often buffed die castings are sprayed with, or dipped in, the hot solvent and then subjected to vapor degreasing to remove the last traces of grease and compound. This method is effective provided that adequate measures are taken to remove the fine abrasive and metallic particles from the parts (Ref 5).

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## Emulsion Cleaning

Emulsion cleaners can be used to soften and remove, to some extent, buffing compounds and other oils and greases (Ref 5, 6). Emulsion soak cleaners usually are made from a hydrocarbon base such as kerosene and a water solution that contains soaps, emulsifiers, and an inhibitor to prevent etching of the zinc and zinc alloy surfaces (Ref 14). They typically are used hot, at 80 °C (180 °F), and with agitation or brushing. The soak time varies from 2 to 5 min (Ref 5). A water-spray rinse should follow emulsion cleaning. The pH of emulsion cleaners should be kept between 7 and 10 to avoid attack of the zinc alloy surfaces.

The compounds not removed by an emulsion cleaner usually are sufficiently softened that they are easily removed in the alkaline spray wash that normally follows. The principal disadvantage of emulsion cleaners is the danger of carryover of hydrocarbon solvent into plating baths (Ref 5). Consequently, it is extremely important that proper alkaline cleaning and rinsing follow emulsion cleaning to ensure solvent removal from recesses and blind holes.

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## Aqueous Detergent Cleaning (Alkaline Cleaning)

Because of the increasing restrictions on the use of chlorinated hydrocarbon solvents for cleaning, water-based alkaline detergent cleaning systems are being used in place of, rather than in addition to, solvent cleaning systems (Ref 16, 17). No other solvents or cleaners match the desired characteristics of the chlorinated hydrocarbon solvents for degreasing, so much effort is being expended to develop suitable alternative cleaners.

For zinc and zinc alloy parts, a number of alkaline cleaning solutions are available and have been used after solvent cleaning processes. The aqueous-based detergents mix emulsifiers and surfactants (wetting agents) with mild alkaline phosphates, borates, or silicates to optimize properties such as oil emulsion, saponification, dirt suspension and dispersion, water softening, and rinsability. These cleaners are used as soak cleaners, often with ultrasonic agitation, or as power-spray cleaners. Some cycles employ a 2 to 3 min soak treatment followed by spray washing with the alkaline cleaner. The solution temperatures usually range from 70 to 80 °C (160 to 180 °F), but slightly lower temperatures may be more suitable for automated cleaning cycles that include more than 30 s of anodic cleaning (Ref 6). Alkaline cleaning solutions for zinc and zinc alloys are listed in Table 1. Proprietary alkaline cleaners also are available. The alkaline cleaners must have controlled pH and contain inhibitors to prevent attack of the zinc.

**Table 1 Alkaline cleaning solutions for zinc die castings**

| **Chemical** | **Soak cleaning** | **Power-spray cleaning** | **Anodic cleaning** |
|---|---|---|---|
| Sodium hydroxide, g/L | . . . | 1.5 | 0.5-2(a) |
| Sodium carbonate, g/L | . . . | 3.5 | 18 |
| Sodium triphosphate, g/L | 35 | 1.0 | 5 |
| Sodium metasilicate, g/L | . . . | 4.0 | 30(b) |
| Wetting agent, g/L(c) | 0.5 | . . . | 0.5 |
| Temperature, °C | 82 | 77 | 71-82 |
| Current density, $A/dm^2$ | . . . | . . . | 1.4-2.3 |
| Time, min | 1 or 2 | 1 or 2 | 0.5 |

(a) Solutions with a higher concentration of sodium hydroxide or a pH>12 might cause etching and the formation of a loose smut difficult to remove by rinsing.

(b) Solutions containing silicates may be more difficult to rinse than nonsilicated cleaners.

(c) Usually an alkyl sulfonate, alkyl aryl ether alcohol, and/or sodium resinate

A typical alkaline precleaning cycle may include a 1 to 2 min washing period followed by a 0.5 to 1 min draining period, a 0.5 to 1 min spray-rinse period, and a final 0.5 to 1 min draining period (Ref 5). If a spray alkaline cleaning step does not follow the soak cleaning treatment, the soak treatment should be followed by a spray rinse with warm water before electrocleaning.

Following alkaline cleaning and rinsing, parts that will be painted are often given a chromate or phosphate conversion treatment in preparation for painting.

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## Electrocleaning

The final cleaning step for zinc alloy or zinc-coated parts prior to electroplating is electrolytic, usually anodic, and is conducted in an alkaline bath (see Table 1). Electrocleaning is necessary to complete the removal of oil, grease, and soil and to ensure good electroplate adhesion (Ref 5, 6). Anodic cleaning of zinc alloys is preferred to cathodic cleaning, because the dissolution of the metal prevents the formation of nonadherent metal films resulting from impurities in the cleaning solution (Ref 6). Anodic electrocleaning also helps to remove metallic smut.

The anodic alkaline electrocleaning baths are operated at temperatures from 70 to 82 °C (160 to 180 °F) with a low direct-current voltage of 3 to 6 V and current densities of 1.4 to 3.2 A/dm$^2$ (15 to 30 A/ft$^2$) (Ref 6). The cleaning time varies from 25 to 45 s. Lower bath temperatures may be required if the cleaning time exceeds 45 s or if the transfer time to the first rinse is greater than 30 s. Operating an anodic electrocleaner at too dilute a concentration may overetch the zinc (Ref 6).

Rinsing following anodic electrocleaning should include a warm-water rinse, a cold-water rinse, and a water-spray rinse. The rinses should be agitated with air to aid in removal of the cleaner solution from holes, grooves, and other surface irregularities. Alkaline solution trapped in those features can result in process blisters following plating or painting. Rinse waters containing high concentrations of dissolved minerals should be avoided.

Electrocleaning may not be required as a pretreatment for the application of conversion coatings.

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## Acid Dipping

Prior to electroplating, the surfaces of zinc alloy parts are activated by acid dipping. This process removes oxides that formed during anodic cleaning and trace amounts of alkaline compounds that were carried over from the cleaning operations due to inadequate rinsing. Dilute sulfuric acid, 0.25 to 0.75 wt%, is most often used; the immersion time ranges from 25 to 45 s with the solution at room temperature (Ref 5, 6). Similar solutions of hydrofluoric acid or a mixture of sulfuric or hydrofluoric acids also are effective. For very mild acid dipping, citric acid can be used. All traces of black films or loosely adherent smut must be removed by the acid treatment. For die castings prone to smut, including alloys containing more than 0.25% Cu, ultrasonic agitation effectively prevents smut formation (Ref 6).

Thorough rinsing must follow acid dipping to remove all traces of acid from surface fissures, porous areas, or holes to prevent blistering of the parts at those locations after plating (Ref 5, 6, 17). A succession of two air-agitated rinses and a water-spray rinse is recommended after acid dipping. A final water-spray rinse should use deionized water that can be recycled for use in an initial rinsing stage.

Following cleaning, acid dipping, and rinsing, no water breaks should occur on the surfaces of the zinc alloy castings, wrought zinc, or zinc-coated parts (Ref 6). If water breaks occur, the parts should be recycled through the alkaline and/or electrocleaning steps after those processes have been checked for proper solution composition and temperature. Tests for cleanliness should be made routinely during production (e.g., wiping with a clean white cloth or paper should result in no soil or smut on the cloth). More sophisticated tests are available to determine the effectiveness of cleaning processes (Ref 18), but they typically are not suitable for assessing cleanliness on the line during production. Most are research tools that are used to assess new cleaning processes or modifications to cleaning solution formulations.

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## Conversion Coating Treatments

Zinc die castings that will be painted with organic coatings must be given a suitable phosphate or chromate conversion coating (Ref 19). Similarly, zinc-coated (galvanized) steel surfaces must be prepared for painting by phosphate or chromate conversion treatments, application of wash primers, annealing treatments, complex oxide treatments, or anodizing (Ref 3, 19, 20). Sometimes the zinc alloy or zinc-coated parts are used after chromating or anodizing without painting. Prior to the various conversion treatments, the zinc alloy or zinc-coated parts are degreased by solvents, alkaline cleaned, and acid dipped using the procedures described previously.

Two types of phosphate treatments are used for zinc alloy or zinc-coated parts: iron phosphate and zinc phosphate. The baths for the iron phosphate, which is applied to steel and sometimes to aluminum and zinc, are proprietary alkali metal phosphate solutions (Ref 3). The baths are operated at temperatures from 16 to 71 °C (60 to 160 °F). The phosphate coating formed is a mixture of oxides and phosphates of the base metal. Technically, there is little or no iron phosphate present on zinc alloys after treatment, but the generic name is commonly used to describe the process on all three metals. The coating weights range from 1.9 to 4.6 mg/m$^2$ (20 to 50 mg/ft$^2$). The baths are relatively simple to control, and the films that form improve the corrosion resistance and adhesion of paints and powder coatings.

Zinc phosphates are more commonly used on galvanized coatings and zinc die castings (Ref 3, 20, 21). The baths contain zinc oxide or phosphate and phosphoric acid in combination with accelerators, refining agents, and other proprietary ingredients. They produce heavier crystalline deposits than do the iron phosphate solutions. The best paint or powder coating adhesion is achieved when the coating weight is kept low, in the range from 9 to 28 mg/m$^2$ (100 to 300 mg/ft$^2$) (Ref 3).

Chromate treatments consist of a dip or spray in a dilute solution of chromium trioxide and other acids, with the proper accelerator for 5 to 30 s (Ref 20). The baths are operated at temperatures from room temperature to 54 °C (130 °F). The process produces a thin, amorphous chromate coating that increases corrosion resistance and paint adhesion.

Aqueous chromic-organic treatments, applied by dipping or roller coating, are solutions of certain water-soluble resins, properly formulated with chromium compounds (Ref 20). The film is cured or baked after application, whichever is required by the paint system to be applied.

A vinyl wash primer also is used to prepare the surfaces of galvanized parts for painting. It involves the application of an acid-bound resinous film 8 to 13 μm (0.3 to 0.5 mil) thick. The treatment is based on three primary components: a hydroxyl-containing resin, a pigment capable of reacting with the resin and an acid, and an acid capable of insolubilizing the resin by reacting with the resin, the pigment, and the zinc surface. This film usually is applied by spraying, but it may be applied by brushing, dipping, or roller coating. Under normal conditions it will dry sufficiently for recoating within 30 min, and within 8 h of application it will not be softened by organic solvents commonly used in paint coatings. It has good adhesion to the metal substrate and promotes good adhesion of most organic coatings.

Hot-dipped galvanized coatings may be given an annealing treatment under controlled conditions to alloy the coating with the base metal and to change the surface character of the zinc coating and make it more receptive to paint (Ref 20). Annealing treatments usually are performed in the mill shortly after galvanizing coils of steel. The surface produced by annealing can further be treated to enhance paint adhesion by the conversion treatment methods described previously.

The amorphous complex-oxide treatment consists of reacting to the zinc surface in an alkaline solution containing heavy metal ions for times between 5 and 30 s at 45 to 70 °C (115 to 160 °F) (Ref 20). The surface of the zinc is converted to a nonmetallic, amorphous, complex-oxide coating that inhibits corrosion and increases the adhesion and durability of paint finishes. This treatment can be carried out by immersion or spray.

Zinc die castings also can be anodized prior to use or prior to painting (Ref 21). Zinc anodizing produces an unusual fritted coating (Ref 22). Anodizing is conducted in a solution of chromic acid, phosphoric acid, and hydrofluoric acid. Alternating current is preferred, although direct current can be used (Ref 21). The anodizing process is conducted at a current density of 4.3 A/dm$^2$ (40 A/ft$^2$) and a bath temperature in the range from 66 to 82 °C (150 to 180 °F). The coating forms during an anodic spark discharge that starts at about 70 V (Ref 22). Because the anodized coating is dielectric, the voltage increases to about 200 V in order to maintain the current density as the fritted coating forms. When the power reaches 200 V (5 to 7 min), the process is terminated. The coating formed is matte green. This coating has very unusual corrosion- and abrasion-resisting properties and can be readily painted.

Following the application of a conversion coating, most commonly zinc phosphate, the treated parts can be coated with most of the organic and water-based systems available. The choice of coating will depend on the service requirements of the coated part.

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## Introduction

VITREOUS CERAMIC COATINGS are applied over substrates for a number of reasons (Ref 1). These coatings may be applied to a substrate surface to render the surface:

- Chemically more inert
- Impervious to liquids and gases
- More readily cleanable
- Smoother and more resistant to abrasion and scratching
- Mechanically stronger
- Decorative
- Aesthetically pleasing

Vitreous coatings are thin layers of glass fused onto the surface of the substrate. When the substrate is a ceramic, the coating is called a glaze. When the substrate is a metal, the coating is called a porcelain enamel. When the substrate is a glass, the coating is called a glass enamel. This article focuses on ceramic coatings for ceramic and glass substrates. Porcelain enameling is discussed in a separate article in the Section "Dip, Barrier, and Chemical Conversion Coatings," in this Volume.

The first requirement is for a strong bond between the coating and the substrate (Ref 2). The composition must fuse to a homogeneous viscous glass (or ceramic) at a temperature that is either coincident with the temperature at which the body matures or at a temperature sufficiently lower to prevent distortion of the substrate during glost firing.

During and after fusion of the coating materials, they must react with the substrate to form an intermediate bonding layer of proper thickness. If the bonding layer or interface is too thin, the coating will flake off after application and subsequent firing. If the bonding layer is too thick, the composition of the body or the coating may be degraded. The coating must also have a coefficient of thermal expansion that coincides or fits the substrate (Ref 3). When the fired ware is cooled, the coated substrate contracts. If the coefficients of thermal expansion of the coating and the substrate are not matched, stresses that lead to spalling or crazing of the coating will be introduced. The coating materials should have a low surface tension to minimize the crawling of the coating away from the edges or any holes present during firing.

The second group of properties are those associated with the use of the product, such as appearance, smoothness, porosity, and corrosion resistance to various liquids and gases. Almost all vitreous coatings are expected to be homogeneous, smooth, and hard and also to resist abrasion and scratching. Such a surface is also more apt to be impervious to liquids and gases and hence more readily cleanable. The sole exception to the desire for a smooth surface is the textured coating in which a pattern is applied for aesthetic purposes.

In many applications, chemical durability in severe service conditions is a principal reason for the selection of a ceramic coating (Ref 4). Vitreous coatings are formulated to be resistant to a variety of reagents ranging from acids, to hot water, to alkalis, to essentially all organic media. The only important exception is hydrofluoric acid, which readily attacks all silicate glasses.

For some applications, the finished ware is to be subjected to elevated temperatures while in service. This is a prime reason for the selection of ceramic coatings for cookware applications and for industrial and military applications.

The optical and appearance properties of any surface coating material are major considerations in determining which coating will be applied. Various possibilities exist for meeting the requirements of a particular application. Because vitreous coatings can be transparent or opaque; high gloss, satin, or matte; smooth, patterned, or textured; and monochrome or multicolored, the combination of requirements that meets each particular application is extensive.

## Acknowledgements

Adapted from R.A. Eppler and L.D. Gill, Glazes and Enamels, *Engineered Materials Handbook,* Vol 4, *Ceramics and Glasses,* ASM International, 1991, p 1061-1068

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## Glazes

A ceramic glaze is a vitreous coating applied to a ceramic substrate (usually a whiteware). A great variety of formulations are used as glazes (Ref 1). Ceramic ware is fired over a wide range of temperatures from 800 to >1400 °C (1470 to >2550 °F). No single glaze composition would be satisfactory over such a wide range of temperatures. A glaze that melts at low temperature will run off the substrate, react with the substrate, or volatilize if fired at a high temperature. A given glaze composition is generally useful over a temperature range of only 30 °C (55 °F). Typical firing temperatures for glazes based on application can be summarized as follows (Ref 5):

- Electronic substrates, ≈600 to 900 °C (≈1110 to 1650 °F)
- Artware glazes, ≈900 to 1050 °C (≈1650 to 1920 °F)
- Dinnerware and tile glazes, ≈1000 to 1150 °C (≈1830 to 2100 °F)
- Structural clay and sanitaryware glazes, ≈1180 to 1250 °C (≈2155 to 2280 °F)
- Porcelain glazes, ≥1300 °C (≥2370 °F)

Because of the toxicity of lead, glazes are often classified on the basis of the presence or the absence of litharge (PbO). Safe working practices require unfired glazes containing litharge to be handled carefully and to have an acceptable level of acid resistance in raw powdered form in the work environment. Finished tableware coated with a lead glaze must also possess an acceptable level of resistance to chemical attack.

Another way to classify a glaze is according to the way it is constituted. Raw glazes are prepared from mineral powders (usually oxides or carbonates) and are chemically limited to elements that can be obtained in materials having low water solubility. Frits are prepared to allow the use of water-soluble materials, which are first melted to an insoluble glass, and then quenched and broken up. For a partially fritted glaze, only the soluble materials and sufficient network former to make an insoluble glass are fritted. In an all fritted glaze, all components are melted into the frit except for necessary suspending agents.

### *Markets for Glazed Ceramics*

The total whitewares market in the United States was reported to be $3.459 billion in 1989 (Ref 6). A breakdown of the U.S. market for products using glazes is shown in the chart of Fig. 1.

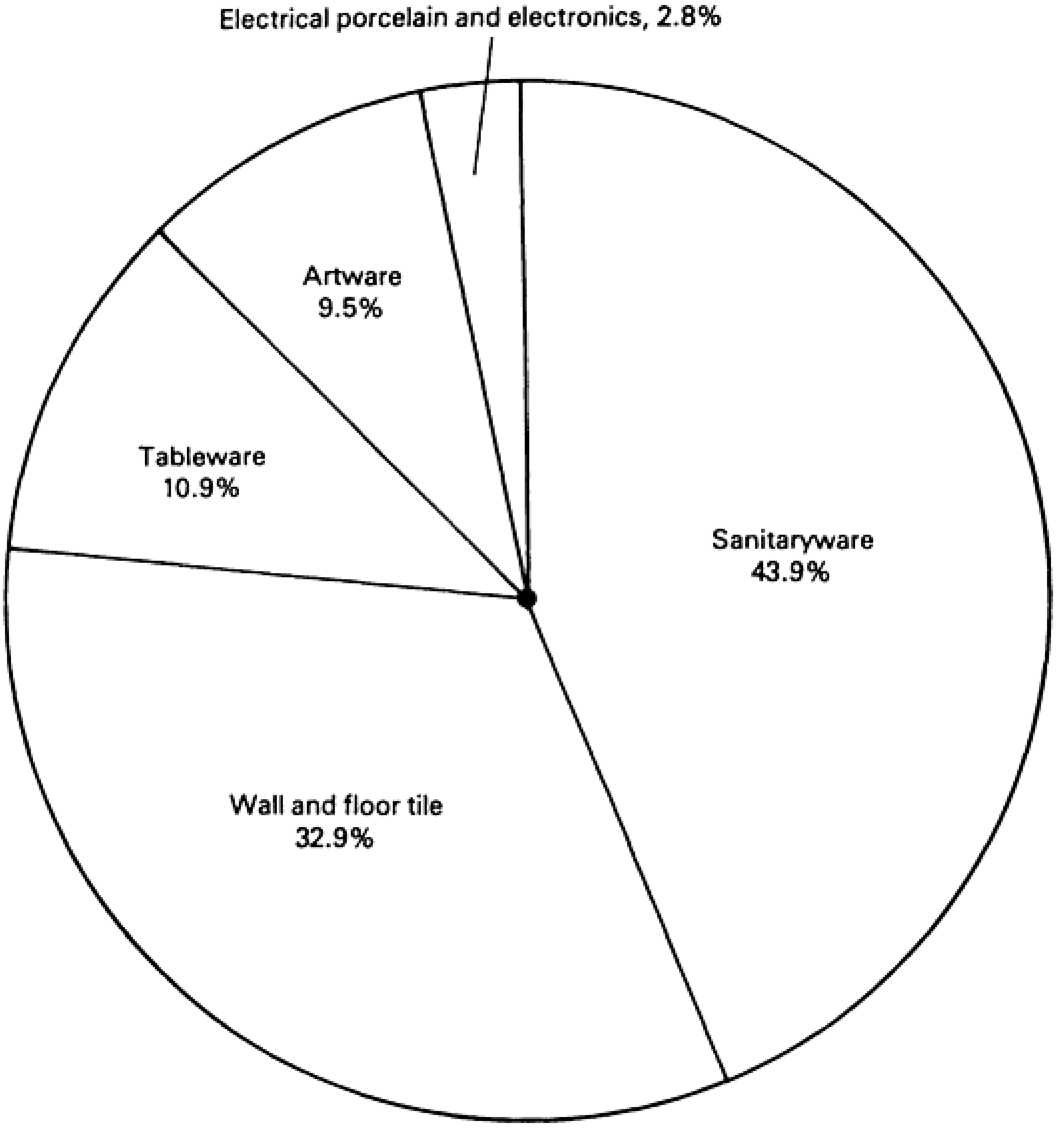

**Fig. 1 Breakdown of key segments of the $3.46 billion glaze market in the United States (1989 data)**

A ceramic coating typically makes up 10 to 15% of the total manufacturing cost of a ceramic product. The value of the properties provided by the coating usually far outweighs this cost. The protective, functional, and decorative surface that is obtained often serves as a primary selling feature of the end product.

Ceramic glazes find their way into a wide range of applications ranging from coffee mugs to automotive sparkplugs. The major markets for ceramic coatings have different requirements, but one common theme is corrosion resistance and cleanability.

Rarely sold in a ready-to-use form, ceramic glazes are usually formulated and processed for application by the end user.

### *Role of Specific Oxides in Glazes*

The commonly used oxides in glazes are $SiO_2$, $ZrO_2$, $Al_2O_3$, $B_2O_3$, CaO, SrO, BaO, MgO, ZnO, PbO, $Li_2O$, $Na_2O$, and $K_2O$ (Ref 7). Small amounts of fluorine are sometimes used as a partial substitution for oxygen.

**Silicon Dioxide.** Most glazes contain more silica than all the other constituents combined. Silica promotes low expansion, high durability, and abrasion resistance. Its only serious deficiency is its high melting point, $T_m$, of 1723 °C (3133 °F).

**Alkali Oxides.** The foremost reason for adding other oxides is to reduce the maturing temperature. The alkalis are powerful fluxes at all maturing temperatures, and their use is limited by the high thermal expansion they impart to a glaze.

**Alkaline Earths.** The alkaline earths and magnesia are effective fluxes only at >1100 °C (>2010 °F).

**Zinc oxide** is effective at >1000 °C (>1830 °F) and in modest amounts it improves the effectiveness of other fluxes.

**Lead monoxide** is a powerful flux from the lowest temperatures to ≈1150 °C (≈2100 °F), above which volatilization becomes excessive.

**Boric oxide** is effective at all temperatures. As a network former, it can be used with other oxides to get a high fluxing level. Above 15% $B_2O_3$ concentration, however, it seriously degrades the durability of the glaze.

**Alumina** contributes to the working properties of a glaze, improves acid durability, and suppresses phase separation and crystallization of the glaze.

**Zirconia** is added to a glaze to improve the alkaline durability, and, in higher concentrations, as an opacifier.

### Leadless Glazes

Tables 1 and 2 give the formulas of a number of commercial ceramic coatings. The first eight of these are leadless glazes. In these glazes, the alkali and alkaline earth oxides, together with MgO, ZnO, and $B_2O_3$, are used to provide the fluxing action.

**Table 1 Compositions of selected glazes based on mole ratio (Seger formula)**

| Oxide | Glazes | | | | | | |
|---|---|---|---|---|---|---|---|
| | **1 Hard porcelain** | **2 Soft porcelain** | **3 Sanitaryware** | **4 Bristol** | **5 Wall tile** | **6 Semivitreous dinnerware** | **7 Vitreous dinnerware** |
| $Li_2O$ | . . . | . . . | . . . | . . . | . . . | 0.047 | . . . |
| $Na_2O$ | . . . | 0.142 | 0.100 | 0.100 | 0.270 | 0.081 | 0.070 |
| $K_2O$ | 0.30 | 0.135 | 0.100 | 0.100 | 0.040 | 0.115 | 0.069 |
| MgO | . . . | 0.043 | . . . | 0.200 | 0.010 | 0.066 | 0.037 |
| CaO | 0.70 | 0.680 | 0.600 | 0.400 | 0.350 | 0.580 | 0.391 |
| ZnO | . . . | . . . | 0.200 | 0.200 | 0.320 | . . . | 0.322 |
| SrO | . . . | . . . | . . . | . . . | . . . | 0.110 | 0.071 |
| BaO | . . . | . . . | . . . | . . . | . . . | . . . | 0.039 |
| $Al_2O_3$ | 1.00 | 0.556 | 0.550 | 0.400 | 0.260 | 0.367 | 0.173 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $B_2O_3$ | . . . | . . . | . . . | . . . | 0.050 | 0.171 | 0.188 |
| $SiO_2$ | 10.00 | 4.570 | 3.000 | 3.500 | 2.650 | 2.721 | 2.224 |
| $ZrO_2$ | . . . | . . . | . . . | . . . | . . . | . . . | 0.011 |
| Ref | 3 | 8 | 2 | 2 | 9 | 10 | 11 |

| **Oxide** | **Glazes** | | | | | | |
|---|---|---|---|---|---|---|---|
| | **8**<br>**Low expansion** | **9**<br>**Cone 4 dinnerware** | **10**<br>**Cone 06 artware** | **11**<br>**Electronic** | **12**<br>**Opacified** | **13**<br>**Zinc matte** | **14**<br>**Lime matte** |
| $Li_2O$ | 0.850 | . . . | . . . | . . . | . . . | . . . | . . . |
| $Na_2O$ | . . . | 0.179 | 0.157 | . . . | 0.111 | 0.087 | 0.040 |
| $K_2O$ | 0.150 | 0.066 | . . . | . . . | 0.083 | 0.052 | 0.059 |
| MgO | . . . | . . . | . . . | . . . | . . . | 0.097 | . . . |
| CaO | . . . | 0.494 | 0.218 | . . . | 0.407 | 0.152 | 0.524 |
| ZnO | . . . | . . . | . . . | . . . | 0.371 | 0.364 | . . . |
| BaO | . . . | . . . | . . . | . . . | 0.028 | . . . | . . . |
| PbO | . . . | 0.261 | 0.625 | 1.000 | . . . | 0.247 | 0.377 |
| $Al_2O_3$ | 0.740 | 0.340 | 0.273 | . . . | 0.406 | 0.443 | 0.262 |
| $B_2O_3$ | 0.200 | 0.314 | 0.507 | . . . | 0.143 | 0.142 | 0.176 |
| $SiO_2$ | 2.510 | 3.369 | 2.792 | 0.500 | 2.019 | 1.566 | 1.746 |
| $ZrO_2$ | . . . | . . . | 0.023 | . . . | 0.248 | 0.210 | 0.211 |
| Ref | 12 | 13 | 14 | 15 | 16 | 2 | 2 |

**Table 2 Compositions of selected glazes based on weight percent**

| **Oxide** | **Glazes** | | | | | | |
|---|---|---|---|---|---|---|---|
| | **1 Hard porcelain** | **2 Soft porcelain** | **3 Sanitaryware** | **4 Bristol** | **5 Wall tile** | **6 Semivitreous dinnerware** | **7 Vitreous dinnerware** |
| $Li_2O$ | . . . | . . . | . . . | . . . | . . . | 0.51 | . . . |
| $Na_2O$ | . . . | 2.24 | 2.05 | 1.98 | 6.54 | 1.81 | 1.81 |
| $K_2O$ | 3.67 | 3.24 | 3.12 | 3.01 | 1.47 | 3.92 | 2.71 |
| MgO | . . . | 0.44 | . . . | 2.57 | 0.16 | 0.96 | 0.62 |
| CaO | 5.10 | 9.71 | 11.15 | 7.16 | 7.67 | 11.76 | 9.16 |
| ZnO | . . . | . . . | 5.39 | 5.19 | 10.18 | . . . | 10.94 |
| SrO | . . . | . . . | . . . | . . . | . . . | 4.12 | 3.07 |
| BaO | . . . | . . . | . . . | . . . | . . . | . . . | 2.50 |
| $Al_2O_3$ | 13.24 | 14.44 | 18.58 | 13.01 | 10.36 | 13.53 | 7.37 |
| $B_2O_3$ | . . . | . . . | . . . | . . . | 1.36 | 4.30 | 5.47 |
| $SiO_2$ | 78.00 | 69.90 | 59.71 | 67.09 | 62.25 | 59.09 | 55.79 |
| $ZrO_2$ | . . . | . . . | . . . | . . . | . . . | . . . | 0.57 |

| **Oxide** | **Glazes** | | | | | | |
|---|---|---|---|---|---|---|---|
| | **8 Low expansion** | **9 Cone 4 dinnerware** | **10 Cone 06 artware** | **11 Electronic** | **12 Opacified** | **13 Zinc matte** | **14 Lime matte** |
| $Li_2O$ | 9.08 | . . . | . . . | . . . | . . . | . . . | . . . |
| $Na_2O$ | . . . | 3.06 | 2.46 | . . . | 2.50 | 1.91 | 0.85 |
| $K_2O$ | 5.05 | 1.72 | . . . | . . . | 2.84 | 1.73 | 1.91 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| MgO | . . . | . . . | . . . | . . . | . . . | 1.38 | . . . |
| CaO | . . . | 7.65 | 3.09 | . . . | 8.29 | 3.02 | 10.08 |
| ZnO | . . . | . . . | . . . | . . . | 10.97 | 10.48 | . . . |
| BaO | . . . | . . . | . . . | . . . | 1.56 | . . . | . . . |
| PbO | . . . | 16.08 | 35.30 | 88.14 | . . . | 19.52 | 28.87 |
| $Al_2O_3$ | 26.98 | 9.57 | 7.04 | . . . | 15.04 | 15.99 | 9.17 |
| $B_2O_3$ | 4.98 | 6.04 | 8.93 | . . . | 3.62 | 3.50 | 4.20 |
| $SiO_2$ | 53.91 | 55.88 | 42.45 | 11.86 | 44.07 | 33.31 | 35.99 |
| $ZrO_2$ | . . . | . . . | 0.72 | . . . | 11.10 | 9.16 | 8.92 |

**Hard Porcelain Glaze.** Glaze 1 is a feldspathic glaze suitable for use only on the highest firing hard paste porcelains (Ref 3).

**Soft Porcelain Glaze.** For porcelains fired at lower temperatures, such as soft paste porcelain or hard stoneware, glaze 2 would be satisfactory (Ref 8). This glaze is typical of that used on medieval Chinese porcelains.

**Sanitaryware Glaze.** Glaze 3 is a sanitaryware glaze (Ref 5). It is derived from the soft paste porcelain glaze by the addition of ZnO in large quantities.

**Bristol glaze** (glaze 4) is used to produce an opaque white coating on stoneware and other dark-colored bodies.

**Fast-fire wall tile glazes** are derived from the Bristol glaze by increasing the amount of fluxes to increase the melting rate (Ref 9). Glaze 5 is a typical example.

**Semivitreous Dinnerware Glaze.** The development of glazes for dinnerware is more difficult because of the lower expansion of the bodies. Glaze 6 is an example of a glaze for semivitreous dinnerware (Ref 10). Several alkaline earths are used to improve the melting and surface properties.

**Hotel China Glaze.** Leadless glazes for vitreous hotel china (such as glaze 7) are a very recent development (Ref 11).

**Low Expansion Glaze.** Zircon and cordierite bodies are even lower in expansion, requiring a semicrystalline glaze, such as glaze 8 (Ref 12).

### *Lead-Containing Glazes*

Litharge is used in glazes for several reasons (Ref 20). The strong fluxing action of PbO allows the formulation of glazes that mature at temperatures lower than their leadless counterparts, thus leading to greater flexibility in the formulation of the glaze to obtain low expansion, smooth surface, and maturing of the glaze over a wider firing range. Litharge imparts low surface tension for a smooth surface and a high index of refraction that results in a brilliant appearance. Glazes containing litharge heal over defects in the glaze surface more readily and are usually more corrosion resistant. This combination of desirable properties is difficult to achieve in leadless glazes on a production scale.

However, litharge also has disadvantages as a glaze constituent. Lead glazed ware must be fired in a strongly oxidizing atmosphere because lead is readily reduced. Lead oxide cannot be used above 1150 °C (2100 °F) due to volatility. Most importantly, litharge is highly toxic. Moreover, lead poisoning is very difficult to diagnose because its symptoms are similar to other ailments. Therefore, every possible precaution must be taken when preparing lead glazes to avoid poisoning, and ware intended for food contact should be tested as noted below to ensure consumer protection.

**Cone 4 Dinnerware Glaze.** Glaze 9 in Tables 1 and 2 is an example of a lead-containing dinnerware glaze for cone 4 (1100 °C, or 2010 °F) (Ref 13). (*Cone* refers to pyrometric cones, which are a traditional means of measuring time/temperature thermal cycles, and are still one on the most accurate methods for recording the amount of thermal "work" applied to a kiln of ware. Pyrometric cones are small, triangular pyramids prepared from carefully formulated ceramic compounds designed to soften and melt under precise conditions of temperature and time. A series of cones, which are given numbers corresponding to temperatures at which they soften, are placed in the kiln with the ware. The cones are observed during firing to assist in temperature control, and are examined after the fire to indicate and record the degree of firing achieved.)

**Cone 06 Artware Glaze.** Glaze 10 is an example of a clear glaze suitable for use on artware and hobbyware bodies at cone 06 (1000 °C, or 1830 °F) (Ref 14).

**Electronic Glaze.** The glazes used on alumina packages for integrated circuits (ICs) to seal the package represent the lowest firing lead-containing glazes. Glaze 11 is an example of such a glaze, which can be fired as low as 550 °C (1020 °F) (Ref 15).

## *Heavy-Metal Release*

If lead-containing glazes are not properly formulated, they may be less resistant to acid attack, which results in the release of lead. If such glazes are used in contact with food or drink, lead poisoning of the user may result. Cadmium oxide, which is considerably more toxic than lead oxide (Ref 21), is only used in ceramic coatings in connection with the use of cadmium sulfoselenide pigments, which already contain large amounts of cadmium.

To control this problem under production conditions, standard tests have been developed for determining the lead and cadmium content released from glazed surfaces (Table 3). A sample is exposed to a 4% acetic acid solution for 24 h at room temperature while covered. The concentration in ppm of lead and cadmium in the solution is then determined.

**Table 3 Standard test methods for determining the lead and cadmium content released from glazed and enamel surfaces used for food preparation when exposed to attack by acetic acid**

| ASTM standard | Test method | Ref |
|---|---|---|
| C 738 | Lead and cadmium extracted from glazed ceramic surfaces | 22 |
| C 872 | Lead and cadmium release from porcelain enamel surfaces | 23 |
| C 895 | Lead and cadmium extracted from glazed ceramic tile | 22 |
| C 927 | Lead and cadmium extracted from the lip and rim area of glass tumblers externally decorated with ceramic glass enamels | 22 |
| C 1034 | Lead and cadmium extracted from glazed ceramic cookware | 22 |

**FDA Guidelines.** The current United States Food and Drug Administration (FDA) standard limits for lead released are 7 ppm average for six samples of flatware, 5 ppm maximum of six samples of small holloware, and 2.5 ppm maximum of six samples of large holloware (Ref 24). The standard limits for Cd are $\frac{1}{2}$ ppm average for six samples of flatware, $\frac{1}{2}$ ppm maximum of six samples of small holloware, and $\frac{1}{4}$ ppm maximum of six samples of large holloware. These limits are currently under review, and lower levels may possibly be applicable by the time this article is published (Ref 25). Because of statistical fluctuations in the measurements, operating standards must be less than half these guideline values (Ref 26).

In the FDA test, lead-containing commercial dinnerware glazes usually release $\frac{1}{2}$ to 2 ppm (Ref 20). Properly designed commercial artware will be somewhat higher. In contrast, ware implicated in health cases have all released in excess of 50 ppm Pb.

Most glazes have no added cadmium oxide. Those that do contain cadmium will release 0.1 to 0.2 ppm even when properly formulated (Ref 21). For this reason, it is best if CdS-Se colors are not used as surface decorations on glass surfaces that will come in contact with food or drink.

The issue of lead and cadmium release from glassware decorated with glass enamels has also been addressed through a voluntary quality-control program adopted by the ceramic industry (Ref 27). The lip and rim area (that is, the top 20 mm, or $\frac{25}{32}$ in.) of the decorated glass must not leach greater than 50 ppm Pb or 3.5 ppm Cd when analyzed by a modification of the existing ceramic ware test (see Table 3). Failure of one glass in a sample of six is cause for rejection.

Numerous factors must be considered in formulating and processing a glaze to achieve low lead and cadmium release:

- Total glaze composition
- Thermal history during processing
- Glaze application techniques
- Glaze-body solution at the interface during firing
- Atmospheric conditions that exist during firing

Of all these parameters, the most important is the glaze composition.

**Heavy-Metal Release Performance Rating.** A figure of merit (FM) has been developed to predict the heavy-metal release or acid resistance of a glaze from its composition (Ref 14). Silica, alumina, zirconia, and similar ions such as titania and tin oxide are effective in lowering the lead release (LR) of a glaze:

$$LR_A = 2[Al_2O_3 + [SiO_2] + [TiO_2] + [ZrO_2] + [SnO_2] \quad \textbf{(Eq 1)}$$

The concentrations given in Eq 1 are expressed in molar ratio. The factor 2 arises from the fact that there are 2 equivalents of aluminum ions per equivalent of $Al_2O_3$.

It has also been shown that alkalis, alkaline earths, $B_2O_3$, fluoride, phosphate, ZnO, CdO, and PbO are all more or less detrimental to the lead release in a glaze:

$$LR_B = ([Li_2O] + [Na_2O] + [K_2O] + [B_2O_3] + [P_2O_5]) + [MgO] + [CaO] + [SrO] + [BaO] + [F] + [ZnO] + [PbO] \quad \textbf{(Eq 2)}$$

Combining these terms gives the figure of merit:

$$FM = LR_A/(LR_B)^{1/2} \quad \textbf{(Eq 3)}$$

When the figure of merit is >2.05, the lead release is below the standard. When it is <1.80, some measurements are always greater than the standard. This figure of merit applies to all single-phase glazes. In a glass-crystal-line system, the formulation of the least durable component must be used in the calculation.

### Opaque Glazes

In opaque glazes, the transmittance of the glaze has been reduced to hide the body. Opacity is introduced into ceramic coatings by the addition of a substance that will disperse in the coating as discrete particles to scatter and reflect the incident light (Ref 5). This dispersed substance must have a refractive index that differs from that of the clear ceramic coating.

The refractive index, $n_D$, of most glasses is 1.5 to 1.6. Typical opacifiers include $SnO_2$ ($n_D$ = 2.04), $ZrO_2$ ($n_D$ = 2.40), $ZrSiO_4$ ($n_D$ = 1.85), and $TiO_2$ ($n_D$ = 2.5 for anatase and 2.7 for rutile). Opacified glaze (glaze 12) in Tables 1 and 2 is an example of a glaze fired at >1000 °C (>1830 °F) where zircon is the opacifier of choice (Ref 16).

In coatings fired at <1000 °C (<1830 °F), titania in the anatase phase is the best opacifier because of its high refractive index. The temperature limit is the point at which anatase inverts to rutile. Rutile crystals are unsuitable because they grow too large in glass for opacification and then have a yellow color.

### Satin and Matte Glazes

Satin and matte effects are also due to dispersed crystals in the glaze (Ref 5). The crystals must be very small and evenly dispersed if the glaze is to have a smooth velvet appearance. Matte glazes are always somewhat opaque. The amount of opacity depends on the difference in refractive index between glaze and crystal and can be fairly small. Glaze 13 in Tables 1 and 2 is an example of a zinc matte glaze where the crystal is willemite ($Zn_2SiO_4$) (Ref 2). Glaze 14 is a lime matte glaze with a wollastonite ($CaSiO_3$) crystal.

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## Glass Enamels

Glass enamels are applied to glass for decorative purposes and not to improve chemical durability or cleanability. Because these coatings are matured at temperatures below the deformation point of the glass substrate (540 to 650 °C, or 1000 to 1200 °F) and require larger quantities of fluxing elements, corrosion resistance can be difficult to obtain.

Glass enamels are produced in ready-to-use form (for example, paste, thermoplastics, spray media, and ultraviolet curable media) by a few select manufacturers. These enamels are rarely compounded by the end user and represent a specialty product that is more akin to organic paints than to other ceramic coatings.

The markets for this specialty product are categorized as tableware, glass containers, architectural, lighting, and automotive. There are no published figures on the value of the specific portion of the glass market that is decorated with glass enamels.

As supplied to the user, glass enamels are mechanical mixtures of pigments (see the section "Ceramic Decoration" in this article), fluxes, and organic suspending media. The requirement for low maturing temperatures necessitates the use of very high lead-oxide containing borosilicates for the flux. The industry relies on in-house control tests to ensure acceptable levels of lead release from decorated areas that might come in contact with food or drink (see the section on "Heavy-Metal Release" in this article).

The organic suspending media for glass enamels are similar to materials used to make organic paints.

## Ceramic Decoration

**Techniques for Coloring Vitreous Coatings.** There are a number of ways to obtain color in a ceramic coating (Ref 28). In one method, certain transition metal ions can be melted into a glass when it is made. While suitable for bulk glass, this method is rarely used for coatings because adequate tinting strength and the purity of color cannot be obtained by this process.

A second method to obtain color is to induce the precipitation of a colored crystal in a transparent matrix. Certain materials dissolve to some extent in a vitreous material at high temperature. When the temperature is reduced, the solubility is also reduced and precipitation occurs. This method is used for opacification (that is, the production of an opaque white color). Normally, some or all of the opacifier added to the coating dissolves during the firing process and recrystallizes upon cooling. For oxide colors other than white, however, this method lacks the necessary control for reproducible results and is seldom used.

The third method to obtain color in a vitreous matrix is to disperse in that matrix one or more insoluble crystals that are colored. The color of the crystal is then imparted to the transparent matrix. This method is the one most commonly used to introduce color to vitreous coatings.

**Pigment Systems.** To be suitable as a ceramic pigment, a material must have a high tinting strength, a high refractive index, and be free of grayness. It must also possess stability under the high temperatures and corrosive environments encountered in the firing of glazes (Ref 29). Most ceramic pigments are complex oxides (see Table 4) with the lone exception being the cadmium sulfoselenide red pigments.

**Table 4 Inorganic pigments to impart colors to ceramic coatings**

| **Pigment system** | **CAS registry number**(a) | **Chemical formula** | **DCMA number**(b) |
|---|---|---|---|
| **Pink and purple** | | | |
| Chrome-alumina-pink spinel | 68201-65-0 | $Zn(Al,Cr)_2O_4$ | 13-32-5 |
| Chrome-alumina-pink corundum | 68187-27-9 | $(Al,Cr)_2O_3$ | 3-03-5 |
| Manganese-alumina-pink corundum | 68186-99-2 | $(Al,Mn)_2O_3$ | 3-04-5 |
| Zirconium-iron pink zircon | 68187-13-3 | $(Zr,Fe)SiO_4$ | 14-44-5 |
| Chrome-tin orchid cassiterite | 68187-53-1 | $(Sn,Cr)O_2$ | 11-23-5 |
| Chrome-tin pink sphene | 68187-12-2 | $CaOSnO_2SiO_2$:Cr | 12-25-5 |
| **Brown** | | | |
| Zinc-iron-chromite brown spinel | 68186-88-9 | $(Zn,Fe)(Fe,Cr)_2O_4$ | 13-37-7 |
| Iron-chromite brown spinel | 68187-09-7 | $Fe(Fe,Cr)_2O_4$ | 13-33-7 |
| Iron-titanium brown spinel | 68187-02-0 | $Fe_2TiO_4$ | 13-34-7 |
| Nickel-ferrite brown spinel | 68187-10-0 | $NiFe_2O_4$ | 13-35-7 |
| Zinc-ferrite brown spinel | 68187-51-9 | $(Zn,Fe)Fe_2O_4$ | 13-36-7 |
| Iron brown hematite | 68187-35-9 | $Fe_2O_3$ | 3-06-7 |
| Chrome-iron-manganese brown spinel | 68555-06-6 | $(Fe,Mn)(Fe,Cr,Mn)_2O_4$ | 13-48-7 |

|  |  |  |  |
|---|---|---|---|
| Chromium-manganese-zinc brown spinel | 71750-83-9 | $(Zn,Mn)Cr_{2}O_{4}$ | 13-51-7 |
| **Yellow** |  |  |  |
| Zirconium-vanadium yellow baddeleyite | 68187-01-9 | $(Zr,V)O_{2}$ | 1-01-4 |
| Tin-vanadium yellow cassiterite | 68186-93-6 | $(Sn,V)O_{2}$ | 11-22-4 |
| Zirconium-praseodymium yellow zircon | 68187-15-5 | $(Zr,Pr)SiO_{4}$ | 14-43-4 |
| Lead-antimonate yellow pyrochlore | 68187-20-2 | $Pb_{2}Sb_{2}O_{7}$ | 10-14-4 |
| Nickel-antimony-titanium yellow rutile | 71077-18-4 | $(Ti,Ni,Sb)O_{2}$ | 11-15-4 |
| Nickel-niobium-titanium yellow rutile | 68611-43-8 | $(Ti,Ni,Nb)O_{2}$ | 11-16-4 |
| Chrome-antimony-titanium buff rutile | 68186-90-3 | $(Ti,Cr,Sb)O_{2}$ | 11-17-6 |
| Chrome-niobium-titanium buff rutile | 68611-42-7 | $(Ti,Cr,Nb)O_{2}$ | 11-18-6 |
| Chrome-tungsten-titanium buff rutile | 68186-92-5 | $(Ti,Cr,W)O_{2}$ | 11-19-6 |
| Manganese-antimony-titanium buff rutile | 68412-38-4 | $(Ti,Mn,Sb)O_{2}$ | 11-20-6 |
| **Green** |  |  |  |
| Chromium-green hematite | 68909-79-5 | $(Cr,Fe)_{2}O_{3}$ | 3-05-3 |
| Cobalt-chromite blue-green spinel | 68187-11-1 | $Co(Al_{2}Cr)_{2}O_{4}$ | 13-29-2 |
| Cobalt-chromite green spinel | 68187-49-5 | $CoCr_{2}O_{4}$ | 13-30-3 |
| Cobalt-titanate green spinel | 68186-85-6 | $Co_{2}TiO_{4}$ | 13-31-3 |
| Victoria green garnet | 68553-01-5 | $3CaOCr_{2}O_{3}3SiO_{2}$ | 4-07-3 |
| Nickel-silicate green olivine | 68515-84-4 | $Ni_{2}SiO_{4}$ | 5-45-3 |
| **Blue** |  |  |  |
| Cobalt-aluminate blue spinel | 68186-86-7 | $CoAl_{2}O_{4}$ | 13-26-2 |

| | | | |
|---|---|---|---|
| Cobalt-zinc-aluminate blue spinel | 68186-87-8 | $(Co,Zn)Al_2O_4$ | 13-28-2 |
| Cobalt-silicate blue olivine | 68187-40-6 | $Co_2SiO_4$ | 5-08-2 |
| Cobalt-zinc-silicate blue phenacite | 68412-74-8 | $(Co,Zn)_2SiO_4$ | 7-10-2 |
| Cobalt-tin blue-gray spinel | 68187-05-3 | $Co_2SnO_2$ | 13-27-2 |
| Cobalt-tin-alumina blue spinel | 68608-09-3 | $CoAl_2O_4/Co_2SnO_4$ | 13-49-2 |
| Zirconium-vanadium blue zircon | 68186-95-8 | $(Zr,V)SiO_4$ | 14-42-2 |
| **Black** | | | |
| Iron-cobalt black spinel | 68187-50-8 | $(Fe,Co)Fe_2O_4$ | 13-39-9 |
| Iron-cobalt-chromite black spinel | 68186-97-0 | $(Co,Fe)(Fe,Cr)_2O_4$ | 13-40-9 |
| Manganese-ferrite black spinel | 68186-94-7 | $(Fe,Mn)(Fe,Mn)_2O_4$ | 13-41-9 |
| Copper-chromite black spinel | 68186-91-4 | $CuCr_2O_4$ | 13-38-9 |
| Chromium black hematite | 68909-79-5 | $(Cr,Fe)_2O_3$ | 3-05-3 |
| Chromium-iron-nickel black spinel | 71631-15-7 | $(Ni,Fe)(Cr,Fe)_2O_4$ | 13-50-9 |
| **Gray** | | | |
| Cobalt-nickel gray periclase | 68186-89-0 | $(Co,Ni)O$ | 6-09-8 |
| Titanium-vanadium-antimony gray rutile | 68187-00-8 | $(Ti,V,Sb)O_2$ | 11-21-8 |
| Tin-antimony gray cassiterite | 68187-54-2 | $(Sn,Sb)O_2$ | 11-24-8 |

Source: Ref 28, 30

(a) CAS, Chemical Abstract Service.

(b) DCMA, Dry Color Manufacturers' Association.

***Red Pigments.*** Orange, red, and dark red colors are obtained only by the use of the cadmium sulfoselenide pigments (Ref 21, 31). Because cadmium compounds are highly toxic (Ref 32), the cadmium sulfoselenide pigments should not be used in applications that will come in contact with food and drink. Moreover, these pigments must also be handled with great care to avoid the possibility of ingestion.

***Pink and Purple Pigments.*** Chrome alumina pinks (Ref 33) impart pink shades in glazes suitably formulated. The manganese alumina pink is a very pure clean pink, but it is difficult to manufacture. The most stable pink pigment is the iron-doped zircon system (Ref 34) in which the shades of color extend from pink to coral. The chrome-tin system is the only family that can produce purple and maroon shades as well as a pink shade (Ref 35).

***Brown Pigments.*** The zinc-iron-chromite spinels (Ref 36) produce a wide palette of tan and brown shades. The other browns are variations of this system for specific applications.

***Yellow Pigments.*** Zirconia vanadia yellows are economical pigments for use with coatings fired at >1000 °C (>1830 °F) when high tinting strength is not required (Ref 37). Tin vanadium yellows are a strong yellow color but are very costly to produce (Ref 38). The praseodymium zircon pigments have excellent tinting strength in coatings fired to as high as cone 10 (Ref 34). For lower-temperature applications, the tinting strength of the lead antimonate pigment is unsurpassed with the exception of the cadmium sulfoselenides. The rutile pigments yield yellow, orange yellow, or maple shades useful in porcelain enamels and glass enamels.

***Green Pigments.*** Green $Cr_2O_3$ may be used in a few applications (Ref 39). The zinc-alumina-chromite blue-green pigments give shades from blue to blue-green when used in strong masstones. The Victoria green gives a transparent bright green color. Because of difficulties inherent in the use of chromium-containing pigments, many green ceramic glazes are now made with zircon pigments (Ref 34). Stable greens are obtained with a blend of about 2 parts of the praseodymium zircon yellow to 1 part of the vanadium zircon blue.

***Blue Pigments.*** Cobalt blues, both the spinel ($CoAl_2O_4$) and the silicate ($Co_2SiO_4$) forms, are the highest tinting strength colors used in ceramics (Ref 40). At the higher firing temperatures used for ceramic glazes, they often cause a bleeding defect. At these specific temperatures, the vanadium-doped zircon blue is used (Ref 34).

***Black Pigments.*** Black ceramic pigments are formed by mixtures of several oxides to form the spinel structure (Ref 41). The one exception is the chromium black hematite, an inexpensive pigment suitable for use in zinc-free coatings (Ref 42).

***Gray Pigments.*** The cobalt-nickel gray periclase uses zirconia or zircon as a carrier for various ingredients of blacks such as cobalt, nickel, iron, and chromium oxides. The titanium-vanadium rutile can be used in porcelain enamels.

**Pigment Application in Coatings.** When selecting pigments for a specific coating application, consideration must be given to the following parameters (Ref 43):

- Processing stability requirements
- Pigment uniformity and reproducibility
- Particle size distribution
- Compatibility of all materials to be used

An engobe or body stain must be stable to the bisque fire. (*Engobe* is a slip coating applied to a ceramic body for imparting color, opacity, or other characteristics.) An underglaze color or a colored glaze must be stable to the glost fire and to corrosion by the molten glaze ingredients. An overglaze or glass enamel must only be stable to the decorating fire and to corrosion by the molten flux used in the application.

For most ceramic pigments, uniform and reproducible manufacture requires great care. To avoid specking in a blend, no component should be <10% of the mix.

Most calcined ceramic pigments are in the 1 to 10 μm (40 to 400 μin.) range in mean particle size, with no residue on a 325 mesh (44 μm) screen. The optimum particle size for an application is the largest size that gives uniform dispersion and adequate strength in opacified coatings.

A ceramic pigment must function as a component in a glaze or porcelain enamel system. Thus, it must be compatible with the other components (that is, the glaze itself, the opacifier(s), and the other additives).

**Pigment Cost Factors Availability.** Owing to the limited market and the variety and complexity of the products, ceramic pigments are manufactured by specialty firms and not by the users. In 1991, the cost of ceramic pigments ranged from $9 to $50/kg ($4 to $20/lb) or even higher, depending on the elemental composition and the processing required.

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## Surface Engineering for Chemical Activity

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### Introduction

A CATALYST is a substance that accelerates the rate of a chemical reaction toward equilibrium without becoming consumed in the process. The process is cyclic, in that an active catalytic site first forms a complex with adsorbing reactants, and then forms products that desorb, restoring the original site. Catalysts are available in many physical forms, including particulates (tablets, microspheres, etc.), powders for slurry-phase reactions, and washcoated honeycombs or monoliths for fixed-bed reactors. The form that is selected strongly depends on the process being catalyzed.

A catalyst must be designed to have high activity and selectivity. (The *activity* of a catalyst refers to the rate at which it causes the reaction to proceed to chemical equilibrium. *Selectivity* is a measure of the extent to which a catalyst accelerates the reaction to form one or more of the desired products.)

The chemical process being catalyzed should have a high productivity within a specified reactor volume, with high reaction rates for the desired reactions and low rates for undesired reaction pathways. A catalyst also must have sufficient durability, that is, a certain lifetime will be required of it, depending on the process in which it is used. Factors that can influence durability include thermal and hydrothermal stability, resistance to poisons, and mechanical strength. Potential poisons can be either inorganic in nature (sulfur, lead, or phosphorus) or organic (carbon deposition), depending on the process. The mechanical strength of a catalyst can sometimes be determined by measuring crushing strength, attrition resistance, or thermal shock.

## Acknowledgement

The authors would like to thank Dr. Robert J. Farrauto for his suggestions and for editing this article.

## Catalyst Preparation

In the past, the manufacturing of catalysts was regarded to be more of an art than a science. Successful recipes were acquired by trial and error, rather than through scientific understanding and careful process design. However, since the 1980s, the design of catalysts with specific and controlled properties has become possible.

In many catalytic processes, the number of reactant molecules that are converted to products in a given time period is directly related to the number of catalytic sites available. To increase the availability of active sites to reactants, catalytic materials are often dispersed on a highly porous, high-surface-area, thermally stable carrier. This generally stabilizes the active sites by preventing their migration and coalescence.

The most commonly used method for preparing supported metal and metal oxide catalysts involves two steps. First, it is necessary to distribute precursor compounds containing the catalytic component (metal salts, cations, or clusters) within the pore structure of the high-surface-area carriers, using impregnation, ion exchange, or precipitation. Second, the supported precursors must be transformed into catalytically active phases using one or more of these pretreatment steps: drying, calcination (heating to high temperatures in air), reduction (treating with reducing agents such as hydrogen gas or hydrazine), and sulfidation.

In some catalytic applications, nonsupported metal oxides or mixed metal oxides can be used. Generally, these catalysts are prepared by precipitation from aqueous metal salt solutions. Some processes use nonsupported metal wire gauzes. For example, platinum-rhodium alloy gauzes are used for nitric acid production by the oxidation of ammonia.

Some important commercial processes that utilize catalysts prepared by the procedures described in this article are given in Table 1. This article is intended as a very short review of the most general catalyst preparation procedures. The references should be consulted as sources of more complete information.

**Table 1 Industrial processes and relevant catalysts**

| **Application** | **Reaction** | **Active catalytic component** |
|---|---|---|
| **Chemicals** | | |
| Steam reforming ($H_2$ production) | $CH_4 + H_2O \rightarrow 3H_2 + CO$ | $Ni/Al_2O_3$ (pellet) |
| Methanol synthesis | $2H_2 + CO \rightarrow CH_3OH$ | Cu, $ZnO/Al_2O_3$ (pellet) |

| | | |
|---|---|---|
| Ammonia synthesis | $3H_2 + N_2 \rightarrow 2NH_3$ | Bulk Fe (pellet) |
| Hydrogenation | (1) Fats and oils + $H_2$ $\rightarrow$ hydrogenated products | $Ni/Al_2O_3$ (powder) |
| | (2) Organic functional groups + $H_2$ $\rightarrow$ hydrogenated products | Pd or Pt/carbon (powder) |
| | | $CuO\text{-}Cr_2O_3$ (powder) |
| Polyethylene synthesis | $CH_2{=}CH_2 \rightarrow CH_3(CH_2)_nCH_3$ | $Cr_2O_3/SiO_2$ (powder) |
| Nitric acid synthesis | $4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$ | PtRh gauze |
| Sulfuric acid production | $SO_2 + O_2 \rightarrow SO_3\ H\,\underline{2}\,O\ H_2SO_4$ | $V_2O_5/SiO_2$ (pellet) |
| **Environmental processes: catalysts on monoliths** | | |
| Three-way catalyst automotive catalyst | CO + hydrocarbons + NO $\rightarrow$ $CO_2 + H_2O + N_2$ | Pt, Rh, $Pd/Al_2O_3/Ce$ |
| Volatile organic compound destruction | Hydrocarbons + $O_2 \rightarrow CO_2 + H_2O$ | $Pt/Al_2O_3$ |
| Selective catalytic reduction of $NO_x$ | $NH_3 + NO_x\ O_2N_2 + 3/2H_2O$ | $V_2O_5/TiO_2$ |
| Ozone abatement | $2O_3 \rightarrow 3O_2$ | $Pd/Al_2O_3$ |
| **Petroleum processes** | | |
| Fluid catalytic cracking to produce gasoline | High- $\rightarrow$ low-molecular-weight hydrocarbon ($C_5$-$C_{13}$) | Acidic *Y* zeolite in |
| | | $SiO_2/Al_2O_3$ matrix (microspheres) |
| Catalytic reforming to produce high-octane gasoline | (1) Dehydrogenation | Pt, PtRe, or PtSn on acidified $Al_2O_3$ (pellet) |
| | (2)Isomerization | |
| | (3)Aromization | |
| Methanol to gasoline process | $CH_3OH \rightarrow$ aromatics | ZSM-5 zeolite (pellet) |
| Paraffin isomerization | Linear $\rightarrow$ branched hydrocarbons | Pt/H mordenite in alumina matrix (pellet) |

**Impregnation** is one of the simplest ways to prepare a supported metal or metal oxide catalyst. A porous carrier with a high internal surface area, such as alumina, silica, and titania, is contacted with an impregnating solution, usually aqueous, of one or more metallic salts or compounds.

The carrier and the impregnated metal compound are then dried and subjected to further pretreatments, such as calcination and/or reduction before use. Drying at approximately 100 °C (210 °F) in air, followed by calcination to higher temperatures, is a common method used to decompose metal salts and to fix active metal oxide components on carriers. For example, silica can be impregnated with an ammonium metavanadate solution, and then dried and calcined to give a catalyst (vanadium pentoxide supported on silica) that is similar to the product used commercially in sulfuric acid production.

***Incipient Wetness Impregnation.*** In this method, impregnating solution is used in a sufficient volume to completely fill the pores of the carrier, without excess solution. This allows the precursor to disperse evenly within the pore structure of the carrier.

In some cases, the active component can be precipitated onto the carrier by adjusting the pH of the impregnating solution. This will immobilize, or fix, the active material on the carrier. For example, it is common to treat noble metals (platinum, palladium, rhodium, etc.) on carriers with hydrazine, in order to reduce the metal, or with acids or bases, in order to neutralize the impregnating solution (i.e., the addition of ammonium hydroxide to a $H_2PdCl_4$ impregnating solution) and precipitate the metal oxide to obtain dispersions. This step is carried out after impregnation, but before drying and further processing.

***Impregnation by Precipitation.*** One modification of the standard impregnation method is achieved by suspending the carrier material (powder or particulate) in a solution of the catalytic precursor materials. The catalytic material is then slowly precipitated onto the carrier by adjusting the pH of the liquid impregnating solution. The resulting catalyst is collected by filtration. Metal oxides supported on zeolites, such as CuO/ZSM-5, can be prepared using this method.

***Eggshell Impregnation.*** Some catalytic reactions are conducted under conditions in which only the exterior of the catalyst particle contains the active component. Thus, the interior of the catalyst particle is inactive, and all of the reaction occurs on its exterior. This procedure is sometimes used to reduce the formation of byproducts and unwanted side reactions that can occur in a pore diffusion controlled reaction. It is also used to prepare catalysts containing expensive noble metals in order to increase the effectiveness per unit of noble metal.

In this process, a carrier, usually particulate, is coated with a thin layer of up to 200 µm (8 mils) of catalytic material. The procedure involves placing the carrier in a rotating drum along with the catalytic material. The degree to which the active component penetrates the carrier can sometimes be controlled by either adjusting the pH of the solution or varying the quantity of alkali metals present on the surface of the carrier. This technique has the advantage of producing catalysts with shallow metal concentration profiles near the surface of the catalyst particles, which decreases pore-diffusion resistance.

**Ion exchange** is a very effective method for dispersing metals, oxides, and cations on carriers. However, only carriers that have cation-exchange capacities can be used. The ion-exchange procedure is often used to prepare metal supported on aluminas and molecular sieves (i.e., zeolites, metallosilicates, etc.). Metal-loaded zeolite catalysts are easy to prepare using this technique because of their unusually high cation-exchange capacity. Catalysts prepared by this procedure initially result in highly dispersed metal cations. Reduction can lead to highly dispersed metal particles. Further oxidation results in highly dispersed oxide phases.

To carry out the exchange procedure, the carrier must possess negatively charged ions to which exchangeable cations are bonded. The cation initially bonded to the surface ($H^+$, $NH_4^+$, $Na^+$) is ion exchanged with the desired cation, maintaining electrical neutrality during the procedure. The exchange is carried out by mixing the carrier with the desired cation salt in a dilute aqueous solution for 1 to 24 h at temperatures up to 100 °C (210 °F). The exchanged carrier is then collected by filtration and washed with excess water before further processing.

Sometimes, a single ion-exchange procedure is not sufficient to obtain the desired level of metal loading. Multiple ion-exchange procedures with optional drying and calcining steps in between can then be conducted.

**Precipitation.** Amorphous and crystalline metal oxide and mixed metal oxide catalysts can be prepared using a variety of precipitation techniques. Examples of these unsupported oxide catalysts include coprecipitated $NiO \cdot Al_2O_3$ for steam reforming to produce hydrogen, $CuO \cdot ZnO \cdot Al_2O_3$ for methanol synthesis, and $SiO_2 \cdot Al_2O_3$ for fluid catalytic cracking (FCC) of heavy oils to lower-molecular-weight fuels.

In a typical procedure, an aqueous solution of one or more metal salts contacts a basic solution, such as an aqueous alkali, ammonium hydroxide, or ammonium carbonate, to cause the precipitation of insoluble metal hydroxides or carbonates. The catalyst is then collected by filtration and washed repeatedly, prior to drying. Catalysts prepared by this method are often calcined at temperatures that exceed 300 °C (570 °F) after drying in order to decompose metal oxide precursors, such as hydroxides, and form the desired oxides. Temperatures that are even higher are used to form crystalline mixed oxides, such as perovskites or spinels. Catalysts that are prepared using these procedures sometimes need to be crushed into powder form prior to use, as in slurry-phase processes.

The precipitation method used to prepare metal oxide catalysts is also used to prepare some standard catalyst carrier materials, such as $Al_2O_3$, $TiO_2$, and $SiO_2$. Their preparation is discussed in detail below.

## Preparation of Common Carriers Used in Supported Catalysts

Catalyst carriers are usually high-surface-area inorganic materials with complex pore structures, into which catalytic materials such as palladium, platinum, cobalt, chromium oxide, and vanadium pentoxide are deposited using the methods described above. At one time, it was thought that catalyst carriers only served to provide inert high surface areas with suitable strength and durability, on which catalytic substances could be dispersed, thus maximizing the number of active sites. However, it is now widely recognized that the carrier often plays a critical role in the performance of the catalyst, in terms of activity, selectivity, and durability.

The selection of the appropriate carrier is the first and most important step in designing a supported metal or metal oxide catalyst. Parameters such as surface area, porosity, thermal stability, acidity, and the inherent activity of the carrier itself are all critical to the carrier selection process. Because reactants and product must diffuse within the carrier, the size of its pores is critical for optimum transport. Carrier materials can be categorized as:

- Active carriers, such as alumina, silica-alumina, zeolites, titanium oxide, and carbon in powder or particulate form
- Inert carriers, such as silica, in powder or particulate form
- Structural supports, such as the monoliths upon which catalyzed carriers are deposited

The most important catalyst supports for experimental and industrial use are high-surface-area inorganic oxides and carbon. Their characteristics and preparations are described briefly below. Structural supports are described in the section "Catalyst Powder Processing" in this article.

**Alumina** ($Al_2O_3$) is one of the most important commercial carrier materials used in industrial applications. It is a component of many environmental catalysts, including automobile catalytic converters and catalysts for the oxidation of volatile organic compounds. It is also used in petroleum catalysts, for hydrodesulfurization and reforming, and in chemical catalysts, for hydrogenation, isomerization, and oxidation reactions.

Aluminas with high surface areas (100-600 $m^2/g$, or 2-14 $ft^2/lb$) are generally prepared by the thermal decomposition of well-crystallized hydroxides or precipitated colloidal gels. The high surface area of alumina is due to a network of $Al(OH)_x$ species (particles of 2 to 5 nm, or 0.08 to 0.2 μin.) bonded together to form polymer-type chains. Precipitation can be performed by the acidification of aluminate, the neutralization of aluminum salts, or the hydrolysis of alcoholate.

The phase of alumina that is formed strongly depends on the pH used in the precipitation step and the thermal history of the resulting solid support. For example, precipitation at a pH of 11, followed by drying, forms aluminum trihydrate, known as Bayerit, whereas precipitation at a pH of 9, followed by drying, forms pseudo-Boehmit, the monohydrate crystal ($AlO{\cdot}OH$). The gamma phase of alumina, obtained by calcining at 350 to 600 °C (660 to 1110 °F), is the most widely used. Treatment at temperatures above approximately 800 °C (1470 °F) results in the conversion to lower-surface-area phases of alumina.

**Silica** ($SiO_2$). The preparation of different silicas has been reviewed in great detail in the literature (Ref 1). Silica is often used in polymerization catalysts, such as 0.1% chromium oxide impregnated on silica, for the formation of polyethylene.

Most silicas used in catalysis are synthetic. Preparation conditions have a dramatic influence on the properties of the silica that is formed. Variations of pH, rate of precipitation, aging of the precipitate, and drying and calcination conditions can lead to silicas with controlled porosities and surface areas.

Silica gel can be prepared by the polymerization of silicic acid or the aggregation of colloidal silica. Alkaline solutions of silicates (pH of 12) can be neutralized with acid, resulting in the formation of polymeric silicic acid, which precipitates as a hydrogel. When chains of silicic acid polymerize, they form a high-surface-area network with interconnecting pores of varying sizes. After controlled drying and calcination, silicas with high surface areas (200 to 600 $m^2/g$, or 5 to 14 $ft^2/lb$) can be obtained.

**Zeolites** are highly crystalline silicoaluminates with well-defined pore structures comprising tetrahedral silicon and aluminum oxide units. They have pore diameters of 0.3 to 1.0 nm (0.01 to 0.04 in.) and surface areas of 300 to 700 $m^2/g$ (7 to 17 $ft^2/lb$), both of which primarily depend on the type of zeolite. Zeolites have a three-dimensional framework structure with this empirical formula:

$$M_{x/n}^{+n}\ [(\mathrm{AlO_2})_x\,(\mathrm{SiO_2})_y]\cdot w\mathrm{H_2O}$$

where $w$ is the number of water molecules associated with the zeolite and the bracketed term is the zeolite framework and the crystallographic unit cell. The cation $M$ with valence $n$ is present to balance the negative charge on the lattice created by the substitution of $Si^{+4}$ by $Al^{+3}$ in the framework structure. Silicon/aluminum ratios vary with the type of zeolite and the preparation conditions.

Zeolites are generally synthesized by a hydrothermal process. Sodium hydroxide is commonly added to sodium silicate and sodium aluminate, causing gelation to occur (Ref 2). The freshly coprecipitated silica/alumina gel is allowed to age at 25 to 200 °C (75 to 390 °F) to cause crystallization. The zeolite is collected by filtration, and then washed, dried, and calcined. The conditions of aging (temperature and pressure), pH, and silicon/aluminum ratio are some of the important factors determining the type of zeolite that is prepared.

Zeolites are of great interest catalytically, primarily because of their high activity and unusual selectivity in a variety of acid-catalyzed reactions. They are also interesting as catalyst carriers for metals, metal cations, and oxides. They are used in the petroleum industry in fluid catalytic cracking (acidic *Y* zeolite) and isomerization catalysts (platinum/mordenite), and for the methanol-to-gasoline process (ZSM-5). Most important, catalytically, are the zeolites from the faujasite group (*X* and *Y* zeolite), as well as chabazite, erionite, offretite, mordenite, and the pentasil zeolites ZSM-5 and ZSM-11.

**Titanium oxide** ($TiO_2$), or titania, is currently used as a catalyst carrier for the selective catalytic reduction of nitrogen oxide ($NO_x$, or NO + $NO_2$) using ammonia in stationary source applications. It has two crystal structures, anatase and rutile. The anatase form is more important catalytically, because of its high surface area (25 to 100 $m^2/g$, or 0.06 to 2 $ft^2/lb$). The rutile structure has a much lower surface area (<10 $m^2/g$, or 0.2 $ft^2/lb$). Titania in the anatase form is prepared by precipitation from boiling titanium (IV) sulfate solution. The rutile form can be prepared directly from the precipitation of a chloride solution or by calcination of the anatase phase at 600 °C (1110 °F) for several hours.

**Carbon** exists in several morphological forms, such as charcoals, carbon blacks, graphite, and molecular sieve structures. Many carbons occur naturally from wood, peat, nuts, shells, and other organic matter. Charcoal, known for its adsorptive properties, is prepared by the pyrolysis of organic polymers. Charcoals are highly porous with surface areas of approximately 1000 $m^2/g$ (25 $ft^2/lb$). Carbon blacks are prepared by the controlled pyrolysis of hydrocarbons. The nature of the precursor hydrocarbon and the pyrolysis conditions determine the surface area, pore structure, and surface chemistry of the carbon black.

Carbon carriers have been used extensively for precious metals, transition metals, and alkali and alkaline earth metals. Carbon-supported catalysts (platinum, palladium, and nickel on carbon) are used in a variety of catalytic processes, such as alkylation, hydroalkylation, and hydrogenation.

**Other inorganic oxides** that are sometimes, but not commonly, used as catalyst carriers include zirconia, rare-earth oxides, alkaline earth oxides, chromia, niobia, tin oxide, and zinc oxide. These are often prepared simply by precipitation of the corresponding metal salts (nitrates or sulfates), followed by washing and calcination. Zirconia can be prepared with a fairly high surface area (approximately 150 $m^2/g$, or 5 $ft^2/lb$), and therefore is finding use in more catalyst applications.

Many of the mixed metal oxide catalysts described in the section "Precipitation" can also serve as potential catalyst support materials.

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## Catalyst Powder Processing

The form of the catalyst used for a specific reaction depends on the type of reactor being used. Powder catalysts are usually used for slurry-phase processes, whereas tablets or extruded catalysts are used in fixed-bed reactors, and microsphere catalysts (50 to 120 μm, or 2 to 5 mils) are used in fluidized bed reactors. Catalyzed honeycombs or monoliths are used in numerous environmental applications. Therefore, catalyst powders are often converted into a suitable form (particulates or washcoats for honeycombs) for a specific reactor design. In general, powder processing techniques are made easier by using powders having well-defined particle sizes in order to yield catalyst products that are homogeneous and have attrition resistance.

**In the tableting process,** the powder is firmly pressed into a die and shaped into small cylinders, rings, or beads. Powders composed of deformable particles acquire reasonable cohesion upon tableting. Plastifying agents (talc, graphite, stearic acid, etc.) are sometimes added to powders to prevent them from sticking to the sides of dies and stamps.

**In the beading or granulation process,** individual particles of different sizes are rotated under a spray of liquid to form larger, more homogeneously sized particles. The operation is done in a horizontal rotating cylinder or pan with a rotation axis of approximately 45° inclined. The particles roll over one another to give almost perfectly spherical particles (0.5 to 20 mm, or 0.02 to 0.8 in.).

**In the paste extrusion process,** catalyst powders are converted into a paste that is used to form larger particles. The paste is moved through a drilled plate and made into cylinders with diameters of 1 to 10 mm (0.04 to 0.4 in.). The paste must have enough plasticity to give granules with sufficient cohesion. The rheological properties of the paste can be adapted by adding volatile materials (acids, stearates, methyl cellulose, or polymers) or other materials that will not influence the activity of the catalyst (colloidal alumina, silica, clays, etc.).

**Spray drying,** a simultaneous drying and shaping procedure, is a widely used technique to produce spherical materials. A suspension or slurry that contains about 20 to 60% solids is sprayed in hot gases (100 to 400 °C, or 210 to 750 °F). The tiny drops that form are dried very quickly, which results in almost perfectly shaped microspheres. This process is used to make catalysts for fluid catalytic cracking (FCC). The average life of an FCC catalyst during use is about 6 mo, during which it experiences temperatures as high as 750 °C (1380 °F). Therefore, a highly attrition resistant and thermally stable catalyst is necessary. Several binders have been developed that can be added to the slurry to substantially increase the hardness of FCC microspheres.

**Catalyzed honeycomb** or monolith structures with parallel channels are utilized in high-flow-rate processes where pressure drops must be minimized. They have been used in numerous environmental applications, including automobile catalytic converters and abatement systems for volatile organic compounds and selective catalytic reduction. In general, honeycombs provide good mechanical strength and resistance to thermal shock. However, because they have low surface areas, a catalyzed carrier (washcoat) must be deposited on their channels. The most widely used monolith is made from cordierite ($2MgO\cdot 2Al_2O_3\cdot 5SiO_2$). Some metallic materials also are being used.

The finished catalyst is prepared by dipping the honeycomb into an aqueous slurry containing catalyzed carriers that will adhere to the walls of each channel. Excess slurry is then blown from the channels to avoid plugging. The washcoated honeycomb is then dried and calcined (300 to 600 °C, or 570 to 1110 °F) to fix the catalyzed washcoat securely to the honeycomb walls and to decompose precursor compounds (Fig. 1).

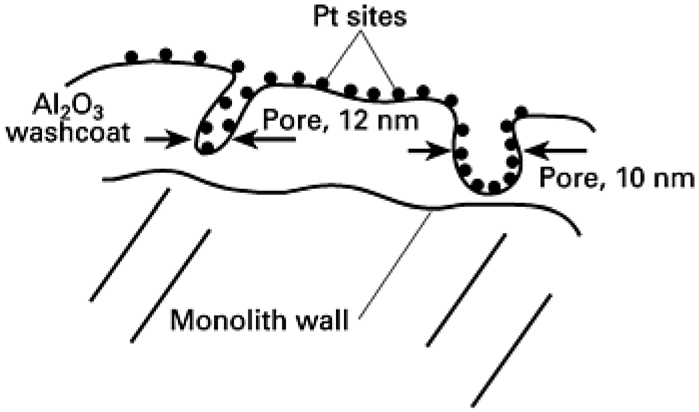

**Fig. 1 Impregnated catalyst washcoated on a substrate honeycomb**

The rheology of the catalyst slurry is determined by its solids content (25 to 60%), the pH, and the particle size of the catalyst (preferably, 10 to 25 μm, or 0.4 to 1 mil). Sometimes the addition of binders, such as alumina or silica sols, is required to improve adhesion onto the monolithic support. The honeycomb has some porosity, which ensures adhesion of the catalyzed washcoat.

## Protective Coatings for Carbon-Carbon Composites

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### Introduction

CARBON-CARBON is a unique composite material in which a nonstructural carbonaceous matrix is reinforced by carbon fibers to create a heat-resistant structural material. The carbon fibers are generally employed as woven fabric in two-dimensional laminates, or as multidimensional preforms created by textile processing of multifilament tows (Ref 1, 2). Composite densification is typically accomplished using phenolic resins in a preforming process, followed by liquid impregnation, vapor phase carbon infiltration, or combinations of the two to achieve pore filling (Ref 3, 4, 5, 6, 7, 8, 9, 10). High-temperature pyrolysis is used to convert liquid impregnants to carbon while vapor phase infiltration is conducted in reduced-pressure reactors where flowing hydrocarbon gas infiltrates the composite and is thermally decomposed to deposit carbon. The result is a low-density (1.5 to 1.9 gm/cm$^3$) composite that derives its mechanical performance from the carbon fiber reinforcement.

Because carbon fibers tend to increase in strength with increasing temperature (Ref 11), carbon-carbon composites retain their tensile strength at extreme temperatures. Carbon-carbon composites provide unmatched specific stiffness and strength at temperatures from 1200 to 2200 °C (2192 to 3992 °F). At temperatures below 1000 °C (1832 °F), carbon-carbon composites exhibit specific strength equivalent to that of the most advanced superalloys (Ref 12). As a result of their carbon constituents and weakly bonded reinforced matrix, carbon-carbon composites also have superior thermal shock, toughness, ablation, and high-speed friction properties. These properties have led engineers to apply carbon-carbon in reentry bodies, rocket nozzles, and exit cones for strategic missiles, and in brake discs for military aircraft (Ref 8, 9, 10, 13). Recently a commercial aerospace application, brake discs for transport aircraft, has become prominent (Ref 14).

Coating technology for carbon-carbon has been driven primarily by the aerospace and defense industries, in applications where the composite is exposed to high-temperature oxidizing environments. Advanced applications include hot-section components for limited-life missile engines, exhaust components for fighter aircraft, hypersonic vehicle fuselage and wing components, and structures for space defense satellites (Ref 13). The most notable application of coated carbon-carbon is for the nose cap and wing leading edges of the Shuttle Orbiter vehicle (Ref 15, 16, 17). Over 40 successful missions have been flown, demonstrating the flight worthiness of coated carbon-carbon in reentry applications.

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## Fundamentals of Protecting Carbon-Carbon

**Historical Development of Protecting Carbon Bodies.** Many of the constituents and approaches for protecting carbon-carbon have grown from early research work aimed at protecting synthetic graphite bodies. Sixty years ago, a patent was issued to the National Carbon Co. (Ref 18) for a coating method to render carbon articles oxidation resistant at high temperatures. Coating systems composed of an inner layer of SiC and outer glazes based on $B_2O_3$, $P_2O_5$, and $SiO_2$ were described. This work demonstrated the utility of glassy materials as coating constituents to enhance oxidation resistance. Work on JTA graphite for reentry applications (Ref 19, 20, 21) was particularly significant. In these materials, refractory compounds containing boron, silicon, zirconium, and hafnium were used as additions to impart oxidation resistance. Oxidation resulted in formation of a borate glass coating that was protective for several hours up to 1700 °C (3092 °F). Enhancement of oxidation resistance through additions of boron to the body of carbon materials was an important contribution of this work.

The investigation by Chown and coworkers of refractory carbides for protecting graphite (Ref 22) was an important early contribution to coating technology. Their results showed that chemical vapor deposition (CVD) of SiC could provide reliable protection for long periods of time at temperatures below 1700 °C (3092 °F). Experiments with a variety of refractory carbides and boride coatings formed by reaction sintering demonstrated that protection for short times up to 2200 °C (3992 °F) could be achieved with sintered ZrC and $ZrB_2$ coatings.

Coatings based on the use of iridium (Ref 23, 24) were investigated in the 1960s to protect graphite up to temperatures as high as 2100 °C (3812 °F). This concept relied on the very low carbon diffusivity and oxygen permeability of iridium as a solid oxygen barrier. While some success was achieved, significant problems associated with volatile oxide formation, adherence, and the high thermal expansion of iridium limited the usefulness of this technology.

Carbon-carbon was thrust into the forefront as a high-temperature materials research topic by the requirement for a reusable, lightweight thermal protection system for the Shuttle Orbiter (Ref 25, 26, 27, 28). The oxidation-protected carbon-carbon presently used for the shuttle nose cap and wing leading edge is based on a substrate containing low-strength, low-elastic-modulus rayon precursor fibers. The coating system is composed of a SiC coating, formed by conversion of the carbon-carbon in a pack process, and an outer silicate glaze coating filled with SiC powder (Ref 25, 26, 27). The process also involves sealing cracks in the coating system with silicon ethoxide (Ref 28). The SiC conversion layer is over 1 mm (0.025 in.) thick.

Throughout the 1980s, a significant level of research activity focused on the protection of high-performance carbon-carbon that used heat-stabilized polyacrylonitrile (PAN) or pitch-based fibers. These composites have higher strength, higher elastic moduli, and lower thermal expansion coefficients than the rayon-based materials. Applications have focused on using high-performance carbon-carbon in structural-weight-critical roles requiring substrates and coatings of minimum thickness. For example, coating thicknesses normally are targeted to be 0.2 to 0.4 mm (0.005 to 0.010 in.). These physical factors, coupled with the significant increase in coating-substrate thermal mismatch stresses, have proved to be significant barriers to acceptable performance and broader use of carbon-carbon composites.

**Carbon-Carbon Constituents and Microstructure.** Applications requiring coatings typically use carbon fibers in laminated woven cloth or three-dimensional woven reinforcements. The fibers used are derived from rayon, PAN, or petroleum pitch and have a wide range of properties. For example, the elastic modulus along the fiber axis ranges from approximately 41.4 GPa (6 Msi) for rayon fibers to 414 GPa (60 Msi) for heat-stabilized PAN to 690 GPa (100 Msi) for pitch fibers. The axial fiber expansion coefficients become lower as the fiber modulus increases.

The characteristics of the matrix vary, depending on the method of densification. Generally, the matrix microstructure spans a range from being glasslike, with small, randomly oriented crystallites of turbostratic carbon, to having strongly oriented and highly graphitized large crystallites. Weak interfaces usually exist between the fibers and matrix, because strong covalent atomic bonding prevents the carbon constituents from sintering, even at very high temperatures. Because the mechanical properties of the matrix are substantially inferior to those of the fibers, the fibers generally control the mechanical performance and expansion characteristics of the composites. A rayon-fabric-reinforced laminated construction typically exhibits the following in-plane properties: a tensile strength of 51.7 MPa (7.5 ksi), a tensile elastic modulus of 13.8 GPa (2 Msi), and a thermal expansion coefficient of $2.4 \times 10^{-6}$ °$C^{-1}$ ($1.3 \times 10^{-6}$ °$F^{-1}$). Laminated constructions that have high-performance fibers exhibit the following typical in-plane properties: a tensile strength of 276 MPa (40 ksi), a tensile elastic modulus of 90 GPa (13 Msi), and a thermal expansion coefficient of $1.4 \times 10^{-6}$ °$C^{-1}$ ($0.8 \times 10^{-6}$ °$F^{-1}$).

**Matrix Inhibition.** Carbon begins to oxidize at measurable rates at approximately 371 °C (700 °F). Carbon-carbon composites exhibit high internal surface areas due to the porous nature of the structure (typical levels of interconnected porosity are 10 to 15%). Adding inhibitor phases to the matrix has become an important facet of an overall oxidation protection system, because inhibitors allow some control of oxidation that can occur through defects in coatings. Inhibitors can also prevent catastrophic oxidation failure due to coating spallation at high temperatures.

Additions of boron, boron compounds, and phosphorus compounds have been effective in protecting carbon bodies (Ref 29, 30, 31, 32, 33, 34) by true chemical inhibition and formation of internal and external glass layers that act as diffusion barriers. The practice of making boron additions to carbon-carbon for improved oxidation resistance was first disclosed in a 1978 patent (Ref 35). Since that time, many improvements and variations on this theme have been reported (Ref 36, 37, 38, 39, 40, 41, 42, 43, 44, 45).

Internal chemical modifications can be made either by mixing the carbonaceous and nonoxide inhibitor powders and consolidating the constituents to form the carbon body, or by impregnating the porous body with liquids that contain the inhibitors, usually in oxide form. Boron and many nonoxide boron compounds are quite refractory, so the powder mixing and carbon processing route has often been used (Ref 32, 33, 34). In composite fabrication, submicron refractory compound additives are normally carried within impregnating resins and are dispersed through the fiber tows as well as between the fabric plies.

**Coating Selection Principles.** The most critical component of any coating architecture is the primary oxygen barrier. The oxygen barrier prevents oxygen ingress to the underlying composite by providing a physical permeation barrier and, in some cases, by gettering oxygen in the process. The critical parameters that guide the selection of the oxygen barrier are its oxidation characteristics, thermal expansion coefficient, and inherent oxygen permeability. A material that forms an adherent, low-permeability oxide scale is preferred as an oxygen barrier because it oxidizes slowly and has the potential to self-heal. An Arrenius plot of rate constants for oxidation of refractory materials typically considered for coating applications (Ref 46, 47) is presented in Fig. 1. Scale growth as a function of time can be estimated from Fig. 1 using the relationship $x^2 = Kt$, where $x$ is the scale thickness, $K$ is the parabolic rate constant, and $t$ is time in hours. The silicon-base ceramics exhibit substantially lower oxide growth kinetics than the aluminum-, hafnium-, or zirconium-base ceramics. Time and temperature of service will dictate material selection and coating thickness. However, from the standpoint of forming thin protective scales in thermal cycles with peak temperatures in the range of 1400 to 1700 °C (2552 to 3092 °F), only $Si_3N_4$ and SiC exhibit sufficiently low rate constants for oxide growth over extended time periods.

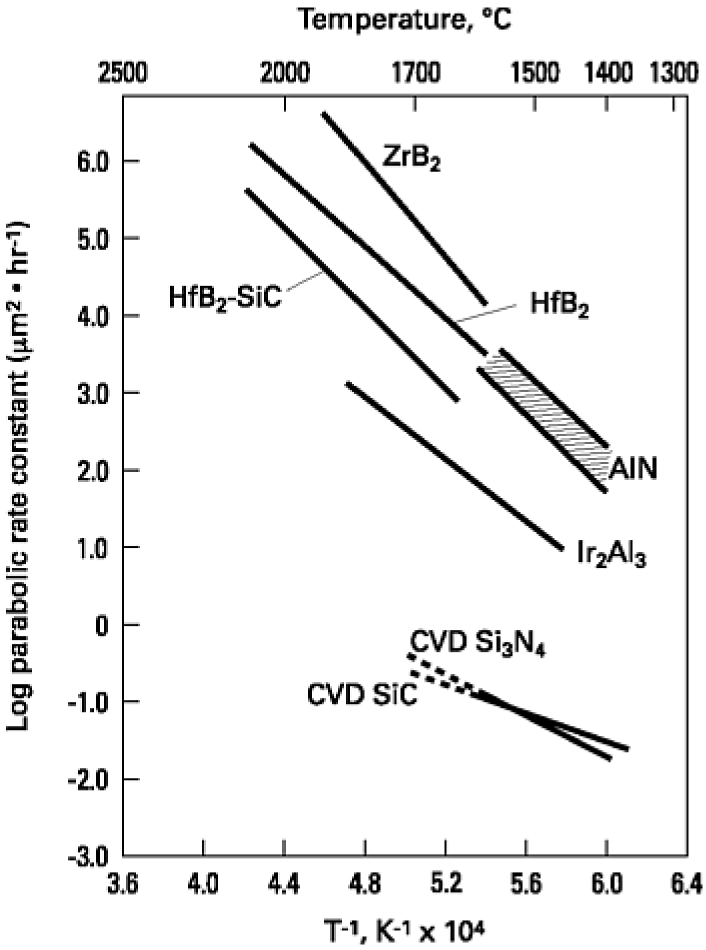

**Fig. 1 Oxidation kinetics of refractory materials. CVD, chemical vapor deposition**

Figure 2 compares the thermal expansion behavior of refractory coating candidates with that measured for high-performance, fabric-reinforced carbon-carbon (Ref 12, 46, 47). The expansion of carbon-carbon in the in-plane directions is substantially lower than for any of the refractory ceramics. This expansion difference, coupled with the high modulus of the refractory materials, results in significant thermal mismatch stresses when they are employed as coatings. An estimate of the thermal mismatch stresses when the coating thickness is small relative to the carbon-carbon substrate thickness can be calculated using the relationship

$$s_c = \frac{E(a_{c-}a_s)\Delta T}{1-v}$$

where $\sigma_c$ is the stress in the coating, $E$ is the coating elastic modulus, $u$ is the Poisson ratio of the coating, $\alpha_s$ is the thermal expansion coefficient of carbon-carbon, $\alpha_c$ is the thermal expansion coefficient of the coating, and $\Delta T$ is the difference between the deposition temperature and the selected temperature for stress calculation.

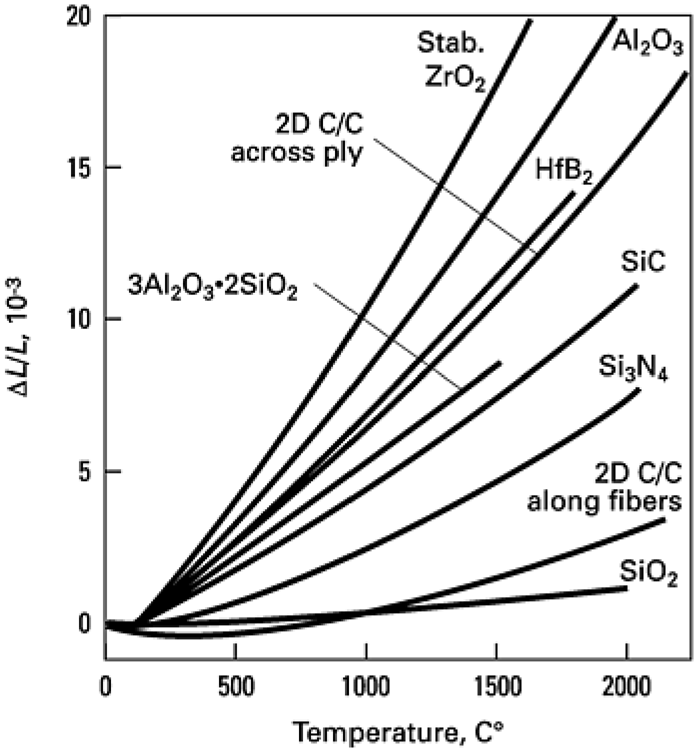

**Fig. 2 Thermal expansion characteristics of ceramics and carbon-carbon laminates. C/C, carbon-carbon laminate; *L*, specimen length**

The properties of refractory materials that have been used in deposition studies are summarized in Table 1. Figure 3 presents the thermal stresses calculated as a function of temperature when these coatings were deposited onto high-performance two-dimensional carbon-carbon laminates. For the refractory ceramics, silicon nitride provides the lowest thermal mismatch stresses of any of the ceramic coating candidates. These stresses are still high enough to cause cracking, however. Therefore, it is usually found that deposited ceramic coatings exhibit microcracking and that the crack pattern depends on the coating thickness and deposition temperature. Iridium metal deposited by electron-beam physical vapor deposition techniques can have low thermal mismatch stresses upon cooling. However, such a coating must then be able to withstand extremely high compressive stresses upon heating. In previously reported work (Ref 47), it has been shown that iridium-base coatings deposited by this technique onto high-performance carbon-carbon fail by compressive spalling at elevated temperatures.

**Table 1 Properties of refractory materials deposited on carbon-carbon composites**

| Materials | Deposition process | Deposition temperature, °C | Bulk properties | | |
|---|---|---|---|---|---|
| | | | Modulus Msi | Poisson's ratio | CTE (20-1900 °C), ppm/°C |
| SiC | CVD | 1050 | 65 | 0.19 | 5.2 |
| TiC | CVD | 1000 | 65 | 0.19 | 9.5 |

| | | | | | |
|---|---|---|---|---|---|
| AlN | CVD | 1250 | 50 | 0.3 | 6.1 |
| $Si_3N_4$ | CVD | 1420 | 46 | 0.3 | 3.6 |
| Ir | Sputtering | 250 | 76 | 0.3 | 7.9 |
| $HfO_2$ | EBPVD | 1000 | 20 | 0.25 | 10.6 |

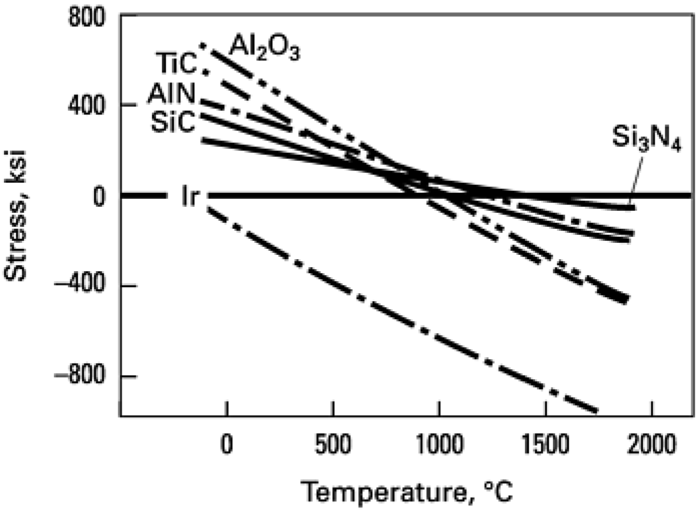

**Fig. 3 Calculated thermal stresses for thin coatings on high-performance carbon-carbon laminates. Ratio of substrate thickness to coating thickness = 20**

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## Preferred Coating Approaches

Coating approaches are dictated by both application requirements and fundamental behavior. Generally speaking, SiC-base and $Si_3N_4$-base coatings have found broad use at temperatures below 1700 °C (3092 °F) because of minimum thermal mismatch stresses and low oxide-scale growth kinetics. In the higher temperature range, 1700 to 2200 °C (3092 to 3992 °F), refractory carbides and borides have been used for short time periods. Coating deposition techniques that have been used include pack cementation, CVD, and slurry processes. Coating architectures are normally built using combinations of these techniques. In the following sections, typical coating architectures are discussed in accordance with the process used to deposit the primary oxygen barrier.

**Pack Cementation.** The coating system used on the Shuttle Orbiter vehicle is the preeminent example of the use of a pack process to create an oxidation protection system for carbon-carbon (Ref 17). In this process, the carbon-carbon part is packed in a retort with a dry pack mixture of alumina, silicon, and silicon carbide. The retort is placed in a furnace, and under argon atmosphere a stepped time-temperature cycle is used to activate conversion of the carbon-carbon surface to SiC. Peak process temperature is approximately 1760 °C (3200 °F). This creates a porous SiC surface nominally 1.0 to 1.5 mm in thickness. Multiple impregnation and curing with an acid-activated tetraethoxysilicate liquid produces $SiO_2$ coating of the porous surfaces. A surface sealant consisting of a mixture of a commercial alkali silicate bonding liquid filled with SiC powder is then applied.

This system was designed to provide protection during multiple reentry cycles where surface temperatures of 1538 °C (2800 °F) are anticipated. The success of the shuttle missions and further testing (Ref 15, 16, 17) has proven this to be an effective approach for low-performance rayon-based composites. Attempts to use similar coatings modified with boron (Ref 48, 49) for other aerospace applications requiring high-performance carbon-carbon have met with only limited success.

**Chemical Vapor Deposition.** Attempts to expand carbon-carbon use to turbine engine hot-section and exhaust components fostered the need for protective coatings that could be applied as thin layers over the structural components without compromising mechanical performance. The coating architectures developed have been dependent on the application lifetime as well as on dynamic or static structural requirements. The CVD coatings are normally applied in multiple cycles to ensure even deposition rates over curved surfaces. A substrate pretreatment is normally used to enhance adherence. Silicon nitride overlay coatings have been shown to be effective for limited-life (<20 h) cycles where heating above the deposition temperature occurs rapidly and peak temperatures reach 1760 °C (3200 °F) (Ref 46, 47, 50). These coatings have employed a thin reaction layer of SiC (formed in a pack process, of the order of 5 μm) to serve as a reaction barrier and to enhance adherence. The $Si_3N_4$ has been applied in thicknesses ranging from 125 to 250 μm (0.005 to 0.010 in.) in a multiple-step CVD process.

Other applications require that carbon-carbon withstand hundreds of hours of exposure to peak temperatures in the range of 1400 to 1500 °C (2552 to 2732 °F) and undergo thermal cycling to temperatures in the range of 600 to 1200 °C (1112 to 2192 °F). In these extended-life applications, a boron-rich inner layer is used to provide a source of glassy phase to seal microcracks in the outer coatings. Elemental boron, boron carbide, and combinations of boron compounds mixed with silicon carbide or silicon are inner layer approaches. These layers are deposited in thicknesses normally in the range of 25 to 50 μm (0.001 to 0.002 in.) using CVD, conversion of the carbon surface, and slurry coating (Ref 51, 52, 53). Depositing SiC or $Si_3N_4$ by CVD is the preferred method to provide hard, erosion-resistant surfaces that cover the boronated inner layers and inhibit vaporization of borate glass sealants (Ref 54, 55). Overlay thicknesses in the range of 200 to 300 μm (0.008 to 0.012 in.) are normally deposited in a multiple-step process. A typical coating architecture on an inhibited composite is shown schematically in Fig. 4.

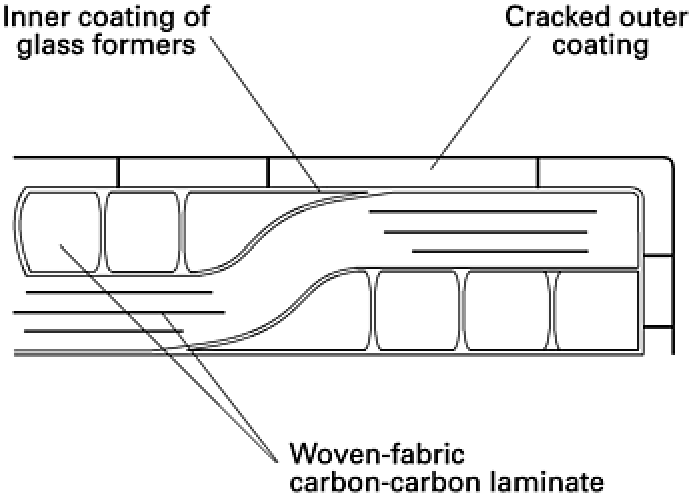

**Fig. 4 Schematic of coating architecture used to protect carbon-carbon for extended-life applications**

Silicate glazes are frequently applied to fill the microcrack network existing in SiC and $Si_3N_4$ coatings. Although the glaze is applied externally and is susceptible to vaporization and physical removal, it has been shown to improve cyclic oxidation lifetimes. Glaze overcoats are normally applied as aqueous sols incorporating boron and silicon that can be painted, sprayed, or dip coated. Typical processing involves air drying and firing above 1038 °C (1900 °F) in an argon atmosphere (Ref 54). The glaze can be periodically replenished.

**Slurry coatings** are produced by dispersing appropriate ceramic or metal powders in a liquid vehicle to make the slurry, applying the slurry as a paint to the component surface, evaporating or gelling the liquid to harden the coating, and then heating to a high temperature to stabilize and densify the coating. Slurries are applied by brushing, spraying, or dipping. The liquids can be water or volatile organics with organic binders in solution, inorganic or organic sols or solutions that form oxides, or thermosetting preceramic polymers or polymer solutions (Ref 56, 57).

Hardening produces a coating that is composed of the powder particles bound together and bonded to the substrate by the solid that is precipitated or condensed from the liquid. Heating to a high temperature decomposes the binder phase to form carbon or a ceramic. The shrinkage associated with binder decomposition and incomplete solid state sintering of the powder particles will result in a cracked, porous, and often weakly bonded coating unless a flowable and wetting liquid is formed by one of the constituents. This can be a glass, molten metal, or ceramic melt.

Coatings meant to provide oxidation protection for graphite and carbon-carbon composite articles at temperatures below 1000 °C (1832 °F) often contain large amounts of boron in the form of elemental boron, $B_4C$, BN, metal borides, or $B_2O_3$ (Ref 58, 59). Employing $B_2O_3$ glass provides a wetting liquid at low temperatures on initial heating, and the nonoxides rapidly oxidize in use to produce the same result. Coatings composed mostly of refractory oxide particles bound together with small amounts of borate glass have shown utility at temperatures in the range of 1200 to 1500 °C (2192 to 2732 °F) in configurations where evaporation of the $B_2O_3$ is inhibited (Ref 38). In making such coatings the boron can be present in the powder constituents, the liquid vehicle, or both. Water or alcohol solutions of boric acid and liquid boron alkoxides are often used (Ref 38, 44). Solutions of preceramic boron polymers are also a possibility (Ref 60, 61).

Slurry coatings meant for higher temperatures, in which borates are replaced by glassy alkali silicates or aluminum phosphate, are prominent (Ref 28, 48). The use of siloxane fluids as preceramic polymers has also been disclosed (Ref 62). Converting the carbon surface to SiC is often recommended as a pretreatment to ensure the adherence of glassy borate, silicate, and phosphate coatings (Ref 28, 48).

The bonding and densification of slurry coatings with molten metal and melted ceramic phases has been used to produce protective layers with intermediate to very high temperature capabilities. Dense, very adherent coatings capable of extreme-temperature service can be made from paints containing fine refractory boride particles (Ref 22). The coatings are fully stabilized by heating the borides in contact with the carbon surface to temperatures over 2000 °C (3632 °F) in an inert environment to form a boride-carbon eutectic liquid. Coatings made by melting certain combinations of metal powders and reacting these with the carbon surface to form refractory carbides (Ref 63) are protective to 1800 °C (3272 °F). Recent work of this type (Ref 64) using a mixture of silicon, hafnium, and chromium powders reacted with the carbon surface at 1450 °C (2642 °F) has produced carbide coatings that provide excellent oxidation protection for short times at 1200 °C (2192 °F).

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## Practical Limitations of Coatings

As mentioned above, carbon-carbon composites can be used as structural materials to at least 2200 °C (3992 °F). At the time of this writing, viable coating concepts to match this capability have not been consistently demonstrated, especially for times greater than a few hours. SiC and $Si_3N_4$ are limited thermodynamically to temperatures of approximately 1800 to 1815 °C (3272 to 3300 °F). At higher temperatures, the $SiO_2$ layers that form and protect these materials are disrupted by CO and $N_2$ interfacial pressures that become greater than $10^{-1}$ MPa (1 atm), causing the coatings to erode by uncontrolled oxidation (Ref 12, 47). Use of more refractory materials such as HfC or $HfB_2$ is limited by the very rapid oxidation rates pointed out in Fig. 1. Rapid conversion of these films to high-expansion oxides leads to severe spallation in thermal cycles. Thus, above approximately 1760 °C (3200 °F), coating lifetimes are currently limited to a few hours.

For the range of applications where coating architectures incorporating borate sealant glasses are used, coating use temperatures are limited to approximately 1500 to 1550 °C (2732 to 2822 °F). When $B_2O_3$ contacts carbon at atmospheric pressure, the CO reaction product pressure will exceed $10^{-1}$ MPa (1 atm) at approximately 1575 °C (2867 °F). Borate glasses also cause dissolution of the protective $SiO_2$ scale forming on SiC or $Si_3N_4$, leading to more rapid corrosion because of the high oxygen permeability of the mixed glass. Experience in test cycles with peak temperatures about 1400 °C (2552 °F) has shown that accelerated dissolution of coatings along microcrack boundaries eventually causes gross oxidation of boron-base inner layers, leading to massive dissolution of the silicon-base overlays.

Moisture sensitivity of borate glasses (Ref 65) can be a major limitation. Hydrolysis at low temperatures in moist air converts adherent $B_2O_3$-containing layers into loosely bonded boric acid particulate. Under long-term exposure, sealant glasses forming beneath the hard overlays undergo moisture attack that leads to spallation. Subsequent heating cycles that rapidly release moisture can cause catastrophic failure. Finally, high-temperature exposure to moist environments makes borate glass susceptible to vaporization by the formation of $HBO_2$ (Ref 44).

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# Plasma Surface Engineering of Plastics

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## Introduction

THE NATURE of the surface of the materials used in a product increasingly determines its success in almost every industry. This is true whether one is dealing with surface cleanliness, bonding of different components, biocompatibility, or mechanical performance of the part under conditions of use. Designers must often select specially formulated and expensive polymeric materials to ensure satisfactory performance, even though these materials often require surface preparation. In some cases, entire design concepts must be abandoned due to the prohibitive cost of the required polymer or the inability of available materials to deliver the desired performance attribute. The alternative to this scenario is to choose the material for its bulk properties and modify the surface of the material to achieve the desired performance attributes. In most cases the final step in the process is the application of a coating that offers the desired performance.

**Conventional Methods.** Historically, surface engineering methods have included mechanical abrasion, solvent wiping to remove surface contamination, solvent swelling, wet chemical etching, and the application of specialized coatings. Application of functional coatings has invariably required surface preparation to achieve an adequate bond between the substrate surface and the coating of choice. Each of these surface engineering methods has limitations, thus providing a strong driving force for the development of alternative surface preparation methods. Many of the common methods mentioned are accompanied by safety and environmental risks, increased risk of part damage, and expensive pollution and disposal problems.

***Abrasion*** only increases the surface area of the part prior to adhesive bonding, and it is thus of limited utility. It often does not reach hidden areas of complex part geometries, and it is operator sensitive, dirty, and difficult to do on small or delicate parts.

***Solvent cleaning*** is useful for removing gross contamination. In ultraclean applications, solvent cleaning merely replaces one contaminant with another. Solvent surface treatment is beneficial in cases where swelling of the polymer substrate can improve adhesion of coatings without adversely affecting the mechanical properties of the substrate. The equipment required is inexpensive, and the process works reasonably well in many cases. The major drawbacks of this technology are the environmental and process hazards associated with the use of large quantities of chemicals. Any savings in equipment cost is usually offset by the increased cost of environmental controls. Solvent-based surface treatment has limited utility when a distinct change in the chemical nature of the substrate surface is desired.

***Acid etching*** is more effective than solvent-based methods, but it can easily result in overtreated and damaged parts, in addition to serious hazard and disposal problems. For example, other than plasma treatment, the most effective method for improving the bonding of materials to fluoropolymers has been to etch the surface with a material commonly referred to as *sodium etch.* The process consists of brief immersion of the component to be bonded in a solution of sodium naphthalene in tetrahydrofuran or another suitable solvent. Although sodium etch is quite effective in treating fluoropolymers, concerns with operator safety and the problems of disposal have caused many users to seek alternatives.

**Energetic Processes.** Flame, ultraviolet (UV), and corona surface treatment have often been suggested as alternatives to wet chemical methods. Of these three methods, flame treatment and corona surface treatment have been adopted on a larger scale. In flame treatment, the surface to be modified is passed through a flame generated by combustion of hydrocarbon gases. In the case of corona treatment, the surface to be modified is exposed to a point discharge across a pair of electrodes. The discharge acts to ionize the gas present in the gap, which subsequently introduces changes in the chemistry of the surface. Flame and corona, although useful in oxidizing the surfaces of plastics, have limited utility in many applications. In addition, the transitory nature of these modifications prevents their widespread use in many applications.

***Limitations.*** Corona treatment is limited by the materials and part configurations that are responsive to this method of surface preparation. Complex shapes cannot easily be treated, because the treatment quality is a function of the distance of the part from the electrode. Thus, small-diameter holes and surfaces that are difficult to access in complex parts prove particularly troublesome. The result is an uneven surface treatment at best. Because corona discharge surface treatments are typically conducted in ambient air, the process is subject to change from day to day as the environment changes in the location where such treatment is being conducted. Finally, the high-voltage discharge often results in thermal damage to sensitive materials such as thin-wall plastics and film.

Flame treatment suffers from many of the limitations of corona treatment: difficulty in reaching recessed areas and evenly treating complex shapes. Thermal damage from overtreatment is another common problem with flame treatment.

**Cold gas plasma technology** is rapidly becoming the preferred industrial process for many applications requiring surface chemical modification. Plasma surface treatment, which is conducted in a vacuum environment, affords a wide latitude of possibilities in chemically changing the surface of a plastic to suit a particular application. Three mechanisms contribute to improvement in the adhesion of two components and the adhesion of coatings:

- Removal of surface contaminants and weakly bound polymer layers
- Enhancement of wettability through incorporation of polar groups that facilitate spontaneous spreading of adhesive or matrix resin
- Formation of functional groups on the surface that permit covalent bonding

When specialized surface characteristics are desired, coatings with unique chemical and physical characteristics can be deposited by plasma polymerization. Examples include antiscratch or antifog coatings, lubricious coatings, biocompatible coatings, and chemical and vapor barrier coatings. Because plasma treatment is a process of surface modification, the bulk properties of the material are retained. The nature of the process also allows precise control of the process parameters and ensures repeatability of the process in industrial applications. Finally, several studies have demonstrated that these surface modifications can be achieved with minimal impact on the environment.

## Plasma Processing Equipment

Most, if not all, plasma equipment consists of similar components, but the design of the reactor chamber, the distribution of power, the excitation frequency, and the gas dynamics can all be critical parameters influencing the efficiency and properties of plasma reactions. An extensive amount of work has been published that shows a direct correlation between excitation frequency and plasma reactivity. Manufacturers of plasma equipment employing radio-frequency (RF) excitation use either low frequencies (i.e., less than 400 kHz) or the higher frequencies 13.56 or 27.12 MHz as specified by the Federal Communications Commission. For applications involving the treatment of plastics, 13.56 MHz is the preferred frequency.

Also important is whether the material being treated is in a primary or a secondary plasma. Older equipment using large cylindrical barrels typically comprises secondary plasma systems (Fig. 1a). The plasma is created either between closely spaced, paired electrodes, which may function as shelves, or in the annulus between the outer wall of the vessel and a ring electrode, when employed. Treatment of materials placed within the working volume depends on the diffusion of active species created in the primary plasma (i.e., within the RF field). Diffusion of these active species is very dependent on pressure; the higher the pressure, the shorter the mean free path. The mean free path is the distance that active species can probably travel before undergoing collisions that deactivate radicals or neutralize ions. Therefore, when using a secondary plasma, the concentration of active species varies either across the diameter of a barrel system or between electrode pairs, as the case may be. Thus, by the physical laws of nature, the treatment within the working volume of a secondary plasma system cannot be uniform.

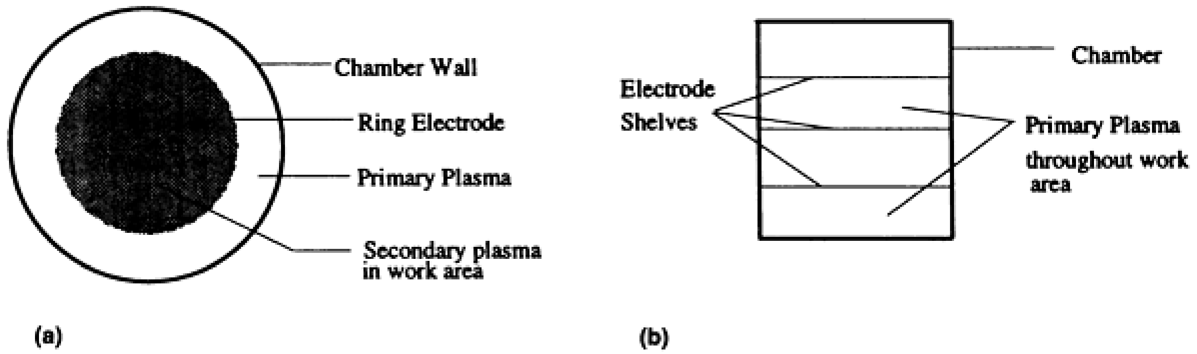


**Fig. 1 Schematic of plasma processing equipment. (a) Barrel-type reactor, typical of secondary plasma systems. (b) Primary plasma reactor**

By contrast, when working within the RF field, or primary plasma, the gas is constantly being excited. Thus, polymeric articles being treated are immersed in a constant concentration of active species. Further, because diffusion is not a mechanistic limitation, significantly higher operating pressures may be used. This allows a higher process gas flow rate, ensuring that out-gassing species from the polymer are sufficiently dilute, providing the full benefits of the desired process gas. In addition, the primary plasma is rich in UV radiation, which is often an important initiation step in polymer reactions. Ultraviolet radiation is line of sight, so uniform treatment of multiple parts can be obtained only when working within the primary plasma. Otherwise, any part in the shadow of another will receive different radiation, and therefore the effectiveness of the treatment will vary.

The types of reactors used for the deposition of plasma polymers have been varied. Glass and/or quartz reactors or aluminum chambers with metal parallel-plate electrodes seem to predominate in the literature, although several investigators have used inductively or capacitively coupled systems with external electrodes. High rates of deposition are found in the glow area, with the rate of deposition decreasing as one moves farther away from the glow discharge region. Consequently, primary plasma systems that use a 13.56 MHz RF source are favored. The RF excitation used by various equipment manufacturers can be as low as 2 to 4 kHz, or it can be the more typical 13.56 MHz (high frequency). Microwave plasma systems have also been used for the deposition of plasma polymers. Previous studies have shown that the densities of films deposited by low-frequency systems are significantly lower than those of films deposited by either the high-frequency or microwave plasma systems. The choice of equipment used for plasma polymerization and deposition is thus dictated by the rate of deposition desired, the film properties that can be obtained by the various systems, and practical considerations such as the size of the parts to be treated and the processing rates that are feasible in any given system.

## Plasma Technology

### *Overview of Plasma Treatment*

There are many definitions of the term *plasma,* according to the various disciplines with which it is involved. It has often been referred to as "the fourth state of matter," the generation of plasma being analogous to the transitions that occur when energy supplied to a material causes solids to melt and liquids to become gases. Sufficient additional energy supplied to a gas creates a plasma. In the case of cold gas plasma, typical of that used in this work, the process is excitation of a gas at reduced pressure by RF energy. Typically, a plasma is composed of a large concentration of highly excited atomic, molecular, ionic, and radical species. On an atomic scale, plasma generation cannot be construed as a room-temperature equilibrium process, because the bulk of the material remains near room temperature. The plasma contains free electrons as well as other metastable particles that break covalent chemical bonds upon collision with the surfaces of polymers placed in the plasma environment, thus creating free radicals on the polymer surface (Ref 1). The free radicals then undergo additional reactions, depending on the gases present in the plasma or subsequent exposure to gases in the atmosphere. The result is that these gas radical reactions form a surface that is potentially very different from that of the starting bulk polymer. Because the process is conducted in a reactor under very controlled conditions, the end result is very reproducible.

Plasma processing is not one process, but rather a "field of opportunities" that can be classified into three overlapping categories: plasma surface modification, plasma-induced grafting, and plasma film deposition. These processes are described in more detail in the section "Plasma Processes" in this article.

**Plasma surface modification (plasma activation)** is the alteration of surface characteristics by the substitution of chemical groups or moieties for groups normally present on the polymer chain being modified. The assumed mechanism is free-radical creation and coupling of these free radicals with active species from the plasma environment. Depending on the process gas selected, a large variety of chemical groups can be incorporated into the surface: hydroxyl, carbonyl, carboxylic, amino, or peroxyl groups. Most important, the insertion or substitution of these groups in the polymer chain is under the control of the operator. In this manner, the surface energies and the surface chemical reactivity of plastics can be altered completely without affecting their bulk properties.

**Plasma-induced grafting** is another method by which plastic surfaces can be modified. If a noble gas is employed to generate a plasma, a multitude of free radicals are created along the polymer backbone. If an unsaturated monomer such as allyl alcohol is introduced into the reaction chamber after the plasma is extinguished, but prior to the introduction of air, it will add to the free radical, yielding a grafted polymer. The range of functional and reactive sites that can be incorporated onto a surface is increased significantly with this technique. This process differs from activation in that instead of functional modification of the surface polymer chains, material is added to the polymer backbone.

**Plasma film deposition (plasma polymerization)** uses gases or vapors that fractionate and undergo polymerization under the influence of RF energy. For example, methane ($CH_4$) under the influence of plasma will deposit as a polyhydrocarbon that has a density approaching 1.6 g/cm$^3$. Any material that can be introduced into the process chamber is a potential candidate as a feed material for plasma polymerization. The properties of materials polymerized in this manner are very different from those of polymers obtained via conventional polymerization methods. These properties include a high degree of cross-linking and the ability to form pinhole-free films that adhere tenaciously to various substrates.

## *Plasma Process Applications*

The particular plasma process used in a given application is dictated by the desired end result. For example, when contamination removal is the primary goal, the process of choice is plasma surface modification. When the goal is to improve the adhesion of two materials, the most commonly used process is surface modification, with plasma-induced grafting offering an attractive alternative. The particular process used is application-specific rather than industry-specific. For example, cleaning processes are used in many industries, such as aerospace, electronics, packaging, and medical products.

All plasma processes have a common thread in that the surface change is accomplished by an ionized gas. As a result of this common basis, it is easy to accomplish several objectives in a single system. For example, surface cleaning and the application of protective coatings is always accomplished in a single reactor with a multiple-step process, instead of using two separate process areas as is common with conventional technology.

Figure 2 illustrates the components of a typical plasma surface treatment system. As described above, the chamber is evacuated to a specified pressure using a mechanical vacuum pump, and gas is introduced into the chamber through flowmeters. During normal operation, gas is continuously introduced into the chamber, and the unreacted species and byproducts are continuously evacuated. The chamber thus operates in a steady state. Application of RF energy to the electrodes ionizes the gas in the reactor. A capacitance matching network tunes the chamber impedance to a constant load.

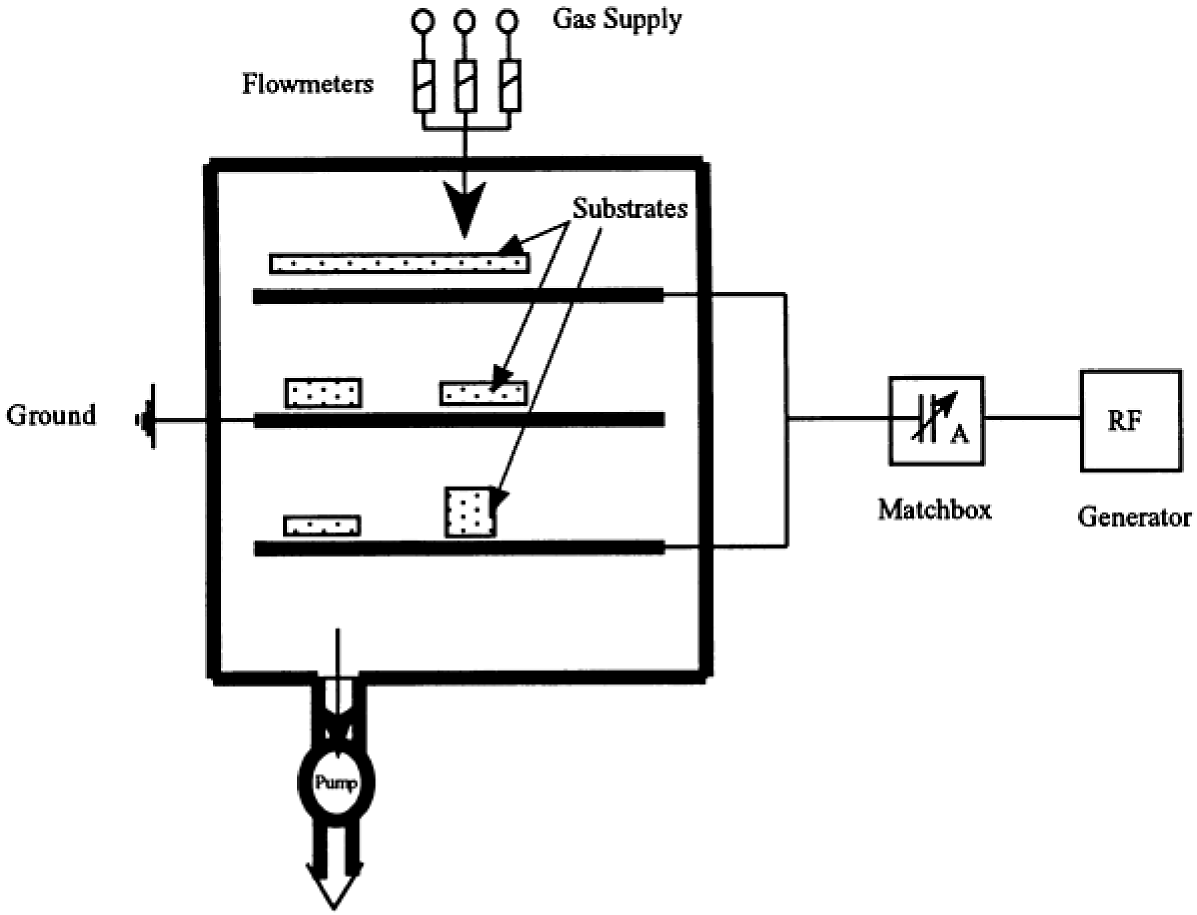


**Fig. 2 Typical plasma surface treatment system**

All commercial reactor systems consist of similar components, but there are variations in design parameters, such as power coupling efficiency and the gas-handling capacity of the vacuum pump. For this reason, it is difficult to translate process conditions from one system design to another. Nonetheless, Table 1 shows suggested starting process conditions for various materials and adhesive systems.

**Table 1 Typical plasma surface treatment conditions**

| Substrate | Adhesive system/ paint system | Process gas | Operating pressure, torr | Radio-frequency power,W | Process time, min |
|---|---|---|---|---|---|
| Polypropylene | Urethane | Oxygen | 0.400 | 200 | 1.0 |
| Nylon | Epoxy | Ammonia | 0.200 | 400 | 3.0 |
| Polyphenylenesulfide | Epoxy | Nitrous oxide | 0.150 | 300 | 0.5 |
| Polytetrafluoroethylene | Epoxy | Ammonia | 0.100 | 550 | 1.5 |
| Polyethylene | Epoxy | $O_2/CF_4$ | 0.200 | 300 | 1.5 |

Adhesion performance for a specific system can be optimized by designing experiments in which the RF power, gas, process pressure, and process time are varied. In the case of plasma-induced grafting and plasma polymerization, process conditions are highly dependent on reactor geometry and reactor design. The experimenter should refer to appropriate references for guidance about starting process conditions.

## *Plasma Discharge Reactions and Surface Interactions*

Although any gas can be ionized using RF excitation, a gas such as $O_2$, $N_2$, He, Ar, $NH_3$, $N_2O$, $CO_2$, $CF_4$, and air, or some combination of these gases, is commonly used in most plasma processes. One of the more commonly used plasma processes is surface treatment in an oxygen plasma, which is aggressive in its reactivity and forms numerous components. Within an oxygen plasma $O^+$, $O^-$, $O_2^+$, $O_2^-$, O, $O_3$, ionized ozone, metastably excited $O_2$, and free electrons are generally observed. The ionization of oxygen into the various species found in an oxygen plasma can be represented by the following reaction scheme:

$$\begin{aligned}
&O_2 + e \rightarrow O_2^- \rightarrow O + O^- \\
&e + O \rightarrow O^+ + 2e \\
&e + O_2 \rightarrow O_2^+ + 2e \\
&e + 2O_2 \rightarrow O_2^- + O_2^- + O \rightarrow O_3 + e
\end{aligned}$$

These reactions represent a small sampling of those that occur in an oxygen glow discharge. As the components formed during the ionization recombine, they release energy and photons, emitting a faint blue glow and much UV radiation. The photons in the UV region have enough energy to break the carbon-carbon and carbon-hydrogen bonds in the materials on the surface that are exposed to the plasma. In the case of contaminants, the net effect appears to be degradative, such that lower-molecular-weight materials are created. These materials are subsequently removed by the vacuum, and in this manner the surface that has been exposed to a plasma is cleaned. Lower-molecular-weight polymer fractions that comprise the weak boundary layers on the surface are also removed in this manner.

Once the contaminants have been removed, the virgin polymer surface is exposed to the plasma environment. The electrons, ions, and free radicals in the plasma act on this exposed polymer, creating free radicals in the molecular chains on the surface (Ref 1, 2, 3). The free radicals that are created on the polymer surface by this process can then react with the various molecular and active species present in the plasma environment. In a low-pressure oxygen plasma, the following oxidation reaction scheme has been suggested:

$$\begin{aligned}
&RH + O\bullet \rightarrow R\bullet + \bullet OH \\
&R\bullet + O_2 \rightarrow RO_2. \\
&RO_2. + R'\,H \rightarrow RO_2H + R'\bullet \\
&RO_2\bullet + R'\bullet \rightarrow RO_2R'
\end{aligned}$$

Here $RO_2H$ and $RO_2R'$ indicate the formation of acids and esters. Not indicated in the above reaction scheme are the possible formation of alcohols, ethers, peroxides, and hydroperoxides.

Thus, besides the reactions resulting from the bombardment of the surface by photons, ions, and neutral particles, all of the active species in the plasma react with the polymer surface. The byproducts that consist of $CO_2$, $H_2O$, and low-molecular-weight hydrocarbons are readily removed by the vacuum system. The use of co-reactants can modify the surface chemistry obtained with a single gas chemistry or accelerate the reaction kinetics. For example, in an oxygen plasma, the breaking of the carbon-carbon and carbon-hydrogen bonds is the rate-limiting step. When tetrafluoromethane is introduced as co-reactant, the $O_2$-$CF_4$ plasma yields excited forms of O, OF, CO, $CF_3$, $CO_2$, and F. Fluorine or fluorine-containing species are more effective in breaking the carbon-carbon and carbon-hydrogen bonds, so the reaction rate is accelerated. These examples illustrate how plasma technology can be used as a "limitless box" to accomplish the desired surface engineering objectives.

## *Contamination Removal*

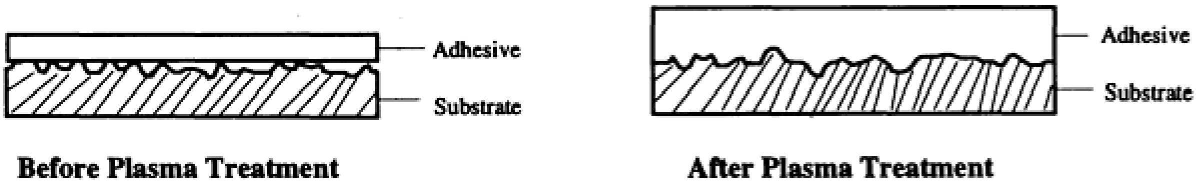
Vapor degreasing or sonication in organic solvents is the most common form of contaminant removal. However, the Montreal protocol on ozone-depleting chemicals has mandated the replacement of chlorofluorocarbon-based cleaning solutions, and use of many of the traditional solvents is also being restricted due to environmental concerns. The alternatives, including water-based systems, have proven to be less effective than expected. Plasma cleaning is now being looked upon as an effective alternative and is beginning to find increasing use (Ref 4, 5, 6, 7, 8).

Ablation is the key process by which contaminants are removed from the surface of materials placed in a plasma (see the description in the previous section about how carbon-carbon and carbon-hydrogen bonds are broken). The choice of gas used for cleaning applications depends on both the contaminant and the substrate to be cleaned. Contaminants that are difficult to remove, such as silicone oils, require aggressive chemistries containing tetrafluoromethane or sulfuroushexafluoride. When delicate materials are to be cleaned, a less aggressive chemistry such as that offered by the noble gases, argon or helium, is commonly used.

## Plasma Surface Modification (Plasma Activation)

Plasma treatment using commonly available gases (air, oxygen, nitrogen, and the others described above) is often referred to as *plasma surface modification.* The distinguishing factor is the absence of reactive gases, such as unsaturated hydrocarbons or saturated hydrocarbons, or any other materials that would result in the deposition of a film on the substrate. In many industries, surface chemical interactions play a central role in the functional performance of the product. For example, the interaction between the surface and a specialized coating is important in the successful performance of the coating. Another example is that in the biomedical industry, one encounters interactions between the surface and proteins or chemical reagents in applications involving cell culture or diagnostic devices (Ref 9, 10, 11, 12). A similar phenomenon exists in adhesive bonding when two dissimilar surfaces are joined. Adhesive bonding represents a large percentage of the applications requiring surface modification, so it will be used to illustrate this process, but the basic principles are equally valid for other applications.

The strength of an adhesive joint is influenced by several factors (Ref 13, 14, 15). Removal of contaminants and process aids provides a means for the adhesive to interlock with the substrate surface rather than with a boundary layer that is merely resting on the surface. In addition, increasing the surface energy of the substrate above the surface tension of the adhesive makes it possible for the adhesive to wet the entire surface of the polymer substrate. The increase in the apparent surface area of contact increases the strength of the adhesive bond (Fig. 3).



**Before Plasma Treatment**

**After Plasma Treatment**

**Fig. 3 Schematic of ablation, or microroughening, of the surface layer of a polymer substrate by plasma surface modification. Microroughening increases the area of contact between an adhesive and a substrate to strengthen the bond.**

Ablation of the surface layers of the exposed polymer can result in a microroughened surface that increases the area of contact between the adhesive and the substrate. Adhesion strength is further enhanced by modification of the surface chemistry in a manner that facilitates covalent bonding between the adhesive and the substrate surface. These changes are accomplished by competing molecular reactions that take place on the surface of a polymer substrate in a plasma. Ablation of the surface layers of the polymer can also take place in a plasma and occur through a similar mechanism. If the substrate consists of a blend or alloy of materials that react differently in a plasma, differential ablation of these components can be used to create a microroughened surface.

Substitution of atoms in the polymer molecule with chemical groups from the plasma is often referred to as *activation.* The surface energy of the polymer placed in a plasma can be increased very rapidly by plasma-induced oxidation, nitration, hydrolization, or amination. The higher surface energy of the polymer surface increases its wettability, which describes the ability of a liquid to spread over and penetrate the surface. The resulting increase in apparent bonded surface area increases the strength of the bond. The process of activation can also be used to replace surface polymer groups with those that facilitate covalent bonding between the polymer substrate and the adhesive.

The use of plasma surface treatment to improve adhesion is well known (Ref 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30), and several literature sources provide an in-depth discussion of the nature of gas plasmas and their chemistries (Ref 1, 16, 18, 21, 22, 23). The gases most commonly employed for surface modification are $O_2$, $N_2$, He, Ar, $NH_3$, $N_2O$, $CO_2$, $CF_4$, and air or some combination of these gases. The first step of the process is contaminant removal by chain scission, and several reports documenting the efficacy of plasma surface cleaning in improving adhesion have been published (Ref 1, 24, 26). Once the contaminants have been removed, the virgin polymer surface is exposed to the plasma environment. The electrons, ions, and free radicals in the plasma act on this exposed polymer, creating free radicals in the molecular chains on the surface (Ref 1, 2, 3). The free radicals that are created on the polymer surface by this process can then react with the various molecular and active species present in the plasma environment.

The permanent nature of these changes on the polymer surface have been confirmed by spectroscopy and documented in several studies (Ref 31, 32, 33, 34). The use of other gases permits the incorporation of other functional groups on the polymer surface. Examples include the use of ammonia, nitrogen, and oxides of nitrogen plasmas that are used to incorporate nitrogen in the surface and create nitrogen-base functional groups such as primary and secondary amines (Ref 35, 36).

One result of modification of the polymer surface is an increase in the surface energy of the polymer and an attendant improvement in surface wetting. As stated above, adequate wetting of the surface by the adhesive contributes to the improvement in bond strength by increasing the apparent area of contact over which the load is distributed. Published studies suggest that this improvement in wetting contributes directly to the observed improvement in the strength of the adhesive bond (Ref 37, 38, 39). As stated above (Fig. 3), another factor that contributes to improved adhesion is an increase in surface area of the polymer surface through microroughening (ablation of the polymer surface through exposure to a plasma). This is particularly the case when the plasma is highly reactive, as when oxygen is used as one of the gas components that is being ionized. The nature of the gas being ionized to create the plasma is not the only factor that determines the extent of ablative etching; the nature of the polymer that is exposed to the plasma also plays a key role. Studies have shown that etching through ablation of surface polymer layers does occur in polymers such as polyethylene, polyethylene terephthalate, and nylon 66 (Ref 22, 40), whereas polyaramid materials such as Kevlar appear to be resistant to microroughening through ablation of the polymer chains (Ref 41).

Evidence presented in several studies indicates that the strength of the adhesive bond depends on the particular functional group that has been created on the surface of the polymer. Some of these studies draw a direct correlation between the nature of the chemical groups on the surface, the nature of the adhesive used, and the observed improvement in adhesion (Ref 22, 39, 42). Other studies relate the improvements to effects of hydrogen bonding and specific surface chemical interactions that do not necessarily result in covalent bonding between the polymer surface and the adhesive (Ref 43). Sometimes it is left to the reader to deduce the conclusions from the adhesion data presented, along with data describing the nature of the surface chemistry (Ref 44, 45).

As these examples illustrate, the selection of the process gas determines how the plasma will alter the polymer. Very aggressive plasmas can be created from relatively benign gases. Oxidation by fluorine free radicals that are generated when tetrafluoromethane is included as one of the gases is as effective as oxidation by the strongest mineral acid solution. The primary difference is that the byproducts of the plasma process do not require special handling, because the active species recombine to their original stable and nonreactive form outside the RF field. In all cases, profound and permanent changes in the chemical nature of the polymer surface are implemented. The stability of these surface changes is a function of the materials themselves and the storage conditions used (Ref 46). For instance, plasticizers that can migrate to the surface, or contaminants in the storage area that can be attracted to these high-energy surfaces, will negate the effects of the chemical changes that have been created on the surface of these materials. Contact angle measurements and electron spectroscopy of plasma-treated surfaces have confirmed the permanent nature of plasma surface modification of polymers. For example, plasma-modified fluorinated ethylene propylene (FEP) was shown to retain its surface chemical characteristics over an 18-month observation period (Ref 47). Similar phenomena have been observed by other investigators for other materials, such as polyethylene and polystyrene (Ref 48). These changes ultimately lead to significant improvements in adhesion strength, as Table 2 suggests.

**Table 2 Lap shear strength of untreated and plasma-treated surfaces**

| Material | Plasma chemistry | Adhesive | Bond strength, MPa | Failure mode | Reference |
|---|---|---|---|---|---|

| | | | | | |
|---|---|---|---|---|---|
| Vectra A625 | Control | Epoxy | 6.47 | Adhesive | 19 |
| | Oxygen plasma | Scotchweld 2216 (3M) | 11.02 | Cohesive | |
| | Ammonia plasma | Scotchweld 2216 (3M) | 8.55 | Cohesive | |
| Noryl 731 | Control | Epoxy | 4.25 | Adhesive | 19 |
| | Oxygen plasma | Scotchweld 2216 (3M) | 10.24 | Adhesive | |
| | Ammonia plasma | Scotchweld 2216 (3M) | 12.40 | Cohesive | |
| Ultem 1000 | Control | Epoxy | 1.28 | Adhesive | 19 |
| | Oxygen plasma | Scotchweld 2216 (3M) | 13.37 | Cohesive | |
| | Ammonia plasma | Scotchweld 2216 (3M) | 14.18 | Cohesive | |
| Rynite 530/935 | Control | Epoxy | 4.71 | Adhesive | 27 |
| | Plasma treatment A | Epoxy | 40.51 | Cohesive | |
| | Plasma treatment B | Epoxy | 41.83 | Cohesive | |
| Tefzel | Control | Epoxy | 0.07 | . . . | 23 |
| | Ammonia plasma | Uniset D276 | 1.39 | . . . | |
| | $O_2/SF_6$ plasma | Uniset D276 | 2.02 | . . . | |

### Plasma-Induced Grafting

As effective as plasma surface modification might be, the extent to which the surfaces of polymers can be modified is limited. Plasma-induced grafting is another method by which chemical functional groups can be incorporated. In this process, free radicals are generated on the surface of a polymer through the use of an inert gas plasma. Because of the nonreactive nature of the inert gas plasma, surface chemical modification of the polymer does not occur. However, if a polymer surface that has been treated in this fashion is exposed to vapors of unsaturated monomers, the monomers get attached to the surface. A variety of vinyl monomers are available, and the possibilities for incorporating many different chemical functional groups are endless. Unlike surface modification, this is a two-step process, which adds a degree of complexity. Few studies have appeared in the open literature; the majority of such processes are being used in proprietary applications (Ref 49, 50, 51).

### Plasma Film Deposition (Plasma Polymerization)

Compared to the processes described above, plasma film deposition is an entirely new avenue for bonding dissimilar materials. For example, films deposited from a methane plasma have been shown to dramatically improve the adhesion properties of many materials when tested in both the dry and wet states (Ref 49). The process of plasma film deposition is often called *plasma polymerization,* although the process that takes place is not polymerization in the classical sense.

Gases in plasma may undergo polymerization, usually through a free radical initiation process. When a gas is ionized by RF energy, the resulting plasma contains free electrons as well as other metastable particles. When the process gas mixture used consists wholly or in part of hydrocarbon gases, the hydrocarbon molecule is fractured into free radical fragments, which become the sites at which the polymerization process is initiated. As the molecular weight of the plasma-polymerized product increases, the product is deposited onto the substrate placed within the plasma chamber. The fragmentation of the feed gas in the plasma generates free radical species for initiating the polymerization process, so gases that have zero functionality, such as methane ($CH_4$), can be used to form plasma polymers. In addition to methane, plasma polymers have been formed from other hydrocarbon gases such as ethylene or propylene, fluorocarbon monomers such as tetrafluoroethylene, and organosilicon compounds such as hexamethyldisiloxane (HMDSO) or vinyltrimethylsilane. Due to the complex nature of the fragmentation process, the resulting polymer structure is unlike any that can be deduced from conventional polymerization mechanisms (Ref 52). The physics of plasma polymerization has been described in depth elsewhere in sufficient detail for the interested reader (Ref 49, 53, 54).

The conditions used during glow discharge polymerization determine not only the structure of the resulting film but also the rate at which these films are deposited onto the target substrate materials (Ref 49, 55, 56). The degree to which the monomer is fragmented depends on the amount of energy supplied per unit weight of monomer that is allowed to flow through the reactor. When sufficient energy is supplied to break all the bonds of the monomer molecule, the recombination or polymerization process becomes atomic in nature. In addition, the structure of the plasma polymers can be varied by changing the reaction conditions, including the use of co-monomers or the introduction of oxygen, nitrogen, or ammonia into the reaction chamber during the polymerization process. Studies have correlated the power input, the type of monomer used, and the monomer flow rate to the density and type of active species in the plasma, and these factors in turn determine the rate of deposition and the film structure (Ref 56, 57). Table 3 shows typical deposition rates for some common plasma-polymerized films.

**Table 3 Deposition rates for various compounds**

| **Compound** | **Deposition rate (D), $10^8 \times$ gm/cm$^2$/min** | **$D/D_0$** |
|---|---|---|
| Hexamethyldisiloxane | $233 = D_0$ | 1.00 |
| Acrylic acid | 28 | 0.12 |
| Styrene | 173 | 0.74 |
| Tetramethyldisiloxane | 191 | 0.82 |
| Divinyltetramethyldisiloxane | 641 | 2.75 |
| Ethylene | 42 | 0.18 |
| Benzene | 110 | 0.47 |

Source: Ref 49

Plasma of ammonia, mixtures of hydrogen and nitrogen, and oxides of nitrogen have been used to incorporate nitrogen atoms in the surface layers of the polymer (Ref 35, 36), but the level of nitrogen incorporation has been less than 10 at.% (Ref 36). In contrast, films deposited from allyl amine have shown to contain up to 25 at.% nitrogen, as measured by spectroscopic methods (Ref 58). Despite this high nitrogen content, however, Ref 58 reports a lower-than-expected concentration of amino groups. Other studies have shown concentrations of up to 2 molecules/nm$^2$ of reactive amine groups on the surface of films deposited from allyl amine onto FEP substrates. These surface concentrations were determined by derivatization of the amine groups with fluoroscein isothiocyanate and subsequent detection of the fluoroscein chromophore by optical spectroscopy (Ref 59). Electron spectroscopy does not always allow precise determination of functional sites, so the earlier data may reflect limitations of the analytical methods used.

In a similar vein, hydroxyl and carboxylic acid functionalities can be incorporated by plasma polymerizing acrylic acid (Ref 60) or allyl alcohol (Ref 58). Another technique commonly employed to incorporate specific atomic species is the use of co-reactants along with the primary monomer. In one such example, ammonia or acrylonitrile was used as the co-reactant during the deposition of films from a methane plasma (Ref 61). Two additional techniques for modifying plasma-deposited films are plasma surface modification of the deposited film in a second process step and wet chemical reaction methods. As an example, carbonyls formed during the plasma deposition of films from N-vinylpyrrolidone were reacted with lithium aluminum hydride and sodium borohydride to convert these carbonyls to hydroxyl groups (Ref 62).

The use of plasma-deposited films for adhesion enhancement is not limited to polymeric substrates. Such films have also been deposited onto inorganic materials, such as mica (Ref 60), and metal substrates, such as aluminum and steel, in an effort to improve adhesion of these materials to polymers (Ref 49).

Plasma film deposition technology has become a significant tool in achieving performance attributes beyond simple adhesion improvement. The diverse applications include biocompatibility, permeation control of films, corrosion resistance of metal surfaces, and hard coats or abrasion-resistant coatings for plastic substrates. Plasma-polymerized films have been successfully used for developing gas separation membranes and as barrier coatings for packaging applications. Such coatings are typically deposited from the plasma polymerization of siloxane monomers (Ref 63, 64, 65, 66). As shown in Table 4, plasma-deposited films offer barrier properties that are significantly better than those obtained by films deposited by evaporative methods.

**Table 4 Oxygen transmission rates of evaporated and plasma-deposited $SiO_x$ coatings on polyethylene terephthalate**

| **Process** | **Material** | **Thickness, Å** | **$O_2$ rate, cc/m$^2$/day** | **$H_2O$ rate, g/m$^2$/day** |
|---|---|---|---|---|
| Resistance evaporation | SiO | 600 | 2.2 | 2.5 |
| Electron-beam evaporation | SiO | 600 | 3.0 | 2.0 |
| Plasma-enhanced chemical vapor deposition | $SiO_2$ | 200 | 1.0 | 1.0 |

Source: Ref 64

Table 5 compares the physical properties and permeation characteristics of plasma-deposited films with those of a silicone rubber membrane for use in gas separation. The membranes prepared from HMDSO are similar to silicone rubber but of a higher density, and they appear to offer better selectivity. Note that the structure of the plasma-deposited film significantly influences the permeation properties, as evidenced by the differences between HMDSO films and hydroxymethyldisilazane films. Other applications include optical coatings (Ref 67), abrasion-resistant coatings (Ref 68, 69), and coatings that act as semiconducting films (Ref 70). As shown in Table 6, plasma-deposited coatings offer a 300% improvement in the abrasion resistance of polycarbonate substrates compared with that of uncoated plastic.

**Table 5 Physical properties and permaselectivity of plasma-polymerized (PP) films**

| **Parameter** | **PP HMDSO, 0.5 µm** | **PP HMDSN, 0.5 µm** | **Silicone rubber, 1.0 µm** |
|---|---|---|---|

| | | | |
|---|---|---|---|
| Film density, g · $cm^{-3}$ | 1.40 | 1.35 | 1.05 |
| C, H, N content, mass % | 32.5, 8.3, 0.0 | 32.0, 8.5, 7.2 | 32.0, 8.1, 0.0 |
| $N_2$ permeation coefficient(a) | $1.3 \times 10^{-15}$ | $0.27 \times 10^{-15}$ | $3.5 \times 10^{-15}$ |
| Separation Factor | | | |
| $CH_4/N_2$ | 2.7 | 1.2 | 2.4 |
| $C_4H_{10}/N_2$ | 21.0 | 9.8 | 7.8 |
| $CO_2/N_2$ | 8.1 | 3.9 | 5.4 |
| $He/N_2$ | 2.8 | 2.3 | 2.8 |
| $O_2/N_2$ | 2.4 | 0.7 | 2.4 |

HMDSO, hexamethyldisiloxane. HMDSN, hydroxymethyldisilazane.

Source: Ref 63

(a) The $N_2$ permeation coefficient is calculated as [$m^3$, STP (m)/($m^2$(s)(Pa)] where STP is standard temperature and pressure.

**Table 6 Haze resulting form abrasion of polycarbonate substrates**

| **Sample** | **Haze, %** | **Notes** |
|---|---|---|
| Uncoated polycarbonate | 5.2 ± 0.8 | Average haze for ten samples |
| Coated polycarbonate | 4.1 ± 0.5 | Average haze for three samples |
| Coated and oxygen-treated polycarbonate | 2.5 ± 0.2 | Average haze for six samples |
| Uncoated and unabraded polycarbonate | 2.3 ± 0.1 | Average haze for ten samples |
| Coated and unabraded polycarbonate | 2.2 ± 0.1 | Average haze for three samples |

Source: Ref 69

Biomedical applications of plasma-polymerized films are primarily devoted to biocompatible coatings (Ref 71, 72, 73, 74). The interaction between plastics and body fluids such as human blood and proteins is complex and not well understood. Because plastic materials offer an opportunity to develop and design lifesaving devices and prosthetics, the focus in these applications has been biocompatibility for both short-term use and long-term implants. Several literature sources offer excellent summaries of these applications (Ref 74).

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# Surface Engineering of Carbide, Cermet, and Ceramic Cutting Tools

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## Introduction

RAPID TECHNOLOGICAL DEVELOPMENT has produced global competition in manufacturing, and the incentive to improve productivity has never been greater. This article discusses the expanding role of surface engineering in increasing the manufacturing productivity of carbide, cermet, and ceramic cutting tool materials used in machining operations.

## Acknowledgements

The authors wish to express their appreciation to P.C. Jindal and W.A. Bryant for their contributions to this article and to E.J. Oles and P.K. Mehrotra for reviewing the manuscript.

## Tool Material Classes

The classes of tool materials currently in use for machining operations are high-speed tool steels, carbides, cermets, ceramics, polycrystalline cubic boron nitrides (CBN), and polycrystalline diamonds (PCD). The different materials vary greatly in wear resistance and toughness. Figure 1 shows schematically their relative application ranges in terms of machining speeds and feed rates. Higher machining speeds require tool materials with greater wear resistance, whereas higher feed rates require tools with increased toughness. High-speed tool steels are the toughest materials; however, their relatively low wear resistance limits their application to low-speed machining. (Cleaning, finishing, and coating of tool steels are discussed in the article "Surface Engineering of Specialty Steels" in this Volume.) At the other end of the spectrum, superhard materials such as CBN and PCD are highly wear resistant and can be employed at high speeds. There is, however, a tradeoff between wear resistance and toughness that can limit the application of these superhard tools to lighter feed rates.

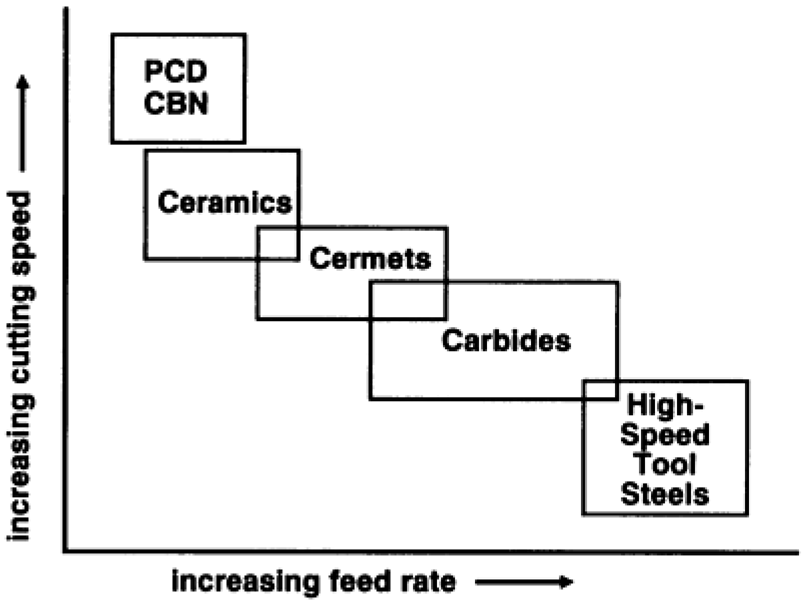

**Fig. 1 Relative machining application ranges of cutting tool materials**

In between the two extremes of high-speed tool steels and superhard materials are carbides, cermets, and ceramic tool materials, which are used over a wide range of speeds and feed rates to suit the diverse machining needs of the automotive, aerospace, and other manufacturing industries. Tables 1, 2, and 3 list the representative properties of carbide, cermet, and ceramic tool materials, respectively. In the past two decades, surface modification technologies have significantly expanded tool application ranges, particularly for carbides, and have dramatically improved manufacturing productivity.

**Table 1 Typical properties of cemented carbides**

| **Nominal composition, wt%** | **Grain size** | **Hardness, HRA** | **Density, g/cm$^3$** | **Transverse rupture strength, MPa** | **Compressive strength, MPa** | **Young's modulus, GPa** | **Relative abrasion resistance(a)** | **Coefficient of thermal expansion(b), μm/m · K** | **Thermal conductivity, W/m · K** | **Palmquist toughness(c), kg/mm** |
|---|---|---|---|---|---|---|---|---|---|---|
| 94WC-6Co | Fine | 92.5-93.1 | 15.0 | 1790 | 5930 | 614 | 100 | 5.9 | 108 | 80 |
| 94WC-6Co | Medium | 91.7-92.2 | 15.0 | 2000 | 5450 | 648 | 58 | 5.4 | 100 | 90 |
| 90WC-10Co | Fine | 90.7-91.3 | 14.6 | 3100 | 5170 | 620 | 22 | 6.0 | 80 | 120 |
| 72WC-8TiC-11.5TaC-8.5Co | Medium | 90.7-91.5 | 12.6 | 1720 | 5170 | 558 | 13 | 6.8 | 50 | 123 |

Source: Ref 44

(a) Based on a value of 100 for the most abrasion-resistant material.

(b) Room temperature to 1000 °C (1832 °F).

(c) Slope of load, $P$, vs. total crack length, $\sum_i l_i$, in a $P$ vs. $\sum_i l_i$ plot obtained in indentation tests.

**Table 2 Typical properties of cermets**

| **Composition** | **Vickers hardness, kg/mm$^2$** | **Modulus of rupture, MPa** | **Fracture toughness $K_{Ic}$, MPa $\sqrt{m}$** | **Young's modulus, GPa** |
|---|---|---|---|---|
| (Ti,Mo/W)CN | 1650 | 1500 | 8.5 | 450 |

|  |  |  |  |  |
|---|---|---|---|---|
| (Ti,Mo/W,Nb,Ta)CN | 1500 | 1800 | 10.0 | 410 |

**Table 3 Typical properties of ceramics**

| Composition | Transverse rupture strength, MPa | Young's modulus, GPa | Fracture toughness $K_{Ic}$, MPa $\sqrt{m}$ | Coefficient of thermal expansion, μ/m · K |
|---|---|---|---|---|
| $Al_2O_3$ | 400 | 390 | 4.0 | 8.2 |
| $Al_2O_3$-TiC | 700 | 420 | 4.5 | 8.3 |
| Sialon[(a)] | 760 | 300 | 6.0 | 3.2 |

Source: Ref 8

(a) Values specific to Kyon 2000 (Kennametal Sialon Grade).

**Cemented carbides** belong to a class of hard, wear-resistant, refractory materials in which the hard carbides of Group IVB-VIB metals are bound together or cemented by a ductile metal binder, usually cobalt or nickel. The first cemented carbide was produced in the 1920s and consisted of tungsten carbide (WC) with a cobalt binder (Ref 1). A remarkable feature of cemented carbides is that they can be tailored to provide different combinations of abrasion resistance and toughness by controlling the amount of cobalt and WC grain size.

Over the years, the basic WC-Co material has been modified to produce a variety of cemented carbides containing WC-TiC, WC-TiC-TaC, WC-TiC-(Ta,Nb)C, and other solid-solution cubic carbides that cover a wide range of applications, including metalcutting, mining, construction, rock drilling, metal forming, structural components, and wear parts. The commercially significant alloys for machining contain 5 to 12 wt% Co and up to 15 wt% cubic carbides. Carbide grain sizes from 0.5 to 5 μm are commonly used.

**Cermets.** The technical definition is that a cermet is a composite of a ceramic material with a metallic binder. Although WC-Co tools also fit this definition, in the North American machining industry the term *cermets* is applied more specifically to TiC-based tools that contain mainly nickel as a binder. Cermet tools have lower density than WC tools but are heavier than ceramic inserts of equal size. The first cutting tool in this family, a TiC-Ni alloy, was commercialized as early as the 1930s, but it could not compete with the inherently stronger WC-Co-based tools. Additions of molybdenum to TiC-Ni alloys in 1960 brought cermets closer in performance to WC-Co-based tools in finish machining of steels.

Titanium carbonitride cermets based on Ti(C,N)-Ni-Mo were introduced in 1970, followed by (Ti,Mo)(C,N)-based compositions that provided a balance of wear resistance and toughness due to their finer microstructures (Ref 2). Continued development in this area has now resulted in complex cermets having a variety of additives, such as $Mo_2C$, TaC, NbC, ZrC, HfC, WC, VC, $Cr_3C_2$, and aluminum (Ref 3). Various mixes of these additives impart different combinations of wear resistance, thermal shock resistance, and toughness, and they allow tools to be tailored for a wide range of machining applications. The newer cermets are used in semifinishing and finishing of carbon and alloy steels, stainless steels, ductile irons, free-machining aluminum and other nonferrous alloys, and some high-temperature alloys. The metal removal operations may include turning, boring, milling, threading, and grooving.

**Ceramic** tools are inherently more stable than carbide tools at high temperatures (high cutting speeds) but are less fracture resistant; hence, recent developments have been focused on improving their fracture toughness. There are basically two classes of ceramic cutting tools: $Al_2O_3$ ceramics and tools based on silicon nitride ($Si_3N_4$) and solid solutions of aluminum and oxygen in silicon nitride (Sialons).

***$Al_2O_3$ Ceramics.*** The white $Al_2O_3$-based ceramics may contain low levels of zirconia ($ZrO_2$) as a sintering aid and are used for machining cast iron. Higher levels are used in tools to machine steels. The $ZrO_2$ improves fracture toughness by a transformation toughening or crack deflection mechanism (Ref 4, 5), but it decreases the thermal conductivity and hardness of the tool.

Additions of up to 30 vol% TiC to $Al_2O_3$ make the inserts black and improve the thermal conductivity, hardness, and toughness of the tools without seriously degrading their chemical stability. $Al_2O_3$-TiC ceramics are employed on a wide range of workpiece materials, including cast iron, steel, and nickel-base superalloys.

SiC-whisker-reinforced $Al_2O_3$ ceramics, developed in the early 1980s (Ref 6), offer better toughness than white ceramics due to crack deflection by the dispersed SiC whiskers in the microstructure (Ref 7). The whiskers also increase hardness and improve thermal shock resistance by increasing thermal conductivity and reducing the thermal expansion coefficient. The major application of these tool materials is high-speed/high-feed machining of nickel-base superalloys. These ceramics can be used on cast irons but are rarely used on steels because of the poor chemical stability of SiC.

***$Si_3N_4$/Sialon ceramics*** were introduced in the early 1980s. Their whisker-like grain structure makes them tougher than the white $Al_2O_3$ ceramics, and they also possess excellent hot hardness and thermal shock resistance. These characteristics permit them to be used at high speeds and feed rates and in interrupted cutting of nickel-base superalloys and cast irons (Ref 8, 9). However, the lower chemical stability of $Si_3N_4$/Sialon tool materials (compared to $Al_2O_3$ ceramics) prohibits their application in most steel machining.

**Superhard Materials.** As discussed earlier, superhard materials are extremely wear resistant. CBN is the tool of choice for machining hard steels (i.e., steels with hardnesses greater than 50 HRC). PCD, on the other hand, cannot be used for steel machining because of diamond's solubility in iron and the catalytic effect of iron, which causes graphitization of the diamond. The primary application of PCD tools is in the very-high-speed machining of aluminum-silicon alloys, composites, and other nonmetallic workpieces.

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## Tool Failure Mechanisms

Machining of metals is a complex process. The cutting tool environment features high localized temperatures (~1000 °C, or 1830 °F) and high stresses (~700 MPa, or 100 ksi). The tool may experience repeated impact loads during interrupted cuts, and the workpiece chips may chemically interact with the tool material. The response of a tool material to the above conditions dictates its performance. High temperatures and stresses can cause blunting from the plastic deformation of the tool tip, and high stresses alone may lead to catastrophic fracture. In addition, the useful life of cutting tools may be limited by a variety of wear processes, such as crater wear, flank wear or abrasive wear, builtup edge, depth-of-cut notching, and thermal cracks (Fig. 2). The origin of the various tool failure mechanisms is now well understood (Ref 10).

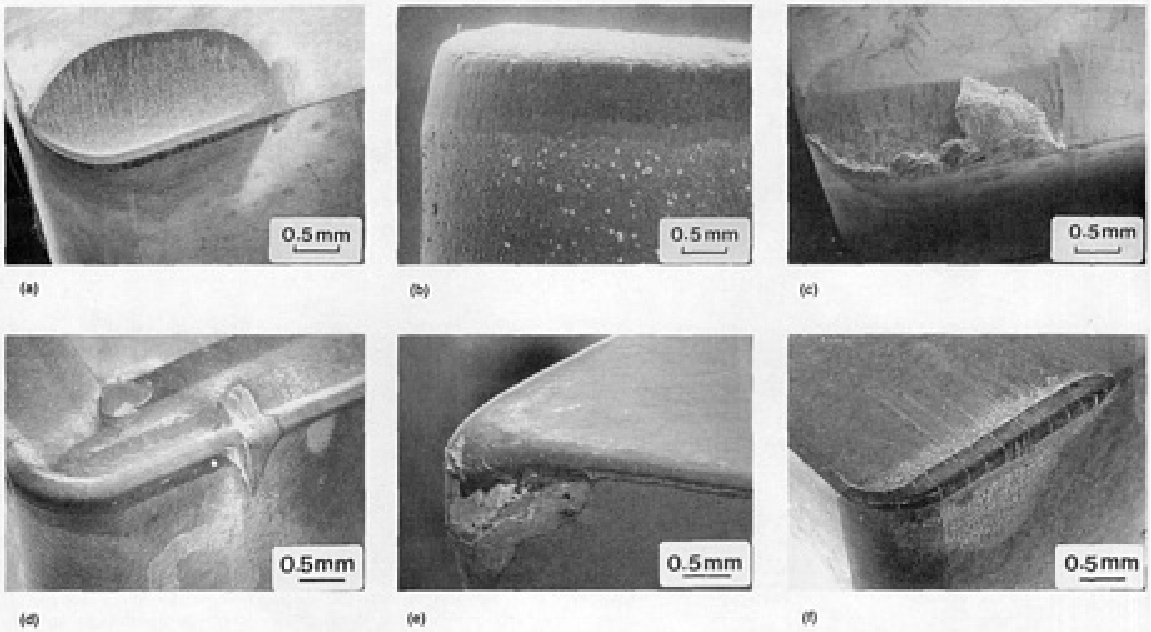

**Fig. 2 Tool wear mechanisms. (a) Crater wear on a cemented carbide tool produced during the machining of plain carbon steel. (b) Abrasive wear on the flank face of a cemented carbide tool produced during the machining of gray cast iron. (c) Builtup edge produced during low-speed machining of a nickel-base alloy. (d) Depth-of-cut notching on a carbide tool produced during the machining of a nickel-base superalloy. (e) Carbide insert showing nose wear (tool-tip blunting) due to insufficient deformation resistance of the tool. (f) Thermal and mechanical cracks in a carbide insert after interrupted cutting of low-alloy steel**

**Crater wear (Fig. 2a),** observed on the rake face of cutting tools, generally occurs during machining of relatively soft steels and ductile irons at high speeds. It is primarily caused by a chemical interaction between the rake face of a metalcutting insert and the hot metal chip flowing over the tool. This interaction may involve diffusion or dissolution of the tool material into the chip. Adhesion of tool material and chip follows, with consequent microfracture of the tool underneath the adhered material.

**Flank wear (Fig. 2b),** on the other hand, is observed on the flank or clearance face of a metalcutting insert and is caused by abrasion of the flank face by the hard constituents of the workpiece. This failure mechanism is commonly observed during machining of cast irons and steels where the abrasive particles are mainly $Fe_3C$ and nonmetallic inclusions.

**Builtup edge (Fig. 2c)** refers to welding of the workpiece material to the tool tip. It typically occurs when soft low-carbon steels and nonferrous materials are machined at low speeds and light feed rates. This may result in attrition wear if small fragments of tool material are carried away as the builtup edge breaks off.

**Depth-of-cut notching (Fig. 2d)** occurs at the depth-of-cut line and is often attributed to the chemical reaction (oxidation) of the tool material with the atmosphere (Ref 11) or to abrasion by the hard, sawtooth outer edge of the chip (Ref 12). Notching is a problem with workpieces that tend to work harden and generate high tool-tip temperatures, such as austenitic stainless steels and nickel-base superalloys. Depth-of-cut notching can lead to tool fracture. Aside from selection of a tool material that is relatively chemically inert and possesses high fracture toughness, notching can be minimized by applying optimized geometries, such as chamfered edges and round insert styles, that spread the depth of cut over a wider area of the cutting edge.

**Nose wear (Fig. 2e),** or tool-tip blunting, results from insufficient deformation resistance of a tool material in a given machining application.

**Thermal cracks (Fig. 2f)** develop when the repeated heating and cooling associated with interrupted cutting, such as milling, create temperature gradients at the cutting edge. With prolonged interrupted cutting, lateral cracks may appear parallel to the cutting edge. The thermal and lateral cracks may join together and cause small fragments of tool material to break away.

Fracture is the least desirable mode of tool failure because it is unpredictable and catastrophic. The preferred mode is flank wear, because it progresses gradually and can be easily monitored for tool-changing protocol. Most tool material development work is focused on minimizing flank wear and preventing unwanted tool failure modes such as catastrophic fracture, gross plastic deformation, builtup edge, crater wear, and depth-of-cut notching.

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## Applicable Methods for Surface Engineering of Cutting Tools

A major breakthrough in controlling cutting tool wear came in the 1960s with the advent of protective hard coatings for cemented carbide inserts. This mode of surface modification increased tool life on steels and cast irons by a factor of at least two to three (Ref 13). Coatings also permitted the use of higher cutting speeds, boosting machining productivity.

The precursor to the development of coated carbide tools occurred in the mid-1960s, when laminated inserts consisting of a base of WC-Co alloy with a sintered layer of high TiC were produced. Although metalcutting productivity increased, thermal stresses during machining often caused the laminate to spall during use.

**Chemical Vapor Deposited Coatings.** Further development of laminated tools was superseded in 1969 by the application of a thin (~5 μm) layer of hard TiC coating to the cemented carbide tool by chemical vapor deposition (CVD) (Ref 13). In the CVD coating process, the tools are heated in a sealed reactor to about 1000 °C (1830 °F) with gaseous hydrogen at atmospheric or lower pressure; volatile compounds are added to the hydrogen to supply the metallic and nonmetallic constituents of the coating.

In TiC deposition, a reaction often occurs in which titanium combines with carbon from the cemented carbide substrate. The resulting surface decarburization leads to the formation of a brittle eta phase and to associated substrate microporosity at the coating-substrate interface. The early coated tools were particularly notorious in this regard and showed inconsistent performance during interrupted cuts (Ref 14). Such performance inconsistencies have now been largely eliminated by a number of metallurgical and processing innovations that have resulted in coatings with greater thickness uniformity, more adherence, and more consistent morphology and microstructure with minimum interfacial eta phase and associated porosity (Ref 15). Additional information is available in the article "Chemical Vapor Deposition of Nonsemiconductor Materials" in this Volume.

***Multilayer CVD Coatings.*** During the 1970s, CVD coatings evolved from single-layer TiC coatings to multilayer hard coatings comprising various combinations of TiC, TiCN, TiN, HfN, and $Al_2O_3$ (Fig. 3). Multilayer coatings, through a combination of properties, suppress crater wear, flank wear, and builtup edge and extend the range of application. A variation of the multilayer coating employs multiple alternating layers. Figure 3(e) shows a coating with alternating layers of $Al_2O_3$ and TiN that is particularly effective in high-speed machining of steels and cast irons (Ref 16).

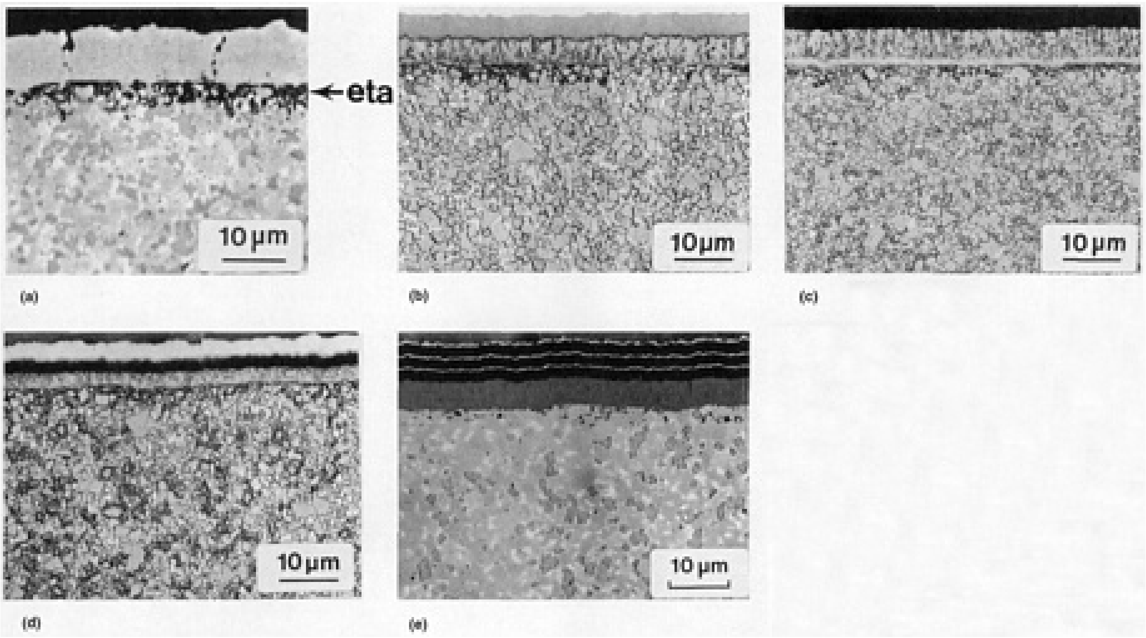

**Fig. 3 Chemical vapor deposition coatings. (a) Cemented carbide insert with TiC coating. Note eta phase at the coating-substrate interface. (b) 73WC-19(Ti,Ta,Nb)C-8Co alloy with a TiC/TiCN/TiN coating about 10 μm thick. (c) 85WC-9(Ti,Ta,Nb)C-6Co alloy with a TiC/$Al_2O_3$ coating about 9 μm thick. (d) 85WC-9(Ti,Ta,Nb)C-6Co with a TiC/$Al_2O_3$/TiN coating about 10 μm thick. (e) TiCN coating supporting multiple alternating coating layers of $Al_2O_3$ and TiN**

The high temperatures employed during CVD coating generally ensure good bonding between the substrate and the coating. The thermal expansion coefficients of the coating materials (TiC, TiCN, TiN, and $Al_2O_3$) are higher than those of the WC-Co-based substrates, so CVD coatings are in residual tension at room temperature. In certain cases, the stresses may be relieved by transverse cracks that form in the coating. These cracks do not affect coating adhesion, but they may initiate tool fracture in interrupted cutting operations in which the cutting edge is subjected to fatigue-type loading. Residual tensile stresses are most severe at tool corners. To minimize their effect, and also to minimize the formation of eta phase, which tends to develop to a greater extent at sharp tool edges, CVD-coated tools are honed before coating.

***Tailored Substrates for CVD-Coated Tools.*** Although the early CVD-coated tools substantially improved metalcutting productivity, they were prone to catastrophic fracture when applied at high feed rates or in intermittent cutting operations. One solution to this problem is to improve the fracture toughness of the substrate by increasing its cobalt content. Unfortunately, this approach decreases deformation resistance, which can result in tool-tip blunting.

A major breakthrough in resolving the conflict between fracture toughness and deformation resistance occurred in the late 1970s, when a TiC/TiCN/TiN-coated tool was developed with a peripheral cobalt-enriched zone, 10 to 30 μm thick (Fig. 4a), that provided superior edge strength while maintaining the deformation resistance of the bulk of the coated tool (Ref 17). This development permitted users to make heavy interrupted machining cuts such as those encountered in scaled forgings and castings at lower speeds. Further advancements in the cobalt enrichment concept (Fig. 4b) have expanded the application range of this type of tool to higher speeds (Ref 18).

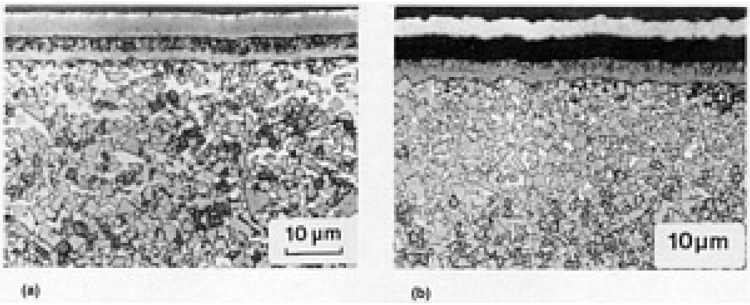

**Fig. 4 Multilayer chemical vapor deposition coatings on cobalt-enriched substrates. (a) 86WC-8(Ti,Ta,Nb)C-6Co alloy with cobalt-enriched periphery and a TiC/TiCN/TiN coating. (b) Second-generation cobalt-enriched cemented carbide tool with TiC/$Al_2O_3$/TiN coating**

***Medium-Temperature CVD Coatings.*** In the mid-1980s a new CVD process for depositing TiCN was commercialized. Using a mixture of $TiCl_4$, $H_2$, and an organic C/N compound such as acetonitrile, it was shown that TiCN can be deposited at moderate temperatures (700 to 900 °C, or 1300 to 1650 °F) at faster deposition rates than in the conventional CVD process (Ref 19). The reduced process temperature and the faster deposition rate minimize the formation of the embrittling eta phase at the coating-substrate interface (Fig. 5) and lessen the thermally induced tensile cracks that are common to higher-temperature CVD coatings (Ref 20).

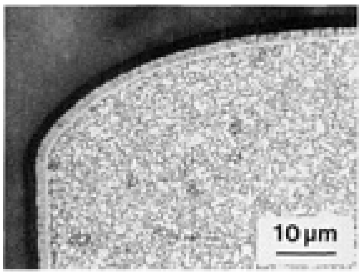

**Fig. 5 Medium-temperature chemical vapor deposition TiCN/$Al_2O_3$ coating on a cemented carbide substrate**

**Physical Vapor Deposited Coatings.** In the 1980s, physical vapor deposition (PVD) emerged as a commercially viable process for applying hard TiN coatings to cemented carbide tools. In this process the coating is deposited in a vacuum by condensation from a flux of neutral or ionized atoms where the metal species are derived from a variety of sources, including electron-beam evaporation, magnetron sputtering, and arc evaporation (Ref 21, 22). In the ion plating variation of the basic PVD process, the flux of atoms and ions is activated by an electrical glow discharge plasma, and the charged species are accelerated toward the substrate by applying a negative bias potential on the substrate. For hard coatings, the evaporated or sputtered metal or cation species (titanium, hafnium, zirconium, etc.) are evaporated or sputtered and are made to react with the gaseous species ($N_2$, $NH_3$, $CH_4$, etc.) introduced into the vacuum chamber. Because PVD coatings are produced at low pressures ($10^{-3}$ to $10^{-2}$ torr), the atoms and molecules have long mean free paths and undergo fewer collisions, making PVD a line-of-sight deposition technique. This necessitates moving the tool fixtures during the PVD deposition to ensure uniformly thick coatings on both the rake and flank faces of tool inserts.

A number of factors make the PVD process attractive for use with cemented carbide tools:

- Lower deposition temperature (<500 °C, or 930 °F) prevents eta-phase formation and produces crack-free coatings with finer grain sizes.
- The coatings are smooth and thus generate less frictional heat during machining.
- Depending on the deposition technique, compressive residual stresses, which are beneficial in resisting crack propagation, may be introduced into the coating (Ref 23).
- PVD coating preserves the transverse rupture strength of the carbide substrate, whereas the CVD

process generally reduces the transverse rupture strength by as much as 30% (Ref 24, 25).

- PVD coatings can be applied uniformly over sharp cutting edges (Fig. 6a). A sharp edge is desirable in a cutting tool because it leads to lower cutting forces, reduced tool-tip temperatures, and finer workpiece surface finishes.

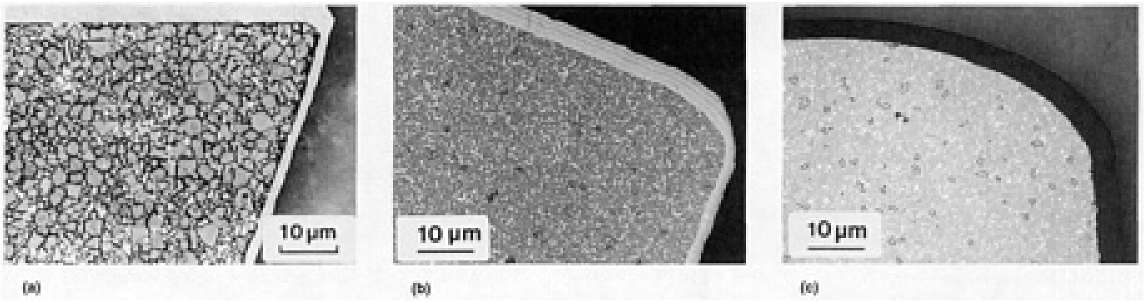

**Fig. 6 Physical vapor deposition coatings on cemented carbide substrates. (a) TiN. (b) TiCN. (c) TiAlN**

In the last three years, newer compositions such as TiCN (Fig. 6b), TiAlN (Fig. 6c), TiZrN, and CrN have been commercialized using the PVD process. PVD $Al_2O_3$ coatings, however, are not yet commercially available.

Additional information about PVD coatings is available in the articles "Growth and Growth-Related Properties of Films Formed by Physical Vapor Deposition Processes" and "Vacuum Deposition, Reactive Evaporation, and Gas Evaporation" in this Volume.

**Plasma-Assisted CVD Coatings.** The high deposition temperatures (~1000 °C, or 1830 °F) of CVD coatings can degrade the strength of the cemented carbide substrate. On the other hand, the PVD coating process, which takes place at lower temperatures (~500 °C, or 930 °F), has a line-of-sight disadvantage. A compromise between the two techniques is the plasma-assisted CVD coating process, which offers a combination of moderate deposition temperature (~600 °C, or 1110 °F) and good thickness uniformity without the need to rotate the tools during the coating process.

In the traditional CVD process, thermal energy activates the chemical reaction that forms the hard coating compounds. In plasma-assisted CVD, lower-temperature activation is enabled by the energetic particles in a plasma, typically an argon discharge. Both direct-current and radio-frequency power supplies are used to deposit the conducting (TiN and TiC) and insulating ($Al_2O_3$) coatings (Ref 26). Use of plasma-assisted CVD for hard coatings on cemented carbide substrates is not yet widespread, probably due in part to the process economics relative to the competing CVD and PVD methods. Additional information is available in the article "Plasma-Enhanced Chemical Vapor Deposition" in this Volume.

**CVD/PVD Coatings.** A recent development in carbide cutting tool coatings combines an outer PVD TiN layer with inner CVD TiN/TiCN layers on a tough cobalt-enriched substrate for interrupted cutting applications such as milling (Fig. 7). The inner CVD layers provide excellent adhesion and wear resistance, and the outer PVD layer offers a hard, fine-grain, crack-free, smooth surface endowed with compressive residual stress. The synergistic effects of this combination contribute to excellent tool performance in milling of steel components at relatively high speeds (Ref 27).

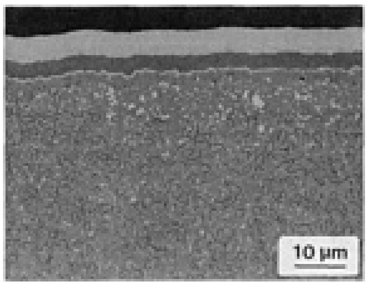

**Fig. 7 Combination of a chemical vapor deposition TiN-TiCN coating and a physical vapor deposition TiN coating on a cobalt-enriched cemented carbide insert**

**Diamond Coatings.** The most recent addition to the development of hard coatings is the low-pressure synthesis of diamond films by carbonaceous gas decomposition in the presence of hydrogen ions. This process is an alternative to the high-pressure, high-temperature synthesis of bulk diamond, which is used to fabricate PCD tips that are brazed onto WC-Co substrates. These PCD-tipped inserts are relatively expensive, but they provide a 20- to 100-fold increase in tool life over uncoated WC-Co inserts in the machining of highly abrasive nonferrous alloys (e.g., aluminum-silicon).

The progress in thin-film diamond coating research has been significant in the last few years. The outstanding problem to date has been unsatisfactory adhesion of the diamond coating to the carbide substrate, partly due to an inherently large mismatch in the coefficients of thermal expansion. Although a ceramic substrate such as silicon nitride presents a better match with diamond, WC-Co-based substrates are more economical when good diamond coating adhesion is obtained. Diamond-coated carbide inserts with good coating adhesion are now being introduced commercially. Recent data from field tests indicate that such diamond-coated inserts can approach the performance of the PCD counterparts (Ref 28). Additionally, diamond-coated inserts will eventually feature chipbreaker designs that are difficult to fabricate in PCD inserts. Research continues regarding the control of diamond grain morphology (Fig. 8) as it relates to the final workpiece surface finish.

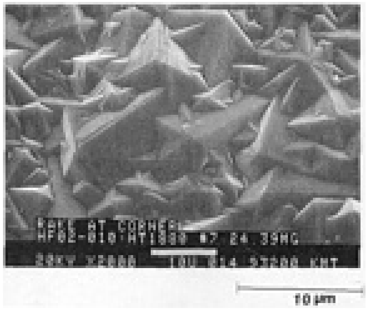

**Fig. 8 Diamond coating on a cemented carbide insert**

**Ion implantation** is a surface modification process that consists of injecting energetic ions into the surface layers of a material. It has been applied to carbide wear products and end mills with limited success (Ref 29). Its main drawback is that the implantation depth and subsurface region disordered by knock-on collisions are no deeper than tenths of a micron. This is much too thin compared to hard coatings that are typically 5 to 10 μm. Ion implantation has therefore not been successfully applied in machining applications. Additional information about this process is available in the article "Ion Implantation" in this Volume.

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## Properties of Hard Coatings

The successful application of hard coatings on cutting tool substrates is due to the combination of physical and mechanical properties of the coating. From a functional standpoint, chemical stability, hot hardness, and good adhesion to the substrate are essential; optimum coating thickness, fine microstructures, and compressive residual stresses can further enhance their performance.

**Chemical Stability.** The criterion for chemical inertness is either a high negative standard free energy of formation of the coating material or low solubility in the workpiece material at temperatures encountered during machining. As can be seen in Fig. 9 and Table 4, CVD $Al_2O_3$ coatings singularly meet these requirements for machining of irons and steels. However, amorphous PVD $Al_2O_3$ coatings are unstable and are not as satisfactory as the crystalline $Al_2O_3$ obtained in CVD. PVD TiAlN coatings are also chemically stable and offer the potential for high-speed machining of steels. Diamond-coated tools are suitable for machining nonferrous alloys containing abrasive second-phase particles (e.g., aluminum-silicon alloys) as well as for machining nonmetallic materials that do not react with carbon (e.g., metal-matrix composites and fiber-reinforced plastics).

**Table 4 Properties of chemical vapor deposited coating materials**

| Material | Room-temperature microhardness kg/mm$^2$ | Coefficient of thermal expansion µm/·K | Thermal conductivity at 1000 K, W/m·K | Relative dissolution rates into iron at: | |
|---|---|---|---|---|---|
| | | | | 500 °C (932 °F) | 1100 °C (2030 °F) |
| TiC | 2800-3200 | 7.7 | 38 | 1.0 | 1.0 |
| TiN | 2000-2200 | 9.4 | 25 | $1.8 \times 10^{-3}$ | $2.2 \times 10^{-1}$ |
| HfN | 1700 | 6.9 | 10 | $3.8 \times 10^{-5}$ | $2.5 \times 10^{-2}$ |
| $Al_2O_3$ | 2100-2300 | 8.4 | 7.5 | $8.9 \times 10^{-11}$ | $4.1 \times 10^{-5}$ |

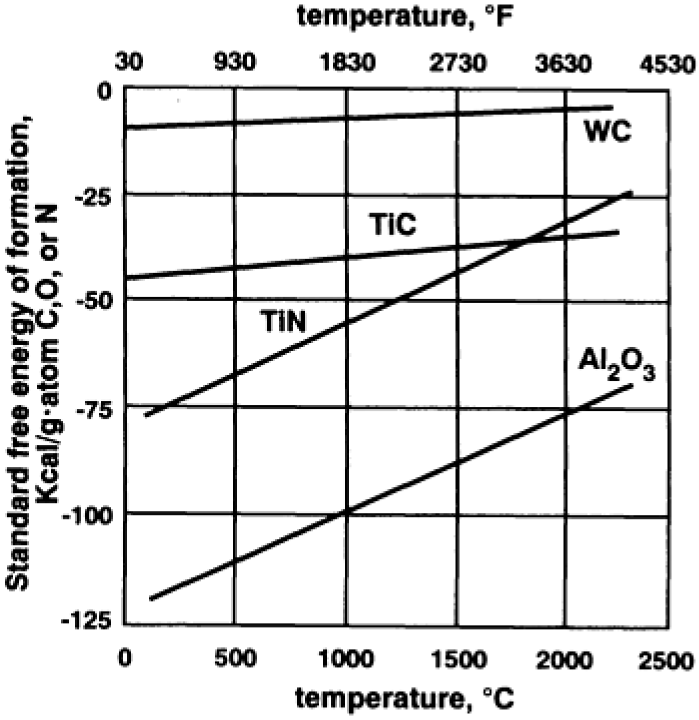

**Fig. 9 Variation in the standard free energy of formation of WC, TiN, TiC, and $Al_2O_3$ with temperature. This parameter gives an indication of the extent to which these materials will undergo diffusion wear.**

**Hot Hardness.** The importance of coating material hardness in resisting abrasive wear has been well documented (Ref 30). High coating hardness is also believed to be beneficial in resisting the abrasive wear component of crater wear (Ref 31). The relevant hardness corresponds to the high temperatures characteristic of those prevalent during machining. Figure 10 shows Vickers microhardness as a function of test temperature for $Al_2O_3$, TiN, and TiC. Although TiC has high room-temperature hardness, it loses hardness rapidly with temperature. Al $_2O_3$, on the other hand, has lower room-temperature hardness but retains its hardness to higher temperatures. The data thus suggest that TiC coatings would be more effective at lower speeds, whereas $Al_2O_3$ coatings, by virtue of high hot hardness and chemical stability, would be most effective for high-speed machining. These concepts have been validated in the machining of 1045 steel and gray cast iron (Ref 32).

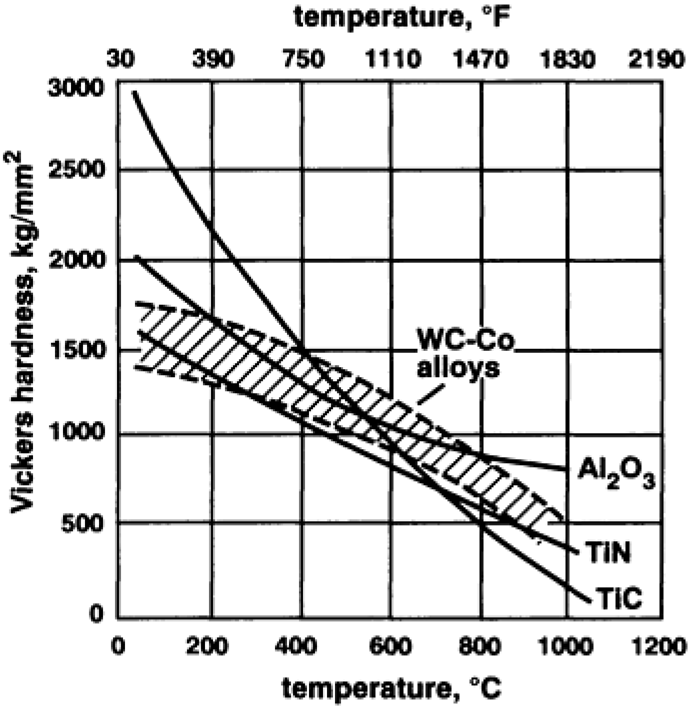

**Fig. 10 Temperature dependence of hardness of TiC, $Al_2O_3$, and TiN. The range of hardness of WC-Co alloys is also shown.**

**Microstructure.** The microstructure of hard coatings controls their mechanical properties and metalcutting performance. A generalized Hall-Petch relationship between grain size of the coating and microhardness has been shown to hold true for CVD and PVD coatings (Ref 33). The higher measured microhardness of PVD TiN relative to that of CVD TiN has been attributed not only to the finer grain sizes obtained in the PVD process but to the presence of compressive residual stresses (Ref 33). Compressive residual stress developed during ion bombardment in certain PVD processes retards crack propagation and thus produces a fracture toughness advantage for PVD-coated tools.

Grain boundary voids developed during columnar growth of some PVD coatings do not allow retention of residual stresses and lead to lower hardness (Ref 34). Likewise, CVD coarse-grain alpha-$Al_2O_3$, which grows with intergranular voids, is not expected to be as hard as the void-free, fine-grain kappa-$Al_2O_3$. Alternating multilayers of CVD kappa-$Al_2O_3$, which have fine grain sizes due to periodic interruption of growth, are harder than $Al_2O_3$ that has been allowed to grow as a single, thick coating (Ref 17). However, transformation from the metastable kappa phase to the stable alpha phase at high temperatures (~1050 °C, or 1920 °F) may induce stresses and a subsequent decrease in coating adhesion.

Coating morphology can also affect surface roughness, which in turn may increase the frictional forces and generate heat at the chip-tool interface. It is known that the relatively smoother PVD TiN-coated carbide tools decrease cutting forces and produce better workpiece surface finishes than CVD-coated tools (Ref 25). In contrast, rough surface morphology is still an issue in diamond coatings (Ref 28).

**Adhesion.** Good coating adhesion to the substrate is a necessary condition for satisfactory performance of the coated tool. It has been shown that varying levels of measured adhesion directly relate to tool life, other variables being constant (Ref 33).

During the high-temperature CVD process, initial coating nucleation on the carbide substrate occurs under conditions that allow interdiffusion of coating and substrate atoms at the interface. In plasma-assisted PVD processes, energetic ion bombardment creates lattice defects that enhance diffusion of coating species at the interface, even at lower deposition temperatures.

It is necessary to choose compatible coating-substrate combinations that accommodate film growth stresses and thermal mismatch stresses at the interface. As noted earlier, coating phase transformations can also induce stresses that may affect adhesion. Substrate surface contaminants prior to coating, particularly in the PVD process, can have detrimental effects on coating adhesion and should be minimized. The use of a thin titanium interlayer to remove residual oxide contaminants, as well as to accommodate interfacial stress, is now common in industrial PVD TiN deposition (Ref 35). Current PVD technology provides well-adhered coatings that are as effective as CVD coatings in demanding applications.

**Coating Thickness.** To achieve maximum metalcutting productivity, the thickness of the modified surface layer has to be optimized. If the modified tool surface region is too thin, the effect persists for a negligibly short time during cutting. If the coating is too thick, the layer acts as a bulk material and the advantage of an engineered composite may be lost. It is established that functional tool coatings should be at least 2 μm thick and that they may be as thick as 20 μm. Coatings deposited by CVD are typically 10 μm thick, while PVD coatings are usually less than 5 μm thick. As mentioned above, ion implantation, which affects no more than 0.1 μm of surface depth, has been found to be ineffective.

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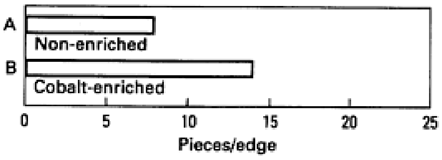
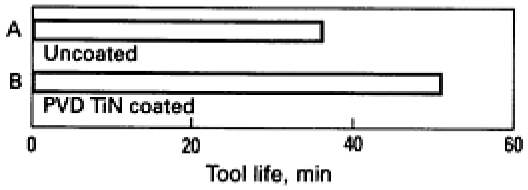
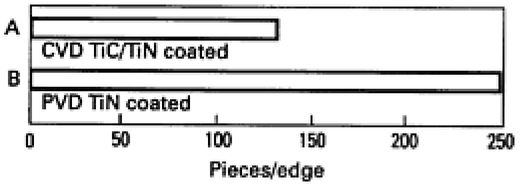
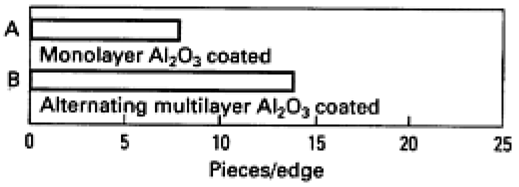
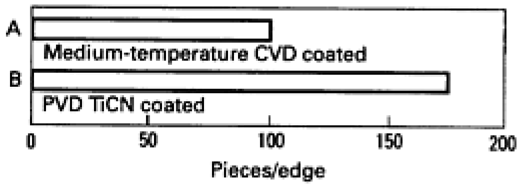
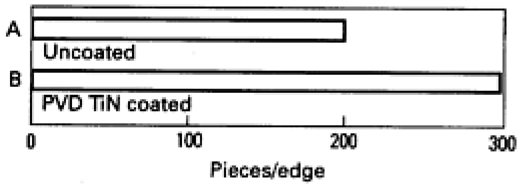
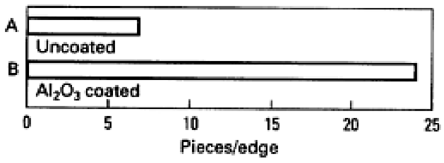
## Application of Coated Tools

The advent and evolution of various coating technologies has produced a wide array of coated carbide tools with broad application ranges. At the same time, specialized areas of application exist where specific coatings and/or substrates offer outstanding performance. Typical applications for each category of coated metalcutting tools are highlighted below. Table 5 gives a few examples of machining productivity enhancements that are due to surface modification of carbide, cermet, and ceramic tool materials.

**Table 5 Effect of surface treatments on the performance of cemented carbide, cermet, and ceramic tool materials**

| Operation | Work material | Cutting speed | | Feed rate | Depth of cut | | ISO No. (ANSI No.) | Results |
|---|---|---|---|---|---|---|---|---|
| | | m/min | sfm | | mm | in. | | |
| **Cemented carbide tool materials** | | | | | | | | |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Turning[a] | 4137H steel forging | 73-98 | 240-320 | 0.76 mm/rev (0.03 in./rev) | 4.6-19 | 0.2-0.7 | TNMG 330924 (TNMG 666) |  |
| Face milling | 1020 steel | 152 | 500 | 0.18 mm/tooth (0.007 in./tooth) | . . . | . . . | SPGN 120308 (SPG 422) |  |
| Camshaft milling | 5150 steel | 274 | 900 | 0.18 mm/tooth (0.007 in./tooth) | . . . | . . . | SPGN 190412 (SPG 633) |  |
| Facing | Ductile iron | 174 | 570 | 0.50 mm/rev (0.02 in./rev) | 9.38 | 0.4 | CNMG 190612 (CNMG 643) |  |
| Face milling | 1020 steel | 330 | 1080 | 0.20 mm/tooth (0.008 in./tooth) | 3.75 | 0.15 | SEHW 1204AFTN (SEHW 43AGT) |  |
| **Cermet tool mateial** | | | | | | | | |
| Turning and facing | 430F stainless steel | 197 | 640 | 0.15 mm/rev (0.006 in./rev) | 1.0 | 0.04 | VNMG 160408 (VNMG 332) |  |
| **Ceramic tool mateial** | | | | | | | | |
| Turning and facing | Gray cast iron brake drum | 550 | 1800 | 0.63 mm/rev (0.025 in./rev) | 3.75-5.0 | 0.15-0.2 | RNGN 120400T (RNG 43T) |  |

(a) CVD TiC/TiCN/TiN coated tool

**CVD-Coated Tools.** Normal-temperature (~1000 °C, or 1830 °F) CVD-coated cemented carbides make up over 80% of all coated carbide metalcutting tools in use. These tools are employed in a variety of metalcutting applications, including turning, boring, parting, threading, grooving, and milling. They are used in machining carbon, alloy, and stainless steels and gray and ductile cast irons, covering a very wide range of speeds and feeds.

**CVD-Coated Tools with Cobalt-Enriched Substrates.** Multilayer CVD-coated tools with specially tailored cobalt-enriched substrates combine the wear resistance of the hard coatings with an edge-toughened substrate. These tools can therefore handle medium to heavy roughing to semifinishing operations on cast irons and high-temperature alloys, as well as stainless, low-carbon, and alloy steels. The broad application range of cobalt-enriched tools enables them to cover a large percentage of the metalcutting operations of a plant, allowing the user to stock fewer grades.

**Medium-Temperature CVD and Plasma-Assisted CVD Coated Tools.** The microstructures of tools coated by medium-temperature CVD and plasma-assisted CVD are characterized by a negligible amount of eta phase at the coating-substrate interface. This permits them to be used in all applications where normal-temperature CVD tools are applied, in addition to those operations that involve interrupted cuts (Ref 26, 36).

**CVD/PVD-coated tools** benefit from the synergistic effects of wear-resistant inner CVD layers combined with a smooth, fine-grain, crack-free outer PVD layer featuring compressive residual stresses. CVD/PVD-coated tools are therefore suited for interrupted cutting operations such as milling of low- and medium-carbon steels and alloy steels (Ref 27). The full potential of CVD/PVD coatings on cemented carbide tools has yet to be determined.

**PVD-Coated Tools.** The PVD coating process offers unique advantages, including the ability to apply a fine-grain, smooth, low-friction, and crack-free coating over sharp edges. When deposited by the ion plating method, PVD coatings also feature compressive residual stresses. These characteristics make PVD-coated tools particularly useful in threading, grooving, parting, finish-turning, and milling operations. Typical workpiece materials include low-carbon and alloy steels, hardened steels, stainless steels, and high-temperature nickel-base alloys.

**Diamond-Coated Tools.** Diamond coatings, with their extremely high hardness, can provide excellent productivity in the machining of nonferrous alloys containing abrasive second-phase particles, such as aluminum-silicon alloys, and in the machining of composite nonmetallic materials that do not have a chemical reactivity problem with carbon. Initial applications of the diamond-coated tools will be similar to those where PCD tools are applied (Ref 37), with the former providing further flexibility in the use of molded chipbreakers, and in rough cuts where surface finish requirement is not stringent.

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## Coatings for Ceramic and Cermet Inserts

Coatings for ceramic and cermet tool materials have not received the extensive development efforts enjoyed by coatings for cemented carbide tools. This is mainly because ceramic and cermet tools amount to less than 10% of the inserts employed in North America and Europe (although they account for about 35% of those used in Japan). Nevertheless, hard coatings for the ceramic and cermet tools can and do provide productivity benefits in certain applications (Table 5).

The chemical reactivity of silicon-nitride-based ceramics is relatively high and limits their usefulness in machining ferrous workpieces. However, application of an $Al_2O_3$ coating (which is chemically inert) enables users to exploit the high hot hardness of the silicon nitride substrate (Ref 38).

Current developments in cermets emphasize raising toughness through increases in nickel and cobalt binder contents. These changes have the desired effect but also raise the tools' chemical reactivity, compromising their usefulness on ferrous workpieces. Coatings can provide a solution to the problem, but the high process temperatures of conventional CVD coatings tend to produce brittle intermetallic compounds involving nickel and titanium. Hence, coatings for cermet tools have focused on those applied by the PVD process.

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## Future Potential

After two decades of material and process innovations, CVD hard coating technology is now mature. The multilayer approach has been very successful in expanding the functionality of the hard coating, and it is anticipated that this design will be duplicated with the newer PVD technology. The property enhancements obtainable in PVD, such as controlled residual compressive stress and fine grain morphology, are expected to be exploited further; indeed, the PVD counterparts may challenge similar CVD coatings as the process economics of the two methods begin to converge. PVD processes are also environmentally cleaner because they do not produce the gaseous effluents characteristic of CVD.

How will the newer coating technologies compare against conventional CVD? To truly compete with all present CVD coatings, an adherent PVD $Al_2O_3$ coating with crystalline microstructure must be developed. Beyond the conventional hard coating compounds, however, PVD techniques offer a larger range of possible compositions, including metastable compounds, that can perhaps be exploited in particular applications (Ref 39). Polycrystalline superlattice coatings such as TiN/NbN, TiN/Ni, and TiN/Ni-Cr are reported to have significantly higher microhardnesses than those of homogeneous nitrides and are promising for metalcutting applications (Ref 40).

The lower-temperature processes, such as medium-temperature CVD TiCN and plasma-assisted CVD, will grow as alternative coating technologies if the ability to deposit a variety of compositions is demonstrated. Combinations of various coating technologies will make sense when material and process economics are justified.

Diamond coatings on metalcutting inserts are expected to be commercially available soon (Ref 28, 41) as upscaling of equipment and optimization of performance are achieved in industrial tests. The major challenge in the coming years will be the successful synthesis of CBN superhard coatings by low-pressure methods. CBN coatings have more industrial potential than diamond because they will be useful in high-volume ferrous cutting applications. Researchers are now taking technical approaches similar to those that led to the realization of diamond coatings (Ref 42, 43), but interrelated issues of film stability, residual stress, coating thickness, adhesion to the matched tool substrate, and upscaling to large-area deposition are still outstanding.

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### Environmental Regulation of Surface Engineering

**David J. Smukowski, Boeing Commercial Airplane Group**

## Introduction

ENVIRONMENTAL PROTECTION REGULATIONS are often related directly or indirectly to surface engineering processes. This article describes selected U.S. environmental statutes and regulations as they are pertinent to material surface finishers. For information about specific regulatory requirements, permitting conditions, and enforcement issues, the reader is advised to seek assistance from federal, state, and local regulatory agencies, consulting engineering firms, and law offices.

## Acknowledgements

The author wishes to acknowledge David J. Wirth for contributing the section on the Clean Water Act and Lorna W. Rubenaker for typing, editing, organizing, and producing the figures and tables.

## Environmental Protection System

U.S. environmental protection has become a complex system of statutes, regulations, guidance documents, executive directives, and standards that are intended to protect human health and the environment. A basic understanding of these requirements will assist those who need to reduce or eliminate the environmental impact of their operations in a cost-effective manner.

**History of the Environmental Movement.** Winston Churchill wrote that "The further back you look, the further forward you can see." The history of the environmental movement shows that environmental management is inextricably linked to population, resources, and technology.

In the 17th and 18th centuries, resources such as land, timber, fish, minerals, and water were considered inexhaustible and free for the taking. This way of thinking changed as the population grew. By the late 18th century, New York, Chicago, and Philadelphia alone contained over one million people. By 1910, 50% of the U.S. population lived in cities.

During the era of the Great Depression, the Tennessee Valley Authority, the Civilian Conservation Corps, the Soil Conservation Service, and the Wilderness Society were created to provide jobs to the unemployed and begin nursing the land. When World War II brought massive industrialization without regard for air or water quality, many states drafted legislation to curtail pollution.

The social revolution of the 1960s and 1970s brought the Clean Air Act and the Clean Water Act, but these did little but divert wastes to landfills. In 1980 the Resources Conservation and Recovery Act (RCRA) was passed for the purpose of tracking hazardous waste from "cradle to grave." The 1990s opened a new era in which we better understand past practices and look less often for end-of-pipe or end-of-stack treatments. We now look at design, materials, and processes to eliminate the root causes of waste production and pollution.

**Environmental Law.** The term *environmental law* does not fully convey its meaning. Once a law is developed, rules for compliance are promulgated, and recordkeeping systems, monitoring procedures, and inspection schedules are developed to enforce compliance. For example, for the eight federal statutes discussed in this article, which constitute some 1,200 pages of text, another 13,000 pages of federal regulations have been developed to carry out the laws (Fig. 1), along with countless more pages of state and local laws, regulations, and guidance documents. These pages have evolved into a web of requirements that constitutes a classic "command and control" system of enforcement.

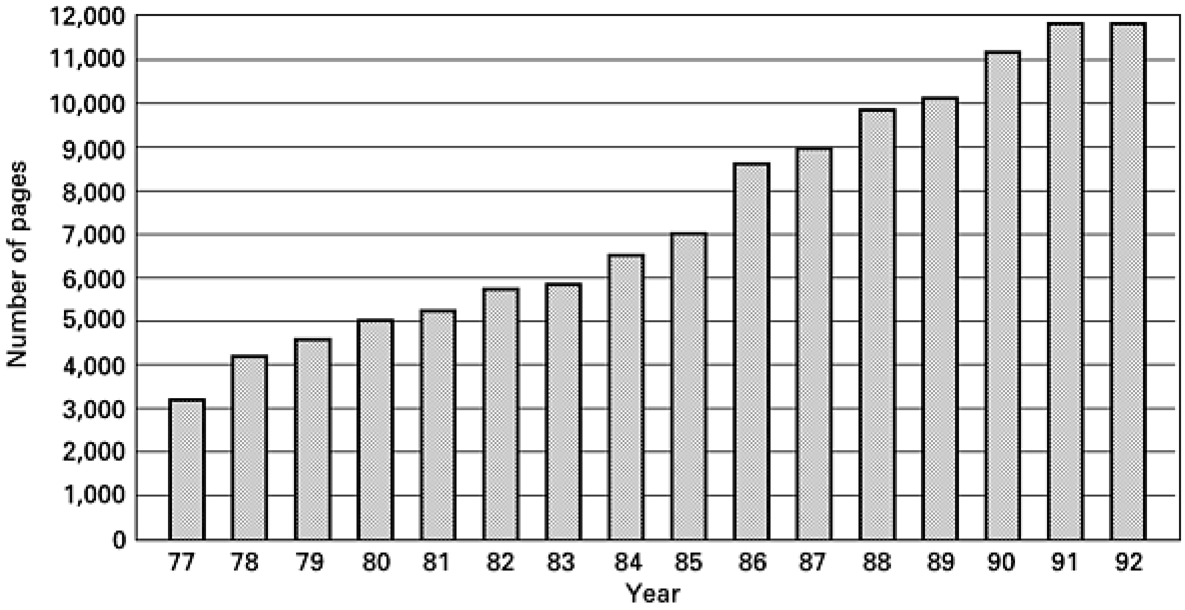

**Fig. 1 Growth of federal regulation. The 1992 figure is given as of July 1. Source: 40 CFR**

***The Legislative Process.*** Federal and state procedures for making laws are similar. The first step in the federal procedure is that a bill is introduced in either the U.S. House of Representatives or the U.S. Senate. Each bill is assigned a number, preceded by an "S" (for a Senate bill) or "H.R." (for a House bill). Bills are then referred to committees of focused expertise for consideration. These committees hold hearings, study, investigate, and issue a report on the bill. When a bill is "reported out" of a committee, it is debated by the House and/or Senate. The House and Senate typically pass different versions of bills, which are then sent to a joint conference committee. When that committee comes to agreement, a bill is sent to the President for signature or veto within ten days. Once signed, a bill is public law.

***State and Local Laws.*** Federal law generally sets only the minimum requirements of environmental law. States and local jurisdictions have the right to exceed federal standards to meet regional needs. In most large metropolitan areas, local rules will be considerably more stringent than the federal requirements in this article.

***The Regulatory Process.*** Environmental laws empower administrative agencies, such as the Environmental Protection Agency (EPA) and the Occupational Safety and Health Administration (OSHA), to promulgate detailed regulations on how to meet the law. Alternatively, the President can write an Executive Order and direct an agency such as the Department of Defense to promulgate regulations.

Rulemaking includes collecting data from industry. The EPA often uses a mandatory questionnaire called a Section 114 request to collect data. The EPA then interprets the data and proposes regulations in the *Federal Register.* After a comment period, final regulations are published in the *Federal Register,* along with preamble discussion of the comments received and their interpretation by the agency. These regulations have the same effect as law and are incorporated into the *Code of Federal Regulations* (CFR).

Figure 2 shows the typical relationships between the legislative and regulatory processes.

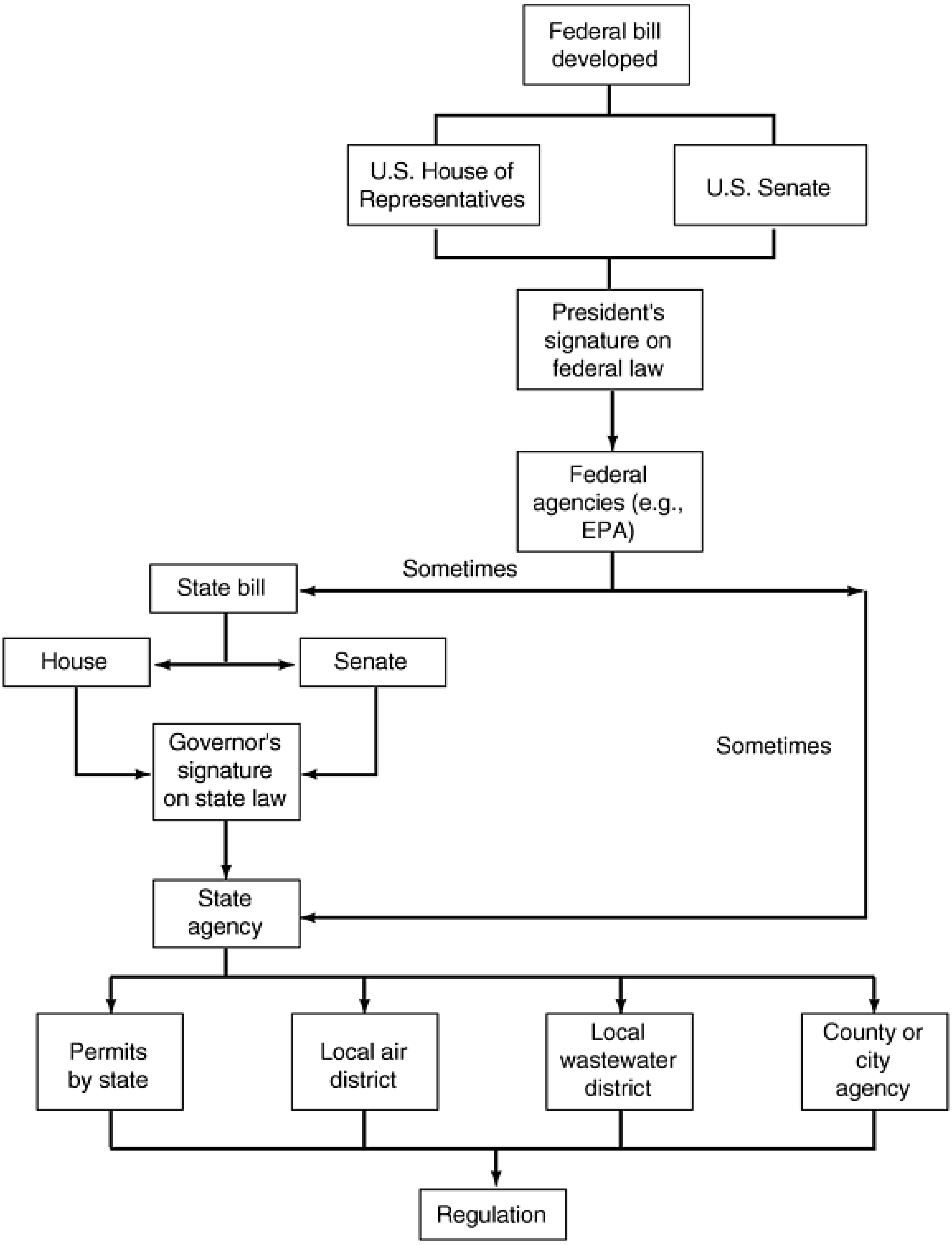

**Fig. 2 Typical relationships between the legislative and regulatory processes**

***Content of Environmental Laws and Regulations.*** Most environmental laws and ensuing regulations contain the same elements:

- Broad statement of purpose
- Inventory of the problem
- Standards of compliance with emissions, discharges, or disposal
- Notification of the public

- Monitoring and records
- Government fee or funding mechanism
- Prohibitions and/or bans
- Technical control equipment and material standards
- Inspection and assistance
- Reports and/or plans
- Enforcement penalty requirements
- Permits
- Detailed compliance requirements, such as labeling and signs

These elements place the burden on the regulated community to provide information to the government that establishes compliance with the law. A facility must inform the government if it plans to engage in any activity that may result in storing, using, or releasing a regulated material. This begins a complex chain of planning, permit seeking, training, self-monitoring, and reporting. Noncompliance typically results in both civil and criminal penalties. Therefore, it is imperative that all surface preparation processes be understood in the context of environmental law.

## The Clean Air Act

The federal Clean Air Act (CAA), written in 1965 and amended in 1970, 1977, and 1990, is the most controversial and industry-intrusive environmental law ever developed. Initially it researched air quality, federalized air pollution control, provided for health protection, and controlled mobile and stationary sources of pollutants (e.g., automobiles and factories).

The 1977 amendments added National Ambient Air Quality Standards (NAAQS), which set criteria for designating regions of the country that do not meet standards for particulates, nitrous oxide (NOX), sulfur oxide (SOX), lead, carbon monoxide, and ozone-depleting substances. These areas of "nonattainment" can then be targeted for stricter requirements.

The 1990 amendments are the most onerous to industry in that they ban, restrict, and/or rigidly control most chemical emissions from industry. Most of the requirements will be effective between 1995 and 2000, posing both drastic changes and opportunities for surface engineering. The basic requirements for surface engineering are scheduled to expand considerably through the year 2000, so the reader should review the most up-to-date literature available.

**Overview.** The CAA requires that material surface finishers:

- Reduce or eliminate the use of volatile organic compounds (VOCs), which create smog through photochemical reactions. Most VOCs will be reduced, categorically, by industry group.
- Control, reduce, or eliminate 189 chemicals determined to be hazardous air pollutants (HAPs). Under the National Emission Standard for Hazardous Air Pollutants (NESHAP), hundreds of regulations are being written for emitting industries.
- Phase out ozone-depleting substances
- Obtain an operating permit for sources of VOCs and HAPs that trigger threshold amounts
- Reduce emissions from power plants, to reduce the generation of "acid rain" from NOX and SOX

**Applicability.** Following are the broad thresholds for determining whether a surface finishing process requires an operating permit and may be subject to additional regulations. These thresholds are presented for general information only; the reader is advised to consult local authorities.

- *Source of VOCs:* Has the potential to emit more than 10, 25, 40, or 100 tons/year of VOCs, depending on the region. VOC emissions are the cumulative weight of chemicals emitted from cleaning, degreasing, painting, wiping, and similar processes, assuming operation for 24 hours/day, 365 days/year.
- *Source of HAPs:* Has the potential to emit more than 10 tons/year of any listed HAP (Table 1) or more than 25 tons/year of a combination of HAPs

- *Source of Ozone-Depleting Substances:* Emits any volume of chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), halons, or methyl chloroform (1,1,1-trichloroethane)
- *Source of NOX or SOX:* Has the potential to emit more than 25 tons/year

**Table 1 List of hazardous air pollutants regulated by the Clean Air Amendments of 1990**

| **CAS No.** | **Chemical name** |
|---|---|
| 75070 | Acetaldehyde |
| 60355 | Acetamide |
| 75058 | Acetonitrile |
| 98862 | Acetophenone |
| 53963 | 2-Acetylaminofluorene |
| 107028 | Acrolein |
| 79061 | Acrylamide |
| 79107 | Acrylic acid |
| 107131 | Acrylonitrile |
| 107051 | Allyl chloride |
| 92671 | 4-Aminobiphenyl |
| 62533 | Aniline |
| 90040 | o-Anisidine |
| 1332214 | Asbestos |
| 71432 | Benzene (including benzene from gasoline) |
| 92875 | Benzidine |
| 98077 | Benzotrichloride |

| | |
|---|---|
| 100447 | Benzyl chloride |
| 92524 | Biphenyl |
| 117817 | Bis(2-ethylhexyl)phthalate (DEHP) |
| 542881 | Bis(chloromethyl)ether |
| 75252 | Bromoform |
| 106990 | 1,3-Butadiene |
| 156627 | Calcium cyanamide |
| 105602 | Caprolactam |
| 133062 | Captan |
| 63252 | Carbaryl |
| 75150 | Carbon disulfide |
| 56235 | Carbon tetrachloride |
| 463581 | Carbonyl sulfide |
| 120809 | Catechol |
| 133904 | Chloramben |
| 57749 | Chlordane |
| 7782505 | Chlorine |
| 79118 | Chloroacetic acid |
| 532274 | 2-Chloroacetophenone |
| 108907 | Chlorobenzene |
| 510156 | Chlorobenzilate |

| | |
|---|---|
| 67663 | Chloroform |
| 107302 | Chloromethyl methyl ether |
| 126998 | Chloroprene |
| 1319773 | Cresols/Cresylic acid (isomers and mixture) |
| 95487 | o-Cresol |
| 108394 | m-Cresol |
| 106445 | p-Cresol |
| 98828 | Cumene |
| 94757 | 2,4-D, salts and esters |
| 3547044 | DDE |
| 334883 | Diazomethane |
| 132649 | Dibenzofurans |
| 96128 | 1,2-Dibromo-3-chloropropane |
| 84742 | Dibutylphthalate |
| 106467 | 1,4-Dichlorobenzene(p) |
| 91941 | 3,3-Dichlorobenzidene |
| 111444 | Dichloroethyl ether (Bis(2-chloroethyl)ether) |
| 542756 | 1,3-Dichloropropene |
| 62737 | Dichlorvos |
| 111422 | Diethanolamine |
| 121697 | N,N-Diethylaniline (N,N-Dimethylaniline) |

| | |
|---|---|
| 64675 | Diethyl sulfate |
| 119904 | 3,3-Dimethoxybenzidine |
| 60117 | Dimethyl aminoazobenzene |
| 119937 | 3,3'-Dimethyl benzidine |
| 79447 | Dimethyl carbamoyl chloride |
| 68122 | Dimethyl formamide |
| 57147 | 1,1-Dimethyl hydrazine |
| 131113 | Dimethyl phthalate |
| 77781 | Dimethyl sulfate |
| 534521 | 4,6-Dinitro-o-cresol, and salts |
| 51285 | 2,4-Dinitrolphenol |
| 121142 | 2,4-Dinitrotoluene |
| 123911 | 1,4-Dioxane (1,4-Diethyleneoxide) |
| 122667 | 1,2-Diphenylhydrazine |
| 106898 | Epichlorohydrin (1-Chloro-2,3-epoxypropane) |
| 106887 | 1,2-Epoxybutane |
| 140885 | Ethyl acrylate |
| 100414 | Ethyl benzene |
| 51796 | Ethyl carbamate (Urethane) |
| 75003 | Ethyl chloride (Chloroethane) |
| 106934 | Ethylene dibromide (Dibromoethane) |

| | |
|---|---|
| 107062 | Ethylene dichloride (1,2-Dichloroethane) |
| 107211 | Ethylene glycol |
| 151564 | Ethylene imine (Aziridine) |
| 75218 | Ethylene oxide |
| 96457 | Ethylene thiourea |
| 75343 | Ethylidene dichloride (1,1-Dichloroethane) |
| 50000 | Formaldehyde |
| 76448 | Heptachlor |
| 118741 | Hexachlorobenzene |
| 87683 | Hexachlorobutadiene |
| 77474 | Hexachlorocyclopentadiene |
| 67721 | Hexachloroethane |
| 822060 | Hexamethylene-1,6-diisocyanate |
| 680319 | Hexamethylphosphoramide |
| 110543 | Hexane |
| 302012 | Hydrazine |
| 7647010 | Hydrochloric acid |
| 7664393 | Hydrogen fluoride (Hydrofluoric acid) |
| 123319 | Hydroquinone |
| 78591 | Isophorone |
| 58899 | Lindane (all isomers) |

| | |
|---|---|
| 108316 | Maleic anhydride |
| 67561 | Methanol |
| 72435 | Methoxychlor |
| 74839 | Methyl bromide (Bromomethane) |
| 74873 | Methyl chloride (Chloromethane) |
| 71556 | Methyl chloroform (1,1,1-Trichloroethane) |
| 78933 | Methyl ethyl ketone (2-Butanone) |
| 60344 | Methyl hydrazine |
| 74884 | Methyl iodide (Iodomethane) |
| 108101 | Methyl isobutyl ketone (Hexone) |
| 624839 | Methyl isocyanate |
| 80626 | Methyl methacrylate |
| 1634044 | Methyl tert butyl ether |
| 101144 | 4,4-Methylene bis(2-chloroaniline) |
| 75092 | Methylene chloride (Dichloromethane) |
| 101688 | Methylene diphenyl diisocyanate (MDI) |
| 101779 | 4,4'-Methylenedianiline |
| 91203 | Naphthalene |
| 98953 | Nitrobenzene |
| 92933 | 4-Nitrobiphenyl |
| 100027 | 4-Nitrophenol |

| | |
|---|---|
| 79469 | 2-Nitropropane |
| 684935 | N-Nitroso-N-methylurea |
| 62759 | N-Nitrosodimethylamine |
| 59892 | N-Nitrosomorpholine |
| 56382 | Parathion |
| 82688 | Pentachloronitrobenzene (Quintobenzene) |
| 87865 | Pentachlorophenol |
| 108952 | Phenol |
| 106503 | p-Phenylenediamine |
| 75445 | Phosgene |
| 7803512 | Phosphine |
| 7723140 | Phosphorus |
| 85449 | Phthalic anhydride |
| 1336363 | Polychlorinated biphenyls (Aroclors) |
| 1120714 | 1,3-Propane sultone |
| 57578 | beta-Propiolactone |
| 123386 | Propionaldehyde |
| 114261 | Propoxur (Baygon) |
| 78875 | Propylene dichloride (1,2-Dichloropropane) |
| 75569 | Propylene oxide |
| 75558 | 1,2-Propylenimine (2-Methyl aziridine) |

| | |
|---|---|
| 91225 | Quinoline |
| 106514 | Quinone |
| 100425 | Styrene |
| 96093 | Styrene oxide |
| 1746016 | 2,3,7,8-Tetrachlorodibenzo-p-dioxin |
| 79345 | 1,1,2,2-Tetrachloroethane |
| 127184 | Tetrachloroethylene (Perchloroethylene) |
| 7550450 | Titanium tetrachloride |
| 108883 | Toluene |
| 95807 | 2,4-Toluene diamine |
| 584849 | 2,4-Toluene diisocyanate |
| 95534 | o-Toluidine |
| 8001352 | Toxaphene (chlorinated camphene) |
| 120821 | 1,2,4-Trichlorobenzene |
| 79005 | 1,1,2-Trichloroethane |
| 79016 | Trichloroethylene |
| 95954 | 2,4,5-Trichlorophenol |
| 88062 | 2,4,6-Trichlorophenol |
| 121448 | Triethylamine |
| 1582098 | Trifluralin |
| 540841 | 2,2,4-Trimethylpentane |

| | |
|---|---|
| 108054 | Vinyl acetate |
| 593602 | Vinyl bromide |
| 75014 | Vinyl chloride |
| 75354 | Vinylidene chloride (1,1-Dichloroethylene) |
| 1330207 | Xylenes (isomers and mixture) |
| 95476 | o-Xylenes |
| 108383 | m-Xylenes |
| 106423 | p-Xylenes |
| 0 | Antimony compounds |
| 0 | Arsenic compounds (inorganic including arsine) |
| 0 | Beryllium compounds |
| 0 | Cadmium compounds |
| 0 | Chromium compounds |
| 0 | Cobalt compounds |
| 0 | Coke oven emissions |
| 0 | Cyanide compounds(a) |
| 0 | Glycol ethers(b) |
| 0 | Lead compounds |
| 0 | Manganese compounds |
| 0 | Mercury compounds |
| 0 | Fine mineral fibers(c) |

| | |
|---|---|
| 0 | Nickel compounds |
| 0 | Polycylic organic matter[(d)] |
| 0 | Radionuclides (including radon)[(e)] |
| 0 | Selenium compounds |

CAS, Chemical Abstract Service. Note: For all listings that contain the word *compounds* and for glycol ethers, the following applies: Unless otherwise specified, these listings are defined as including any unique chemical substance that contains the named chemical (that is, antimony, arsenic, and so forth) as part of that chemical's infrastructure.

Source: Public Law 101-549, Title II

(a) X'CN where X = H' or any other group where a formal dissociation may occur [e.g., KCN or $Ca(CN)_2$].

(b) Includes monoethers and diethers of ethylene glycol, diethylene glycol, and triethylene glycol $R\text{-}(OCH2CH2)_n\text{-}OR'$ where n = 1, 2, or 3; R = alkyl or aryl groups; and R' = R, H, or groups which, when removed, yield glycol ethers with the structure $R\text{-}(OCH2CH)_n\text{-}OH$. Polymers are excluded from the glycol category.

(c) Includes mineral fiber emissions from facilities manufacturing or processing glass, rock, or slag fibers (or other mineral-derived fibers) of an average diameter of 1 µm or less.

(d) Includes organic compounds with more than one benzene ring and which have a boiling point greater than or equal to 100 °C (212 °F).

(e) A type of atom that spontaneously undergoes radioactive decay.

**Requirements for VOCs under NAAQS.** In general, under NAAQS an operation that releases VOCs is required to:

- Install and maintain emissions control and monitoring equipment
- Adhere to the regulations for emission limits and control
- Undergo inspections
- Pay emission fees to fund governmental programs
- Before increasing VOC emissions, offset new emissions at a ratio of 1.1 to 1, 1.15 to 1, 1.2 to 1, 1.3 to 1, or 1.5 to 1, depending on local air quality

In addition, existing sources must meet reasonably available control technology (RACT) standards defined by the control techniques guidelines (CTGs) of the EPA. New or modified sources must meet the lowest achievable emission rates (LAERs), typically identified as best available control technology (BACT). For example, control requirements include:

- Limiting the VOC solvent content of paint
- Limiting the vapor pressure of solvents
- Using a hood to capture emissions, which in turn are forced through carbon absorbers or ultraviolet oxidation systems
- Using high-transfer-efficiency application equipment
- Maintaining spent wipe solvent rags in closed containers

- Limiting plantwide emissions

Imposition of a permit incorporates all requirements such as offset limits, BACT and/or RACT, recordkeeping, and fees. These requirements are predicated on local air quality according to the NAAQS. Sections 181 to 185 of subtitle D of the CAA discuss these standards and their applicability.

**Requirements for HAPs under NESHAP.** Table 1 lists 189 chemicals determined to be HAPs. The EPA has published a list of sources that are to be covered under industry-specific regulations:

- Halogenated solvent cleaning (vapor degreasing)
- Aerospace components and assembly
- Chromic acid anodizing
- Hard chrome plating
- Reinforced plastic parts

By way of example, the following table lists many of the chemicals used in aerospace production:

| **Process** | **Chemicals** |
|---|---|
| Raw materials | . . . |
| Machining/etching | Chlorofluorocarbons, volatile organic compounds, acids, oils |
| Cleaning | Volatile organic compounds, chlorinated solvents, chlorofluorocarbons, alcohol |
| Plating/anodizing | Heavy metals, acids |
| Coating/painting | Heavy metals, volatile organic compounds, chlorinated solvents |
| Stripping | Chlorinated solvents |
| Assembly | Glues, sealants, lubricants |
| Painting | Heavy metals, volatile solvents, chlorinated solvents |
| Maintenance | Halons, freons, oils, solvents |

Regulations are required on a statutory timeline that began on November 15, 1992 and is scheduled to end on November 15, 2000. To determine whether a particular industry is covered by all or some of these regulations, the reader should consult local air authorities.

***Maximum Available Control Technology.*** The sources listed above are required to use an emission standard known as maximum available control technology (MACT). For new facilities, MACT is the best demonstrated control technology and practices in a category or subcategory of emission sources. For existing facilities, MACT is defined, in theory, as the average emission limitation of the best controlled 12% of existing sources in the category or subcategory. In developing MACT standards, the EPA can consider:

- Process changes
- Materials substitution
- Enclosed systems and processes
- Collection, capture, or treatment of pollutants
- Design, equipment, work practice, or operational standard
- A combination of the above

***Area Source Program.*** If a particular process does not fall into an identified category or subcategory, but a HAP from Table 1 is in use, it will probably be regulated by 1995 by an area source program. Such programs identify the emission of HAPs from sources that are believed to pose significant health risks even though they are not major sources. A rule of thumb is that if a HAP cannot be eliminated or replaced with a non-HAP, it will eventually be regulated by one or more regulations under NESHAP.

***Accidental Releases.*** A forthcoming EPA regulation, which was due in November 1993, will address the prevention of accidental releases of any of 160 hazardous chemicals. As of this writing, the proposed regulation covers risk management, hazard assessment, training and procedures, emergency response, and the use, operation, replacement, and maintenance of equipment to monitor or prevent releases.

**Requirements for Ozone-depleting Substances.** Ozone-depleting substances are halogenated compounds that are stable in the lower atmosphere where we live (the troposphere) but are highly unstable at higher levels (the stratosphere). There they react with ozone and form new compounds that deplete the ozone layer, which screens much ultraviolet radiation from reaching the earth. Ozone-depleting substances include CFCs, HCFCs, halons, carbon tetrachloride, and methyl chloroform (1,1,1-trichloroethane).

To prevent further damage to stratospheric ozone, the United States has joined with most other industrialized countries to phase out ozone-depleting substances through production bans. This agreement, which was accomplished at a United Nations meeting, is known as the Montreal Protocol. The U.S. Congress accelerated the production ban schedule to January 1, 2000, and former President Bush, through executive order, further shortened the schedule to December 31, 1995. The phaseout of HCFCs is not scheduled to occur until the year 2015, but in all likelihood it will be rolled back.

**Operating Permits.** Operating permits are, or will be, required for any source that is subject to NAAQS or NESHAP. Permit programs fund state and local air quality authorities and give them enforcement tools.

Permits were required as early as November 15, 1993, depending on the status of EPA, state, and local rule development. If a source is identified as requiring a permit, it has 12 months to submit an application. The minimum requirements are that:

- A permit application and compliance plan must be prepared and submitted.
- Monitoring and reporting requirements are established and submitted at least every six months.
- Permit holders must certify annually that the facility is in compliance with permit requirements.
- A fee of at least $25/ton of pollutant must be paid annually.
- Permits are valid for no more than five years.
- Public comment periods and hearings are required.

**Other Requirements.** Regional offices of the EPA can provide detailed information about the subjects discussed in this section, as well as information about acid rain, mobile sources of pollutants, enforcement, and miscellaneous regulations.

## The Resources Conservation and Recovery Act

The Resources Conservation and Recovery Act (RCRA, pronounced "rick-rah") is the primary law that governs the management of waste, both hazardous and solid. It provides for technical and financial assistance to resource programs, minimization of waste, safe disposal of waste, and regulation of hazardous waste. RCRA is known as the "cradle to grave" law in that as soon as a waste is conceived (a material is no longer useful) it must be documented and tracked through its storage, transport, treatment, and final disposition (normally by landfill, incineration, or deep-well injection).

Although signed into law in 1976, RCRA regulations were first published in 1980, when day-to-day waste management concerns for industry began. RCRA was amended in 1984 with the Hazardous and Solid Waste Amendments (HSWA), and it now controls the generation, treatment, storage, transportation, disposal, training, and labeling of waste. It also controls underground storage tanks, sumps, pollution prevention, recyclers, and transporters of waste.

The discussion of RCRA in this section is limited to very simple concepts, and the reader should consult a regional EPA office or equivalent state agency for detailed information.

**Definition of Hazardous Waste.** Fundamentally, once a material is discarded, it is a waste. RCRA regulates solid waste, which includes hazardous waste (such as sludges and spent acids) and nonhazardous waste (such as household garbage). The determination of whether a waste is hazardous (and therefore whether the facility will be subject to the requirements of RCRA) depends on whether the waste is a threat to human health and the environment. A hazardous waste is one that meets any of the following criteria:

- Appears on an EPA list ("F," "K," "P," and "U" lists are found in 40 CFR 261.3)
- Exhibits a hazardous characteristic (flammability, corrosivity, reactivity, or toxicity)
- Is a mixture of solid waste with hazardous waste. The resultant mixture is hazardous with some exceptions.

These criteria are summarized in Fig. 3. As with all environmental regulations, a variety of exclusions apply. If a waste is not hazardous, it generally can be discarded as municipal waste. If it is hazardous, the facility is regulated.

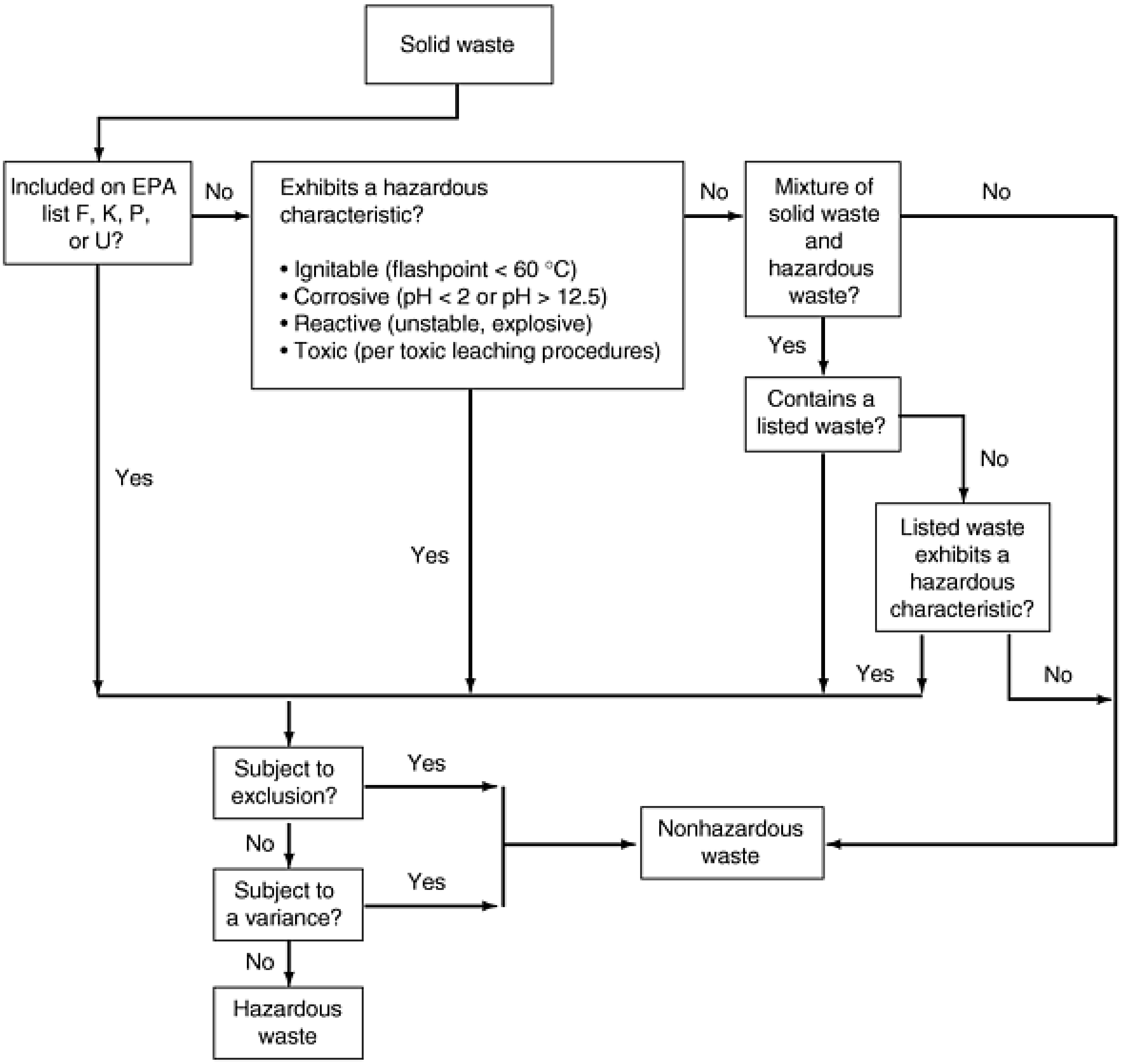

**Fig. 3 Criteria for determining whether a solid waste is hazardous**

**Requirements for Hazardous Waste Generators.** If a facility creates a hazardous waste, it must obtain an EPA identification number and follow regulations about such matters as containers and storage tanks, inspections, employee training, waste minimization, transportation, recordkeeping and recording, and selection of treatment, storage, and disposal (TSD) sites. How a facility is regulated depends on the amount of waste generated.

***Large-quantity generators*** produce more than 1000 kg/month of hazardous waste or more than 1 kg/month of acutely hazardous waste. They may store wastes for only 90 days. In addition, they must:

- Use approved containers that are compatible with the waste and are marked with specific information. Storage procedures must meet fire code satellite requirements.
- Comply with sump and tank requirements. Hazardous waste tanks must meet requirements for secondary containment, leak detection, cathodic protection, overfill alarms, spill prevention, labels, integrity, and so on.
- Conduct a daily inspection of hazardous waste storage areas, transfer areas, and tanks.
- Create an emergency response program that includes a preparedness program, a prevention program, and a contingency plan that is carried out whenever there is a release of hazardous waste.
- Develop, and repeat annually, employee training programs for identifying, packaging, labeling, and transporting hazardous waste, as well as training programs about waste handling, identifying the

properties of waste on-site, and the use of safety equipment.
- Employ programs to minimize waste, including an annual report.
- Comply with transportation and packaging requirements.
- Comply with prohibitions on the disposal of certain wastes in landfills.
- Send wastes to a TSD facility that is approved to handle the types of wastes generated.
- Comply with a host of recordkeeping and reporting requirements.

***Small-quantity generators*** produce between 100 and 1000 kg/month of hazardous waste. They may store up to 6000 kg of waste for up to 180 days (270 days if it is to be shipped more than 200 miles to a TSD). Small-quantity generators are subject to most of the same requirements as large-quantity generators, with some exceptions.

***Conditionally exempt small-quantity generators*** produce no more than 100 kg/month of hazardous waste, no more than 1 kg/month of acutely hazardous waste, and no more than 100 kg/month of waste debris such as contaminated soil. They may store 1000 kg of hazardous waste for any period. While exempt from most requirements, they must determine which wastes are hazardous, keep records, store wastes legally, and transport wastes to an approved TSD facility.

**Requirements for TSD Facilities.** RCRA defines treatment, storage, and disposal as follows:

- *Treatment:* "Any method, technique, or process including neutralization, designed to change the physical, chemical, or biological character or composition of any hazardous waste so as to recover energy or material resources from the waste, or so as to reduce such waste to non-hazardous or less hazardous; safer to transport, store, or dispose of; amendable for recovery or storage; or reduced in volume."
- *Storage:* "The holding of hazardous waste for a temporary period, at the end of which, the hazardous waste is treated, disposed of, or stored elsewhere."
- *Disposal:* "The discharge, deposit, injection, dumping, spilling, leaking, or placing of any solid waste or hazardous waste into or on any land or water so that such solid waste or hazardous waste or any constituent thereof, may enter the environment or be emitted into the air or discharged into any waters, including ground waters."

A TSD facility uses surface impoundments (such as sludge ponds), waste piles, landfills, chemical/physical/biological treatment, and/or incineration to treat, store, or dispose of waste on-site. It is subject to extensive permit application requirements and conditions if it:

- Stores waste longer than 90 days
- Uses surface impoundments or waste piles
- Stores recyclable materials longer than 90 days
- Treats or disposes of hazardous waste

Such facilities typically specialize in waste management, due to the high cost of maintaining permit conditions. However, a manufacturing site can also use one or more of these TSD methods, and if so it is subject to the same rigorous requirements. All TSD facilities must have permits, which regulate such matters as waste analysis, inspections, security, training, waste management, facility maps, emergency response, air emission control, recordkeeping systems, groundwater monitors, infrastructure, containment, financial assurances, and closure. Unless TSD operations are primary to the business, it is unlikely that a surface treatment facility would want or need to maintain a TSD permit.

## Superfund Amendments and Reauthorization Act

In December 1980, the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), commonly known as "Superfund," was passed into law. It established a program to identify sites where hazardous materials are released into the environment and ensure that they are cleaned up by responsible parties.

What has more bearing on surface engineering processes is the 1986 reauthorization of CERCLA, known as the Superfund Amendments and Reauthorization Act (SARA). In addition to extending CERCLA, SARA Title III created the Emergency Planning and Community Right to Know Act (EPCRA), a sweeping system for informing. community emergency planners and the public about what chemicals are being used, where they are being used, and how much are being released into the air, water, or land as pollution.

Publicity of "SARA 313 releases" has done more to motivate research into alternative surface finishing processes than any other mechanism.

**Overview.** The EPCRA section of SARA includes two sets of significant requirements:

- *Requirements about release notification and emergency response planning:* Facilities must inform government agencies of hazardous material releases and have the appropriate equipment, personnel, and training to respond to a cleanup.
- *Requirements about reporting,* which are divided into three sections: 311, 312, and 313. Section 311 requires that material safety data sheets for chemicals used at a facility be given to the local fire department or an emergency planning committee. Section 312 requires a facility-wide inventory of what chemicals are where within the facility. Section 313 requires that an annual report about toxic releases be submitted each July 1 to the federal government.

**Section 313.** A U.S. facility is required to submit the annual toxic chemical release report if it has more than 10 employees, falls into certain industry categories (Standard Industrial Codes 20 to 39), uses a toxic chemical in excess of 10,000 lb/year, or manufactures a toxic chemical in excess of 25,000 lb/year. For each chemical used at the facility, an EPA form R must be submitted that shows:

- EPA permit numbers
- Storage and treatment data
- A pollution prevention report for the chemical
- The quantity of chemical released to air, water, or offsite transfer
- Business information
- Executive certification of the report's accuracy

## Clean Water Act

Protection of water resources is a critical issue in the design and operation of a manufacturing facility that uses surface engineering processes. Nearly every facility of this type uses water in a variety of ways: for cooling, cleaning and rinsing, anodizing, and plating baths. Even facilities that do not use water directly in manufacturing processes should be aware of water issues because of concerns about stormwater and groundwater quality.

**Wastewater Discharge.** The primary water-related concerns about surface engineering processes are the quality and quantity of wastewater discharges and the design and operation of the facility to protect stormwater and groundwater. The procedure that is most heavily regulated by the Clean Water Act, and probably most costly to deal with, is the discharge of wastewaters to either surface waters or to publicly owned treatment works (POTWs).

***NPDES Permits.*** Federal regulations (40 CFR 122) prohibit the discharge of wastewater to any surface water body without a National Pollutant Discharge Elimination System (NPDES) permit. The permit is administered by either the EPA or a designated state agency, depending on the location of the facility. It requires the discharger to characterize the volume and composition of the discharge, sets maximum discharge temperatures and flow rates, outlines how the discharger must monitor the discharge, and specifies maximum pollutant compositions based on either technology or water quality. (Technology-based limits are established by determining the level of treatment that is both technically and economically feasible for a particular industry. Water-quality-based limits are based on minimizing the potential effects of the discharge on the receiving water body.) NPDES permits remain in effect for five years, and the requirements of subsequent permits are typically stricter, as more aggressive technology-based or water-quality-based standards are developed.

***Requirements of Dischargers.*** Wastewater discharges to POTWs do not require an NPDES permit but are regulated by comparable pretreatment standards imposed on specific industry categories (40 CFR 403). Many states or municipalities have permit programs to regulate these discharges. Pretreatment standards are technology-based and are calculated by determining the level of treatment that is both technically and economically feasible for a particular industry. They are set in a manner that prevents the discharge of materials that would adversely impact the operation of the POTW or that would pass through the POTW without receiving adequate treatment.

Facilities often have the option of discharging treated wastewater either directly to surface waters or to a POTW for further treatment prior to discharge. NPDES-permitted discharges to surface waters usually require more extensive treatment and monitoring than discharges to POTWs. On the other hand, indirect dischargers must pay a fee to the POTW to help cover the costs of its operations. The preferred choice is the option that allows all regulatory requirements to be met at a lower cost.

***Requirements of Technology.*** The pollutants of most concern to operations using surface engineering processes are metals and toxic organics. Treatment technologies are available to remove these materials from wastewater streams.

The traditional method of removing metals is to modify the pH of the wastewater stream to precipitate insoluble metal hydroxides. The principal drawback is that significant quantities of hazardous sludges are formed that are costly to dispose of. These disposal costs can be reduced by using filter presses or dryers to reduce sludge volumes. Other treatment techniques have been developed to more cost-effectively remove, and even recycle, these pollutants.

A variety of techniques are available to remove or destroy toxic organics in wastewater: chemical oxidation, ozonation, and biological treatment. Each treatment process has different capabilities, and the preferred process will be a function of the characteristics of the wastewater stream and discharge requirements.

The costs of complying with increasingly complex safety, health, and environmental regulations are powerful incentives for implementing pollution prevention programs. Many products can be either redesigned or modified to allow the use of more environmentally acceptable materials and processes in manufacturing operations. The use of these materials and processes can help the manufacturer reduce or eliminate the need for additional wastewater treatment equipment. Many of these efforts are win-win situations, where implementing the new material or process results in both reduced emissions to the environment and lower costs to the manufacturer. Examples of successful pollution-prevention efforts are the use of boric-sulfuric acid anodizing to replace chromic acid anodizing operations and the use of zinc-nickel plating to replace cadmium plating.

**Stormwater Discharge.** Wastewater discharges are not the only area in which facilities are affected by water-related environmental concerns. Most facilities containing typical surface engineering processes need an NPDES permit for stormwater discharges. Facilities are required to obtain NPDES stormwater discharge permits if three conditions are met:

- The Standard Industrial Code of the facility is on the list of regulated operations, as given in 40 CFR 122.
- Stormwater from the facility is discharged to surface waters.
- Operations have the potential to cause stormwater contamination by allowing stormwater to contact hazardous materials at the facility. Examples of this include storing drums of hazardous materials in covered outdoor areas or having uncovered loading docks where hazardous raw materials or finished products are transported.

The NPDES stormwater discharge permit program requires dischargers to develop and implement stormwater pollution prevention plans to identify and correct problem areas.

**Water Supply Issues.** In addition to the water quality issues described above, water quantity issues are becoming increasingly important. In many areas of the country, water supply costs are rising dramatically, and in some areas increased supplies of water are simply unavailable. While reducing the water usage of a facility is typically not a regulatory concern, strong economic drivers exist for implementing water conservation programs. Many opportunities to cost-effectively reduce water consumption are available, including the use of double (and even triple) countercurrent rinsing, the replacement of once-through cooling systems with closed-loop systems, and the use of wastewater treatment techniques that recycle the treated effluent for use elsewhere in the facility.

**Other water-related concerns** at a typical facility include the potential impact of leaking sumps and underground storage tanks on groundwater. Requirements for the design, construction, operation, maintenance, and removal of underground storage tanks and sumps are outlined in 40 CFR 280. Recordkeeping and release reporting are also required.

## Other Environmental Statutes

Several other federal statutes are germane to this article:

- The Safe Drinking Water Act (SDWA) provides substantial requirements for public water supply systems.
- The Toxic Substances Control Act (TSCA) regulates the invention, use, marketing, and importation of chemicals and evaluates health and environmental effects of chemicals. It requires a chemical manufacturer or importer to provide health and environmental data, limit how much chemical is used, have approval for distribution, provide warnings, and maintain test results. Engineers who reformulate materials are advised to understand TSCA.
- The Federal Insecticide, Fungicide, and Rodentacide Act (FIFRA) regulates the manufacture and use of pesticides.
- The National Environmental Policy Act (NEPA) declares national environmental policy and requires federal agencies to consider environmental concerns when taking actions such as issuing permits.

Local officials and environmental consulting firms can provide information about whether these statutes apply to a particular operation.

# Cadmium Elimination in Surface Engineering

**Mark W. Ingle, Corrpro Companies, Ocean City Research Corporation**

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## Introduction

CADMIUM is a soft, blue-white metal widely used as a corrosion control coating on ferrous (e.g., mild and high-strength steel) substrates. Electroplated cadmium coatings are typically applied at thicknesses of between 5.1 and 12.7 $\mu$m (0.2 and 0.5 mil) (Ref 1). Chromate treatments (based on hazardous chromic acid) are frequently applied to cadmium coatings as a final passivation process. Cadmium coatings have historically provided effective substrate corrosion control performance when applied to threaded fasteners, connectors, and general hardware (Ref 2, 3). The technical performance benefits and limitations associated with cadmium coatings are well established.

However, over the past decade, environmental and worker health regulations affecting cadmium use have been promulgated in the United States and in Western Europe. These regulations have increased the costs associated with cadmium coating application and cadmium-bearing waste disposal, creating economic incentives for industrial users to seek cadmium plating replacements. Unfortunately, no universal cadmium replacement has yet been identified. Thus, viable cadmium replacements must be identified on a case-by-case basis in which technical performance requirements, environmental issues, and costs are considered. Identification of effective cadmium replacements can reduce product costs and minimize regulatory compliance problems. Ineffective cadmium replacements can lead to degraded component-corrosion control performance and, in extreme cases, catastrophic component failures.

## Acknowledgements

The author acknowledges the assistance of Earl C. Groshart, Boeing Defense and Space Group; Caroline Freeman, Occupational Safety and Health Administration; and James E. Ellor, Corrpro Companies/Ocean City Research Corporation.

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## Rationale for Replacing Cadmium Coatings

Historically, cadmium coatings have been applied to mild and high-strength steel components as an economical and effective means of controlling in-service substrate corrosion (see the article "Cadmium Plating" in this Volume). Although cadmium coating performance has not changed over the years, recent revisions to environmental and worker health laws in the United States and other countries have created a regulatory climate in which continued cadmium use is becoming cost-prohibitive:

- The U.S. Occupational Safety and Health Administration (OSHA) released the "Occupational Exposure to Cadmium; Final Rules" in 1992. OSHA estimates that compliance with these rules will cost domestic industry $159,616,000/year (Ref 4).
- Environmental laws in the United States make cadmium-bearing waste disposal or emissions expensive. In addition, 29 states have passed pollution prevention acts that mandate reductions in hazardous waste (such as waste that contains cadmium) (Ref 5, 6).
- The Swedish Ban on Cadmium was enacted in 1985. Based on this ban, Sweden can forbid the import of certain products containing cadmium (Ref 7).

These laws may increase operating costs, create liability risks, and restrict markets for certain cadmium-coated products. The following sections of this article provide additional details about regulations in the United States and Europe.

**Cadmium Worker Health Effects and Laws.** OSHA has evaluated the health effects of cadmium on workers and has determined that exposure to respirable particles/fumes represents the most significant risk factor. Cadmium and its compounds are not readily absorbed through the skin, but they can be ingested. Inhaling cadmium or its compounds can directly cause lung cancer, and it also allows the toxic metal to enter the bloodstream. Once in the blood, cadmium readily accumulates in the kidneys, degrading their function. Table 1 shows the estimated levels of lung cancer and kidney dysfunction resulting from varying levels of cadmium exposure.

**Table 1 Impact of cadmium exposure levels on worker health**

| Cadmium TWA PEL(a) | Effective dates | Excess lung cancer rate per 1000 workers(b) | Excess kidney dysfunction rate per 1000 workers(b) |
|---|---|---|---|
| 100 μg/m$^3$ | 1971-1992 | 58-157 | 900 |
| 5 μg/m$^3$ | 1993-present | 3-15 | 14-23 |

Source: Ref 4

(a) TWA PEL, time-weighted average permissible exposure limit.

(b) Based on 45-year workplace exposure history.

From 1971 to 1992, OSHA defined the permissible exposure limit (PEL), over an 8-h time-weighted-average day, as 100 μg of cadmium fumes per cubic meter of workplace breathing air (Ref 4, 8). OSHA redefined the acceptable workplace cadmium exposure limits in 1992 by reducing the allowable airborne concentrations of cadmium in the workplace by 95%, from 100 to 5 $\mu g/m^3$ (Ref 8). In addition to redefining the PEL, the document "Occupational Exposure to Cadmium; Final Rules" includes extensive provisions for engineering controls on workplace breathing-air cadmium levels, worker safety training, medical monitoring requirements, and, as a worst case, employee respirator use. The current OSHA PEL of 5 $\mu g/m^3$ is one of the lowest for common industrial metals. OSHA estimates that compliance with the revised worker safety requirements will cost industries that produce, use, and dispose of cadmium approximately $159,616,000/year (Ref 4).

OSHA data show that the implementation of the 5 $\mu g/m^3$ PEL will reduce workplace health risks. Table 1 summarizes the OSHA health impact data and shows that by reducing cadmium exposure from the earlier 100 $\mu g/m^3$ to 5 $\mu g/m^3$, worker kidney dysfunction and lung cancer rates will decrease appreciably (Ref 4).

**Environmental Regulations Related to Cadmium--United States.** Table 2summarizes the impact of selected federal laws on cadmium production, application, and waste disposal. As shown, cadmium is considered a hazardous material and is regulated as a "hazardous chemical" or "toxic substance" (Ref 9). The federal laws shown in the table are typically administered on a state or local level through facility permits. Depending on specific permit requirements, the economic impact on facilities can be significant. Compliance costs for permits vary from state to state and are difficult to assess. However, the general consensus in the metal coating industry is that costs for hazardous materials handling and waste disposal are increasing.

**Table 2 Federal environmental laws that affect cadmium use, emission, and waste disposal**

| **Federal law** | **Acronym** | **Potential impact** |
|---|---|---|
| Resource Conservation and Recovery Act | RCRA | Hazardous waste disposal regulations create overhead costs and compliance risks. |
| Comprehensive Environmental Response, Compensation, and Liability Act (Superfund) | CERCLA | Cadmium is a Section 304 hazardous substance. Applicable only to certain releases of cadmium compounds. |
| Superfund Amendments and Reauthorization Act (Title III) | SARA | Cadmium is a Section 313 toxic chemical. Emissions must be reported. |
| Clean Water Act and Amendments | CWA | States are reducing allowable cadmium concentrations in facility effluent. Compliance with the new limits may require additional cadmium recovery equipment. |
| Clean Air Act and Amendments | CAA | Recent amendments define cadmium as a hazardous air pollutant. Cadmium emissions may be taxed. |

Source: Ref 9

In addition to the federal regulations, 29 states have enacted pollution prevention laws (Fig. 1). These laws affect cadmium-bearing hazardous wastes specified by the Resource Conservation and Recovery Act and toxic materials specified by the Superfund Amendments and Reauthorization Act, Title III, including cadmium particulates or solutions (Ref 6). State pollution prevention laws generally require industrial facilities to achieve percentage reductions in hazardous material consumption and hazardous waste generation via "source reduction," but the degree to which these laws encourage source reduction varies. Some states offer incentives and funding grants to eliminate hazardous materials, others employ user fees, and some mandate civil fines (e.g., a $15,000 fine for "blatant violators" of the New Jersey Pollution Prevention Act) (Ref 6, 10). These federal and state laws create a significant incentive for industrial users to replace cadmium coatings.

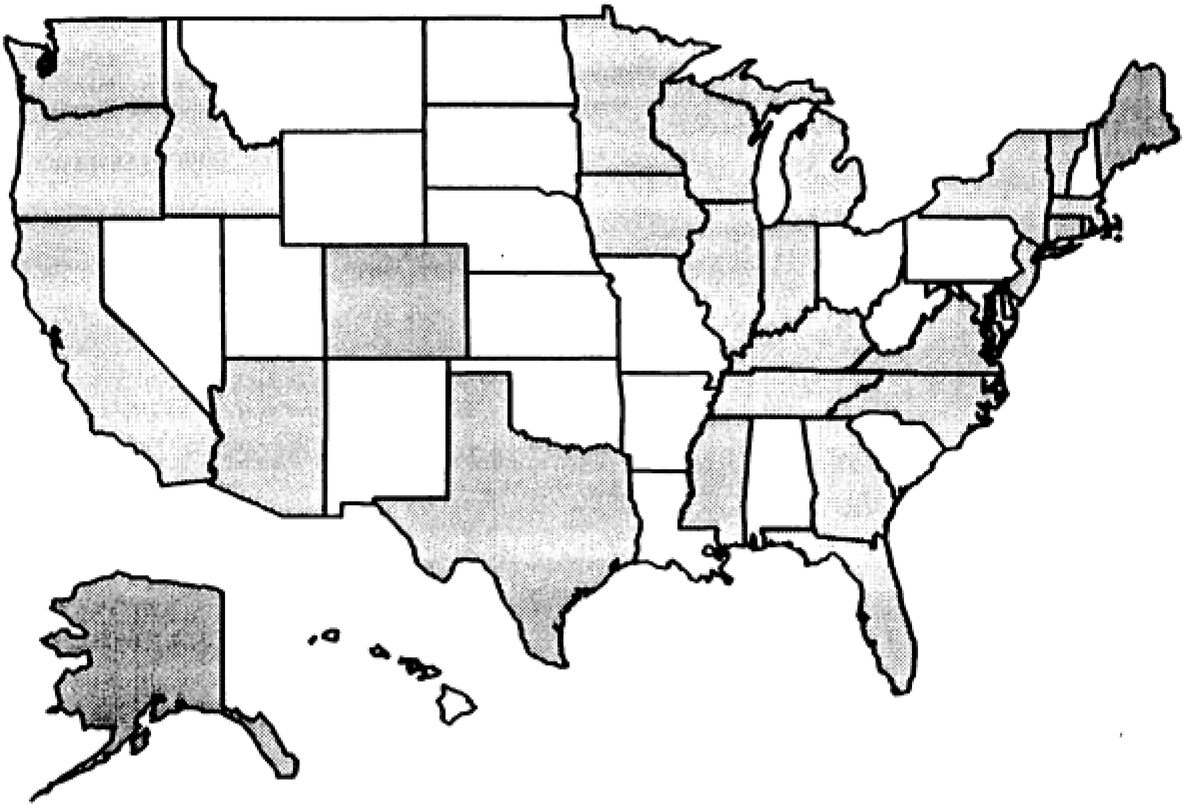

**Fig. 1 States that have pollution prevention or hazardous waste minimization laws as of 1994 (shown in gray). Source: Ref 5,**

**Environmental Regulations Related to Cadmium Use--Europe.** Certain European countries have taken more direct steps than the United States to control cadmium use and resulting environmental impacts, including a ban on cadmium use in Sweden, restrictions on cadmium use in Finland, and a virtual ban on cadmium chloride in Germany (Ref 5, 7, 11).

The Swedish Ban on Cadmium summarizes the environmental and worker health risks posed by the metal and then selectively forbids the production or importation of specific items containing cadmium (Ref 7). The following are some specific provisions of the ban:

- Section 45(j)--"The substance cadmium [defined as cadmium plating in Appendix 2 of the Swedish Ban] may not be used for surface treatment, as a stabilize, or as a pigment" (Ref 7).
- Section 45(j)--"Products whose surface has been treated with a cadmium substance or which contain such a substance as a stabilizer or pigment may not be imported commercially" (Ref 7).

The Swedish statute does not ban nickel-cadmium storage batteries and includes exemptions for certain safety products, but its effect on markets for cadmium-plated parts in Sweden is clear.

The trend toward restricting cadmium use is currently spreading throughout Europe. The German government has virtually banned the use of cadmium chloride and is reducing acceptable workplace exposure levels for other cadmium compounds (Ref 4). Finland has announced "prohibitions and restrictions" on products containing cadmium (Ref 11). These actions reflect a trend in the European Economic Community (EEC) that is effectively summarized in the following conclusion from a 1991 EEC report (Ref 12): "There is a significant threat of long term damage to man and the environment by cadmium if appropriate steps are not taken to reduce environmental contamination by this metal."

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## Cadmium Coating Specifications

Cadmium coatings are applied in accordance with both consensus specifications (e.g., Society of Automotive Engineers) and federal and military specifications. Table 3 lists representative cadmium and cadmium alloy coating specifications. Unless directly specified, cadmium coatings are unlikely to be applied to a component, because cadmium electroplating costs are generally one to two times higher than those for conventional zinc electroplating (Ref 7, 13).

**Table 3 Cadmium coating specifications**

| **Specification** | **Title** |
|---|---|
| **General plating** | |
| SAE AMS 2416 | Plating, Nickel-Cadmium, Diffused |
| QQ-P-416E | Plating, Cadmium (Electrodeposited) |
| MIL-P-23408B | Plating, Tin-Cadmium (Electrodeposited) |
| SAE AMS 2400S | Cadmium Plating |
| **Plating to minimize potential substrate embrittlement** | |
| AIA NAS 672 | Plating, High-Strength Steels, Cadmium |

| | |
|---|---|
| ASTM B 696 | Standard Specification for Coatings of Cadmium, Mechanically Deposited |
| MIL-C-8837B | Coating, Cadmium (Vacuum Deposited) |
| MIL-C-81562B | Coatings, Cadmium, Tin-Cadmium, and Zinc (Mechanically Deposited) |
| MIL-STD-870 | Cadmium Plating, Low Embrittlement, Electrodeposition |
| MIL-STD-1500 | Cadmium-Titanium Plating, Low Embrittlement |
| SAE AMS 2401D | Cadmium Plating, Low Hydrogen Content |

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## Cadmium Replacement Identification

Identification of viable cadmium replacements requires engineering analysis of technical performance issues, environmental considerations, and economic factors. As such, a significant portion of the process of identifying cadmium replacements is based on qualitative data and engineering judgment. There is no direct or "one for one" cadmium replacement, so multiple replacements, or no viable replacements, may be identified for specific cadmium applications. This section provides general, qualitative guidance regarding potential cadmium replacements in terms of general performance, environmental, and economic factors. *Caution: Replacing coatings inherently creates performance risks that must be evaluated and accepted by qualified engineers before any coating or material change is implemented*.

To assist with the identification of cadmium replacements, key technical performance, environmental, and economic data have been collected and summarized in Table 4. These data are presented in a qualitative matrix in which the performance of replacements is rated relative to that of cadmium coatings. Because so many of the factors affecting the selection of cadmium replacements are based on case-specific issues, such as substrate material/heat treatment, component configuration, and production volume, specific references are provided to allow engineers to collect additional information. To improve clarity and provide information on how the qualitative ratings were generated, the following paragraphs discuss each column of the table, along with important issues that could affect cadmium replacement decisions.

**Table 4 Cadmium replacement identification matrix**

| **Cadmium replacement** | **Specifications** | **Corrosion control performance** | **Environment-assisted cracking** | **Coating lubricity** | **Environmental/ worker health regulations** | **Cost/ performance factors** |
|---|---|---|---|---|---|---|
| Zn, Zn-Ni, Zn-Co, or ion vapor deposited | Commercial; MIL-C-83488 with MIL-C-81751 (Ref 3, | Better/comparable (Ref 3, 24) | Worse/comparable (Ref 3) | Comparable or more lubricious (Ref 12, 24) | Better, although some lubricious topcoats may be subject to volatile | Significantly higher costs (Ref 3, 23) |

| | | | | | | |
|---|---|---|---|---|---|---|
| aluminum coating with lubricious topcoat (Ref 3, 24) | 24) | | | | organic compound regulations (Ref 24) | |
| Solid alloy without coating (e.g., nickel alloy, stainless steel) (Ref 17, 18) | QQ-N-281, QQ-N-286 (nickel alloy); AISI 304, AISI 316 (stainless steel) | Better (stainless steel may pit) (Ref 17, 18) | Better (Ref 17, 18, 28) | Not applicable; stainless steel and nickel alloys have been used as fasteners (Ref 17, 18) | Better, no coating process | Initial cost significantly higher; life cycle cost may be comparable |
| Zinc plating (Ref 7, 11, 21) | ASTM B 633[(a)] | Comparable/worse (Ref 3, 16) | Worse (Ref 7, 21) | Less/comparable (Ref 3, 24) | Better, although the type II or III chromate post-treatment is hazardous (Ref 9, 29, 30) | Initial costs lower; zinc coatings generate voluminous, white corrosion products (Ref 16) |
| Zinc-nickel plating (Ref 3, 25) | ASTM B 841; commercial (Ref 27) | Comparable (Ref 3, 25) | Worse/comparable (Ref 3, 25) | Less/comparable (Ref 3, 24) | Better, although nickel is included in EPA "Toxic 17" list; chromate post-treatment hazardous (Ref 9, 29, 30) | Initial costs may be higher; life cycle costs comparable (Ref 16) |
| Tin-zinc plating (Ref 3, 26) | Commercial (Ref 26) | Comparable/worse (Ref 3) | Worse/comparable (Ref 3) | Less/comparable (Ref 3, 24) | Better, chromate post-treatment hazardous (Ref 9, 29, 30) | Initial costs may be higher; life cycle costs comparable (Ref 3) |
| Ion vapor deposited aluminum (Ref 3, 23) | Commercial; MIL-C-83488 (Ref 23) | Comparable (Ref 3, 23) | Worse/comparable (Ref 3, 23) | Less; ion vapor deposited aluminum coatings on threaded fasteners can gall (Ref 3, 23) | Better, chromate post-treatment hazardous (Ref 9, 29, 30) | Significantly higher costs (Ref 23) |

Note: See text for extensive detail.

(a) Specific bath chemistry is not specified and would have to be agreed on with vendors.

**Cadmium Replacement.** This column in Table 4 briefly describes materials or processes that have proven to be viable replacements for cadmium coatings on steel substrate components. The options presented range from simply substituting common zinc plating to employing solid, inherently corrosion-resistant materials (e.g., nickel alloys or stainless steel) to replace plated components.

Implementing a major design change (e.g., replacing a cadmium-coated fastener with a solid nickel alloy fastener) is sufficiently complex to require component-specific engineering review. To assist with this process, Table 4 lists references for commercial and federal agencies that are using cadmium replacements in specific applications. Generic terms are used to describe replacements; if required, the listed reference may be consulted to identify specific products or processes.

The only cadmium replacements included in Table 4 are those specifically applicable to steel substrates. Cadmium applications to nonferrous parts are typically intended to address complex performance parameters that are beyond the scope of this article.

**Specifications.** This column in Table 4 provides a brief list of consensus or military specifications for the cadmium replacements. The term *commercial* denotes specifications developed by individual corporations, which are generally available from the referenced sources.

**Corrosion Control Performance.** This column in Table 4 summarizes the results of corrosion control tests conducted in realistic or natural marine and/or industrial atmospheres. These atmospheres are widely regarded as the most aggressive natural environments used to test coatings. Cadmium replacements that provide effective substrate corrosion control in these atmospheres will perform even more effectively in less harsh environments, such as those that might be encountered inside a climate-controlled building or sheltered compartment.

Corrosion control data generated using artificially accelerated or salt fog tests (e.g., ASTM B 117) are not included because such data have no demonstrable correlation with actual field performance. Figure 2 shows that salt fog and natural marine atmosphere data for an 18-day exposure period are inconsistent and contradictory (Ref 14). Similar data generated by an SAE-AISI task force on corrosion testing led to the following conclusion (Ref 15): "The ASTM B 117 salt spray (fog) gives a very poor simulation of on-vehicle behavior and thus should not be used for ranking the cosmetic corrosion resistance of automotive sheet steel products."

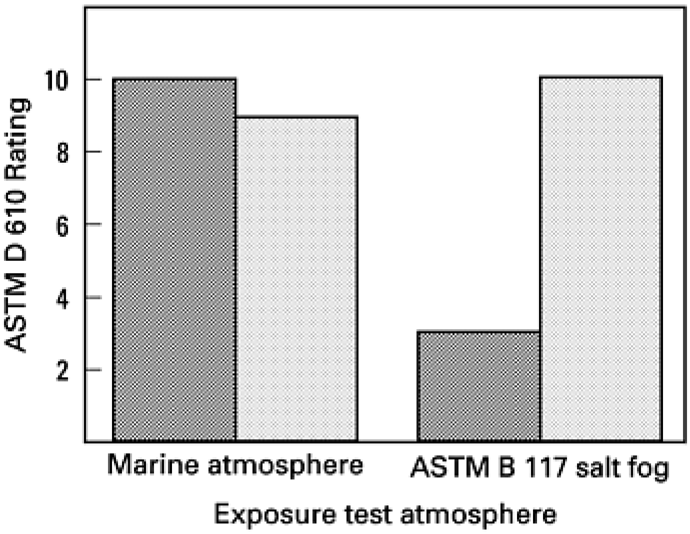

**Fig. 2 Lack of correlation between ASTM B 117 salt fog test results and natural marine-atmosphere exposure test data for cadmium-plated (light-shaded bars) and zinc-plated (dark-shaded bars) mild steel. The ASTM D 610 rating scale extends from severe substrate corrosion (rating 1) to no substrate corrosion (rating 10). Source: Ref 14**

As such, Table 4 summarizes only data generated by comparing the natural-atmosphere corrosion control performance of the listed replacements with that of the cadmium-coated experimental controls (e.g., AISI 1010 steel specimens coated with QQ-P-416, type I cadmium plating at thicknesses of 5.1, 12.7, and 25.4 μm, or 0.2, 0.5, and 1.0 mil). Only cadmium replacements that could be applied at thicknesses of 12.7 μm (0.5 mil) or less were included in the analysis. Following are the terms used to describe the qualitative ratings:

- *Better:* The replacement (applied at thicknesses similar to those of cadmium) controls steel substrate corrosion for a longer period of time than cadmium.
- *Comparable:* The replacement (applied at thicknesses similar to those of cadmium) controls steel

substrate corrosion as effectively as cadmium for a similar period of time. Coating self-corrosion or cosmetic appearance data did not influence this rating. For example, a zinc-base coating was considered comparable to a cadmium coating if it provided the same degree of protection to the substrate, even if it produced greater amounts of white corrosion product than a cadmium coating.

- *Worse:* The replacement (applied at thicknesses similar to those of cadmium) did not control steel substrate corrosion as effectively as cadmium. Because all of the systems included in Table 4 have already been used to replace cadmium in some applications, a rating of *Worse* typically signifies that thin layers of the replacement did not perform as effectively as thin layers of cadmium, even though thicker layers of the replacement may have been equivalent (Ref 3). Even if a system is rated *Worse* in this table, it still could be considered a viable cadmium replacement in applications that could accept thicker coatings, or applications in less corrosive environments.

As these ratings suggest, the coating thickness of cadmium replacements exerts a significant influence on corrosion control performance. Cadmium and virtually all of the replacement coatings sacrificially corrode to protect the substrate, so coating thickness exerts a significant influence on coating service life. In general, thicker sacrificial coatings contain more metal (i.e., greater coating weight) and will sacrificially corrode to protect the substrate steel for a longer period of time.

Figure 3 shows the relationship of zinc coating weight to service life (Ref 16). Although cadmium is a sacrificial coating, data from natural atmosphere exposure tests do show that cadmium coatings tend to provide effective corrosion control when applied in thin layers, whereas many of the cadmium replacements did not perform as effectively at comparable thicknesses. To maximize the service life of components coated with cadmium replacements, specifications should require the thickest layer possible that does not adversely affect fit or function.

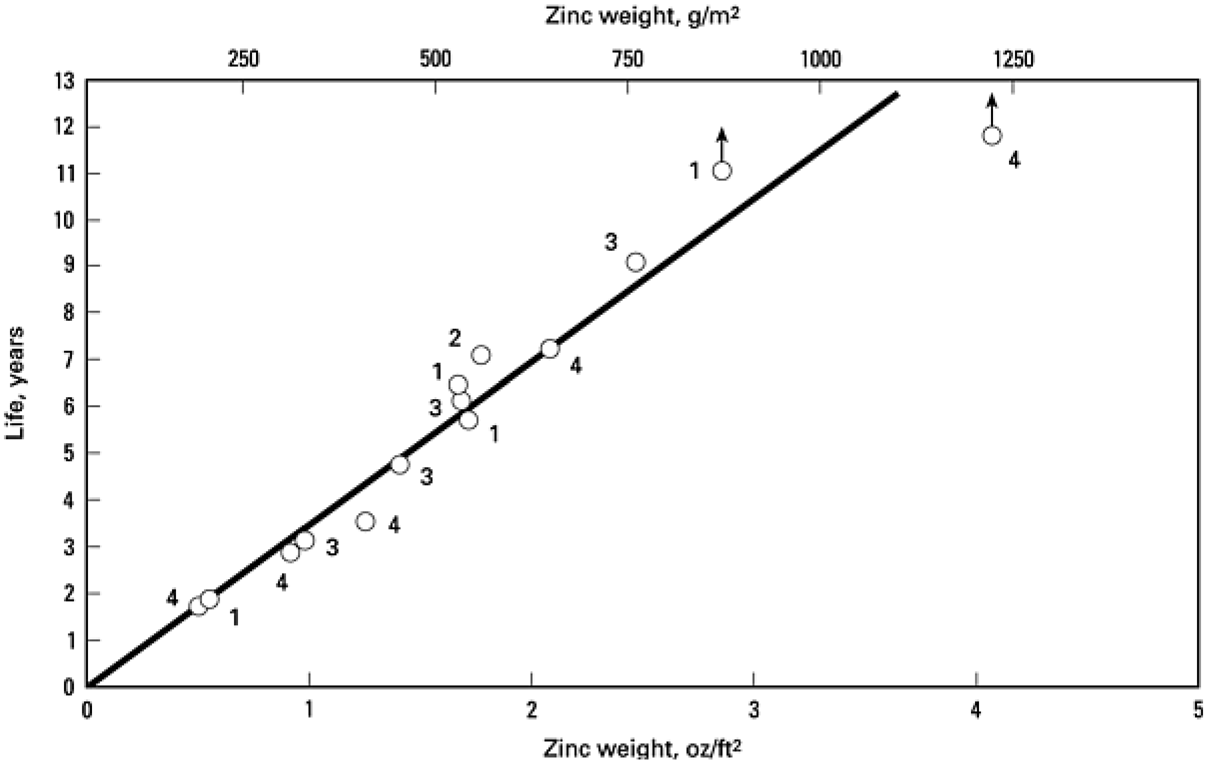

**Fig. 3 Service lives of various zinc coatings according to the weight of the zinc present. Results are for exposure in a very aggressive industrial atmosphere. 1, electrodeposited; 2, electrodeposited (passivated with chromate solution); 3, hot-dip galvanized; 4, sprayed. Source: Ref 16**

**Environment-Assisted Cracking (EAC).** This column in Table 4 compares the influence of cadmium replacement coatings on hydrogen embrittlement or overall EAC of a substrate steel. Again, Table 4 compares the performance of replacement coatings to that of cadmium coatings under similar test conditions. A comprehensive analysis of hydrogen embrittlement and EAC is presented in Volume 13 of the *ASM Handbook* (Ref 17, 18), so a similar discussion is not presented here. However, for steels, susceptibility to hydrogen embrittlement or EAC generally correlates with increasing yield strength and hardness. Thus, any analysis of cadmium replacements intended for use on high-strength steels must consider the issues presented in this table.

In general, the Table 4 data were developed by evaluating AISI 4340 steels, heat treated to between 1241 and 1379 MPa (180 and 200 ksi), using constant extension rate tests (CERT) or other applicable EAC tests. Data regarding EAC of the solid nickel and stainless steels are not presented in Table 4 but are available in Ref 17 and 18.

Figure 4 shows how test data were summarized to create the qualitative Table 4 ratings. It presents CERT results from coated, high-strength steel specimens immersed in an aqueous 3.5% NaCl solution and/or an inert medium (Ref 19). The test specimens were baked after plating to reduce hydrogen mobility and/or drive off process hydrogen (Ref 19, 20). Thus, the results show how sacrificial corrosion can embrittle high-strength steels. Reduced CERT times to failure for coated specimens, relative to those for uncoated experimental control specimens, are associated with embrittling effects. Figure 4 shows that cadmium plating (QQ-P-416, type I) caused the least substrate embrittlement.

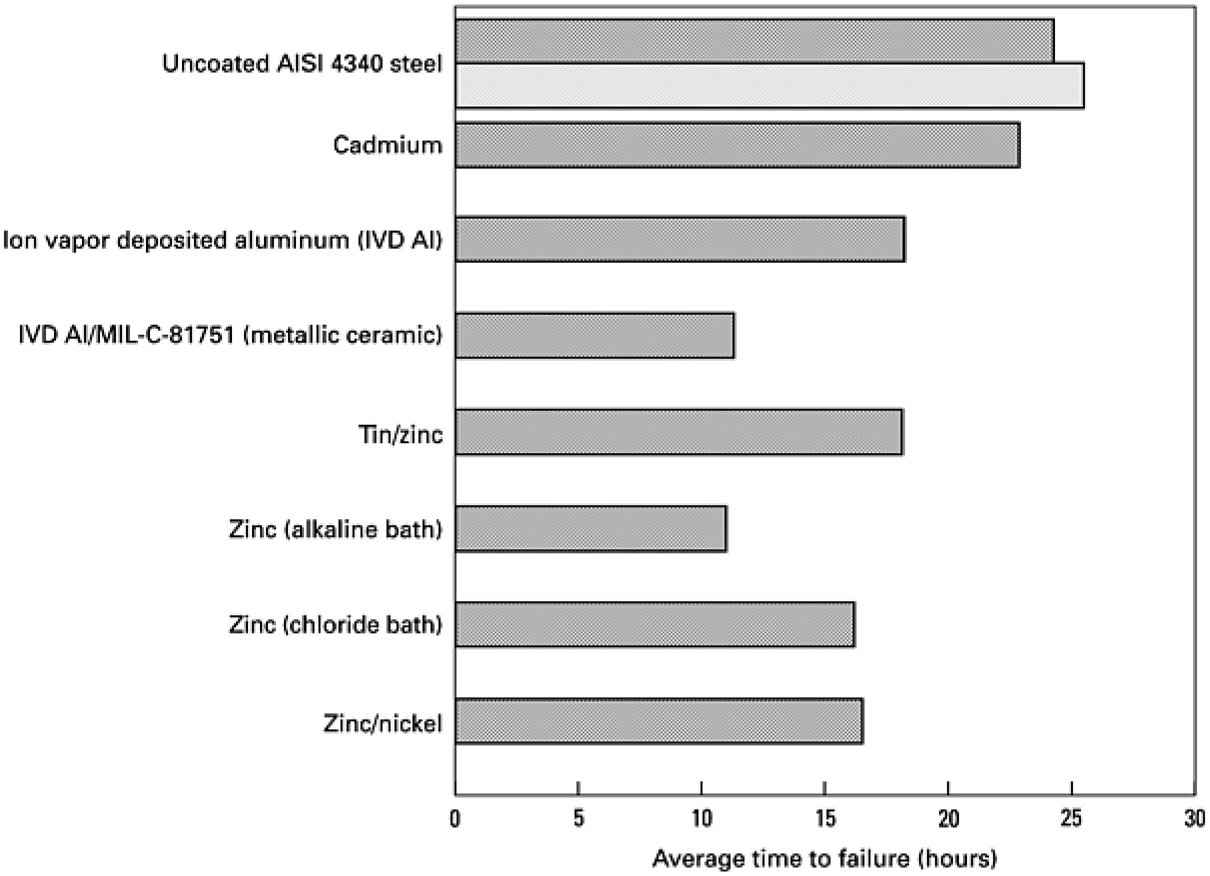

**Fig. 4 Results of constant extension rate tests (2.5 × $10^{-2}$ μm/s, or 2.5 × $10^{-6}$ in./s) of AISI 4340 steel specimens (1241 MPa, or 180 ksi) with cadmium and replacement coatings evaluated in aqueous 3.5 NaCl (dark bars) and/or an inert medium (light bar). Source: Ref 19**

These results are not surprising, given that cadmium has historically been used as a high-strength steel coating. The usefulness of cadmium as a coating for high-strength steels is reflected in the numerous low-embrittlement specifications listed in Table 3. Because cadmium coatings may be applied in accordance with specifications that minimize production-process-induced or corrosion-induced hydrogen charging, and because none of the alternative specifications minimizes embrittlement, any cadmium replacements intended for use on high-strength materials must be evaluated before coating changes are authorized. The evaluation process must consider component strength level, configuration, and intended service environments. *Caution: Failure to evaluate cadmium replacements applied to high-strength steels could result in* *catastrophic component failures.* Analysis of Table 4 data suggests that on some high-strength, high-performance parts for which solid alloys are not acceptable, cadmium may be the only viable, currently available plating process.

**Coating Lubricity.** This column in Table 4 addresses the established usefulness of cadmium as a threaded fastener or connector coating (Ref 21). Because lubricity is such a complex and difficult-to-define performance parameter, the ratings specifically summarize threaded fastener performance, as measured by differences in curves showing the tensile load created in a threaded fastener as a function of applied torque. Replacement coatings are rated *less* lubricious if they exhibited lower fastener tensile loads for given torque levels than cadmium fasteners subject to the same test conditions. To ensure that the data reflect significant performance differences between coating systems, not simply an effect caused by the test conditions, only results from unlubricated tests (i.e., no added oil or grease) are summarized. Adding lubricants such as grease or oil to threaded fastener systems exerts a significant influence on torque-tension behavior and creates an added degree of complexity which is beyond the scope of this article (Ref 22).

Figure 5 shows the type of data summarized in Table 4 and shows how added lubricants influence threaded fastener lubricity. The average tensile load created in H-11, 22-4-22 threaded bolts is shown as a function of applied torque. The data show that the application of cetyl alcohol (a lubricant) had more impact on the torque-tension relationship for threaded fasteners than the metal coating type. The data also show that for a given torque level, the specimens coated with ion vapor deposited (IVD) aluminum exhibited far less tensile load than the cadmium-coated experimental controls. As a result, IVD aluminum was rated less lubricious than cadmium in Table 4. Any potential use of IVD aluminum as a cadmium replacement on threaded fasteners must account for the inherent limited lubricity of the aluminum coating (Ref 23).

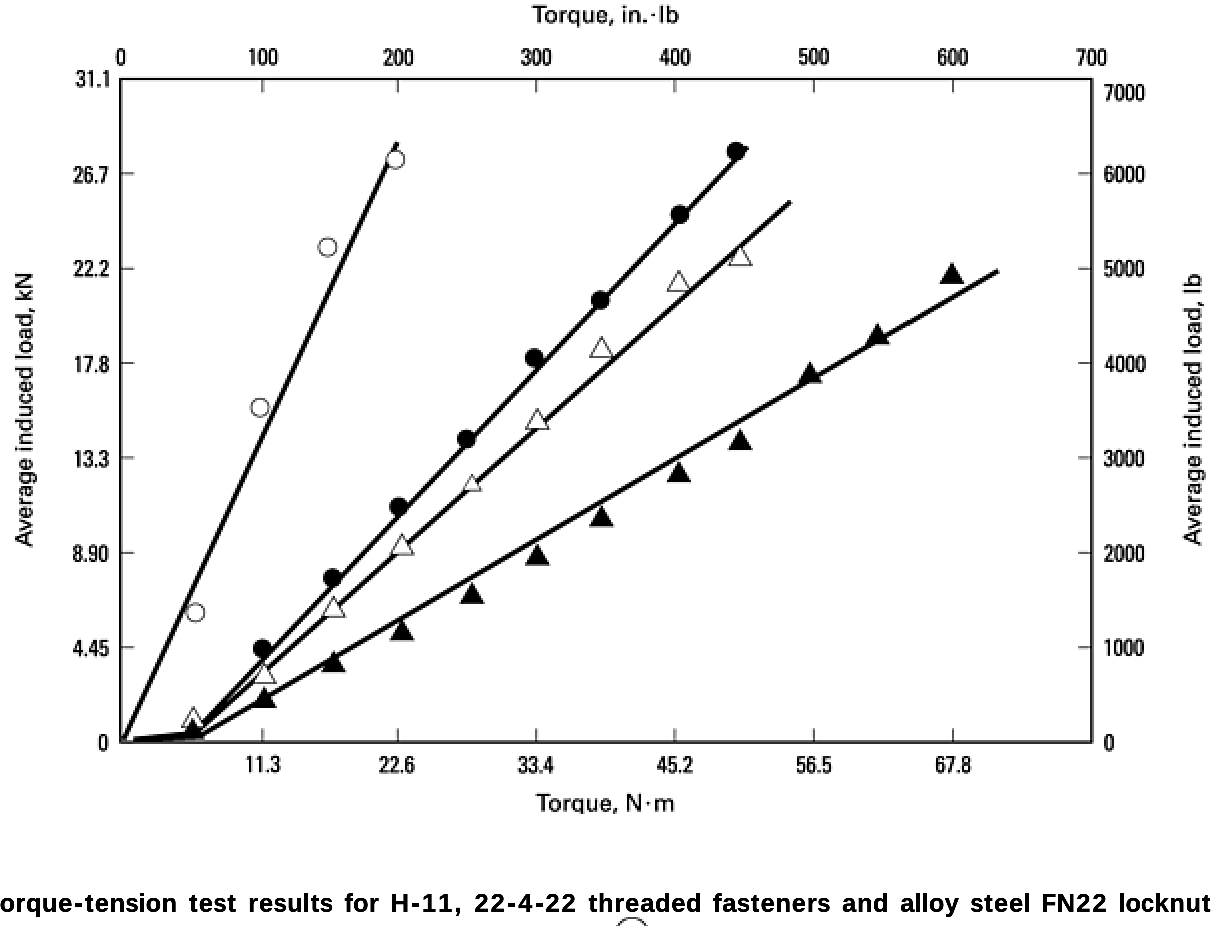

**Fig. 5 Torque-tension test results for H-11, 22-4-22 threaded fasteners and alloy steel FN22 locknuts, coated with ion vapor deposited (IVD) aluminum or cadmium. ○, bolt and nut with IVD aluminum and cetyl alcohol; •, bolt with cadmium and nut with cadmium; △, bolt with IVD aluminum and nut with cadmium; ▲, bolt and nut with IVD aluminum. Source: Ref 23**

Although results generated using added lubricants (e.g., grease or cetyl alcohol) are not summarized in Table 4, the application of a solid, dry film lubricant as part of the fastener production process was considered. Figure 6 shows average torque-tension curves generated from testing replicate $\frac{1}{2}$-20-UNC, grade 5 fasteners plated with cadmium, zinc-nickel, and zinc-nickel with additional lubricious topcoats (i.e., dry film lubricants and polytetrafluoroethylene, or PTFE, systems) (Ref 24). Although only the averages are plotted in Fig. 6, standard deviation data show a considerable degree of variation around the mean. The standard deviation for the cadmium-plated fasteners (one of the most consistently lubricious or "well behaved" coating systems) was typically in excess of 15% of the average. The threaded fasteners coated with replacement systems demonstrated a similar, or even larger, range in tension for a given torque. Although the considerable data range is significant, the most important conclusion is that addition of a dry film lubricant or PTFE-type product over any sacrificial coating can create a system that is more lubricious than cadmium (Ref 24). The significant influence of dry film lubricants on overall system lubricity shows that cadmium should not be considered a unique or irreplaceable lubricious fastener coating.

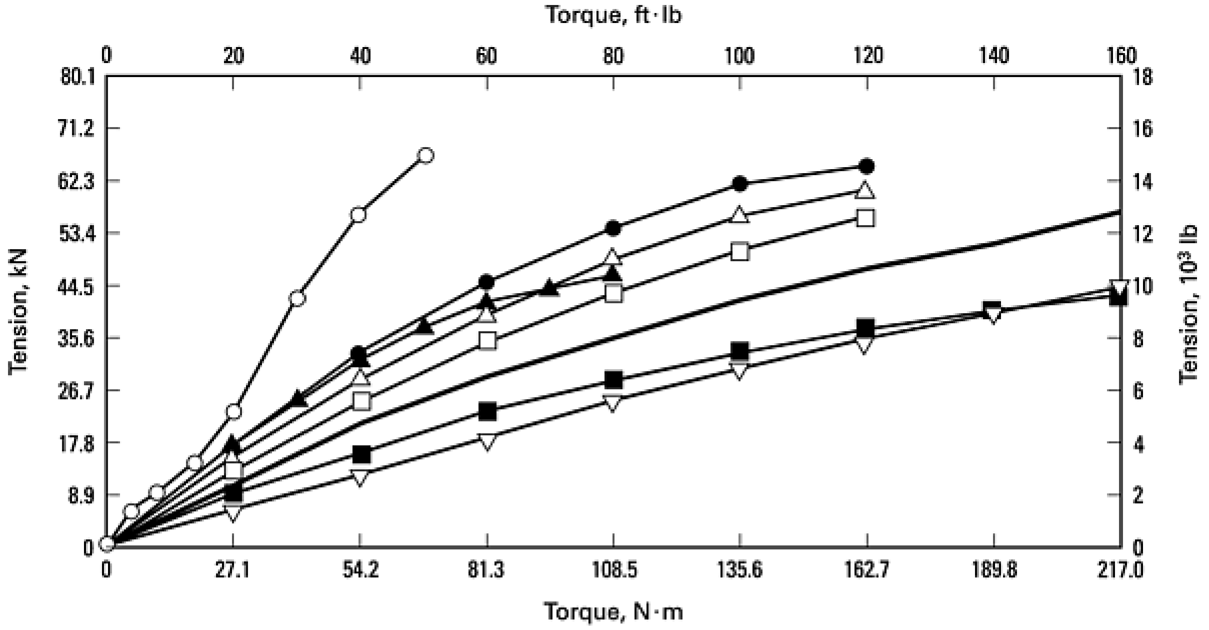

**Fig. 6 Average torque-tension data from five replicate $\frac{1}{2}$-20-UNC grade 5 fasteners plated with cadmium, zinc-nickel, or zinc-nickel with lubricious topcoats. ○, dry film lubricant (MIL-L-56010); •, dry film lubricant (MIL-C-85614); △, organic sulfamate emulsion; ▲, aqueous polytetrafluoroethylene (PTFE)/phenolic; □, PTFE/phenolic A; ■, PTFE/phenolic B; ▽, zinc-nickel; thick line, cadmium. Source: Ref 24**

**Environmental and Worker Health Regulations.** This column in Table 4 compares the environmental compliance risks and potential worker health hazards created by the replacement coatings. Of course, all of the replacements shown in Table 4 create far fewer environmental and worker health risks than cadmium. However, when applicable, there are comments about potential environmental and worker health issues that could affect replacement coatings.

For all plating processes described in Table 4, a comment is provided regarding the hazards posed by the chromate passivation treatment. Chromate passivation treatments based on hexavalent chromium-ion solutions are frequently used as a final step in the plating process and are subject to many of the same environmental and worker health regulations as cadmium. Although chromate passivation treatments do improve the corrosion-control performance of plating systems, the Table 4 data were developed using both chromated and nonchromated plating layers (Ref 3). Replacing cadmium with one of the replacement plating processes shown in Table 4, along with eliminating the chromate passivation process, minimizes hazardous materials handling and disposal costs and simplifies regulatory compliance.

**Cost and Performance Factors.** This column in Table 4 compares the application costs for the replacement processes to those for cadmium. The summaries are based on numerous analyses. Some of the data were inconsistent or contradictory, and as such, specific cost estimates must be developed on a case-by-case basis before any cadmium replacements are used.

Table 4 shows that the costs of using solid alloy components are higher than those for cadmium-coated parts. Although the costs for solid stainless steel or nickel alloy components are typically higher than those for cadmium-plated items, the life cycle costs (i.e., the costs associated with recurring maintenance and repair) for these solid alloy parts may be lower than those for cadmium or other replacement plating processes. The costs for IVD aluminum coatings are also shown to be higher than those for cadmium plating, primarily because the IVD aluminum application process is conducted in a vacuum chamber under the influence of an electric field. The significant investment in sophisticated equipment makes the IVD aluminum coating process approximately 33% more costly than QQ-P-416 cadmium plating on a per-part basis (Ref 23).

Other comments in this column relate to issues that might affect the cadmium replacement selection process. A key noneconomic issue that could affect cadmium replacement selection is the in-service appearance of the sacrificial layer. Zinc coatings are known to develop voluminous white corrosion products while sacrificially corroding (Ref 16). These corrosion products may interfere with the function of precision components, or they may simply be cosmetically unappealing. Decisions about whether these products might affect the performance of individual components should be made by engineering staff.

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# Chromium Elimination in Surface Engineering

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## Introduction

CHROMIUM has been widely used in surface finishing of metals because of the favorable properties it imparts to substrates and because the processes used are relatively mature, well understood, widely specified, and cost-effective. In recent years, however, the use and emission of hexavalent chromium has come under increased scrutiny by various regulatory bodies due to its adverse health and environmental effects. Indications are that regulatory agencies will continue to require significant reductions in the emissions of chromium in the future. Typical solutions to this problem range from the addition of emissions control devices, to a change in the method of application of a material, to the complete re-engineering of the surface finishing process through process and material substitution.

Major uses of hexavalent chromium in surface finishing are in chromium plating and chromate conversion coating. Chromium plating is electrolytically applied to steel parts and can be either hard (engineering) plating, which is applied relatively thickly to impart desirable wear and abrasion resistance, or decorative plating, which, as the name implies, is for aesthetic purposes. (See the articles "Industrial (Hard) Chromium Plating" and "Decorative Chromium Plating" in this Volume.) Chromate conversion coating is a nonelectrolytic process in which the conversion coating is applied to light metals (aluminum, magnesium, cadmium plate) and alloys for corrosion resistance and/or as a paint base. (See the article "Chromate Conversion Coatings" in this Volume.) To a lesser extent, chromium is used in chromic acid anodizing, which also imparts corrosion resistance and paint adhesion properties to aluminum but, unlike conversion coating, is an electrolytic process.

This article focuses on alternatives to chromium in both hard chromium plating and chromate conversion coating. It addresses material and process substitutions that can be used to eliminate the use or emissions of chromium in the industrial processes described above. Other uses of chromium, such as in paints, are not covered. The focus of the article is on comparing the physical characteristics of each coating and the economics, environmental impact, advantages, and disadvantages of alternative processes.

## Alternatives to Hard Chromium Plating

Hard chromium plating is the most widely used application of chromium in surface finishing. It is routinely used for applications that require hard, wear-resistant coatings on either new or refurbished parts. The coating applied is relatively thick (as opposed to decorative chrome), generally between 0.25 and 0.76 mm (10 and 30 mils), which makes it good for dimensional restoration. In aerospace applications, chromium plating is the preferred wear-resistant coating for hydraulics, landing gear, rotating shafts, gears, and surfaces subjected to sliding or rolling wear. The plating characteristics of chromium plating are shown in Table 1. The thickness buildup, coating adhesion, hardness, and abrasion resistance properties are especially favorable.

**Table 1 Plate characteristics of hard chromium plating and prospective alternative processes**

| **Characteristic** | **Chromium electrodeposition** | **Low-phosphorus electroless nickel (generic)** | **Ni-W-B electrodeposition (Amplate)** | **Ni-W-SiC electrodeposition (Takada)** | **Plasma spray (general)** | **High-velocity oxyfuel (general)** |
|---|---|---|---|---|---|---|
| Thickness buildup, mm (mils) | Up to 0.8 (up to 30) | Up to 0.5 (up to 15) (more uniform than chrome) | Up to 0.25 (up to 10) (more uniform than chrome) | Up to 0.4 (up to 15) (more uniform than chrome) | Up to 1.3 (up to 50) (rougher than chrome) | Up to 1.3 (up to 50) (rougher than chrome) |
| Coating adhesion, MPa (psi) (ASTM C 633) | >70 (>10,000) | >70 (>10,000) | >70 (>10,000) | >70 (>10,000) | >55 (>8000) (coating-dependent) | >70 (>10,000) (coating-dependent) |
| Hardness | 800-1000 HV | 670-750 $DPH_{300}$; with heat treatment, 980-1050 $DPH_{300}$ | 600-950 $DPH_{300}$(with heat treatment) | 800 to >1000 $DPH_{300}$ | 800-1200 $DPH_{300}$ (coating-dependent) | 800-1450 $DPH_{300}$ (coating-dependent) |
| Machine finish, $\mu$m ($\mu$in.) (RHR rms) | <0.2 (<8) | <0.2 (<8) | <0.2 (<8) | <0.2 (<8) | <0.2 (<8) | <0.2 (<8) |
| Corrosion resistance, h (ASTM B 117) | >24 | >96 | >400 | >24 | >24 | >48 |
| Porosity, % | <2 | <1 | <1 | <1 | 5-13 | <2 |
| Abrasion resistance, mg (Taber CS-10, 1 kg, avg per 1000 to 10,000 cycles) | <25 | <35 (dependent on heat treatment and composite additives) | <25 | <20 | <20 (coating-dependent) | <20 (coating-dependent) |
| Coefficient of friction | 0.16 | <0.20[(a)] | 0.13 | 0.13 | 0.25[(a)] | <0.20[(a)] |
| Falex wear rate | Good | Moderate/poor | Excellent | Excellent | Moderate/poor | Good[(a)] |
| Threshold galling wear | Good | Moderate/poor | Excellent[(a)] | Excellent[(a)] | Good[(a)] | Good[(a)] |
| Chemical | Fair | Good | Excellent | Excellent | Good | Excellent |

| | | | | | | |
|---|---|---|---|---|---|---|
| resistance | | | | | | |
| Coating stripping ability | Good | More difficult | More difficult | More difficult | Difficult | More difficult |
| Fatigue loss, % | As high as 60 | Less than for chromium(a) | Less than for chromium(a) | Less than for chromium(a) | Less than for chromium(a) | Less than for chromium(a) |

RHR, roughness height rating.

(a) Needs additional testing

The chromium plating process is inexpensive, well understood (it has been widely used for many years), and easy to perform. The process involves degreasing, masking, and cleaning prior to plating. The parts are then racked and immersed in the plating bath for up to 24 h, depending on the desired thickness. Following the plating step, the parts are removed from the bath, masking is removed from the part, the part is baked for embrittlement relief, and finishing (such as grinding, lapping, polishing) is completed.

Several disadvantages of chromium plating are its high fatigue life debit, marginal corrosion resistance due to microcracking, high power consumption, nonuniform coverage, poor penetration into holes and tube bores, and the evolution of hydrogen in the process. As a result of the hydrogen evolution, misting occurs, which leads to high air emission rates and associated adverse health, safety, and environmental risks.

Potential process substitutions for hard chromium plating are discussed below. These include electroless nickel in certain applications, several nickel-tungsten composite plating options, and spray applications such as plasma spray coatings. (There are other possible substitutions, such as vacuum deposition processes and cobalt alloys, that are not discussed.) None of these has exhibited all of the desirable qualities of chromium plating. Certain tradeoffs, such as somewhat poorer physical properties, increased process time, and increased costs, are to be expected. Clearly, no one alternative should be viewed as a "drop-in" replacement for the elimination of all chromium in hard chromium plating.

**Electroless nickel (EN) plating** has been in existence for several decades. In this autocatalytic process, nickel ions are reduced to metal by the action of chemical reducing agents, without the need for an electric current. A commonly used reducing agent is sodium hypochlorite, which donates electrons to the metal ions with the substrate acting as a catalyst for the reaction.

The use of EN as an alternative to chromium plating is severely limited by its somewhat poorer physical properties. As is evident from Table 1, the hardness and abrasion resistance of low-phosphorus EN are good but lower than those of chromium plating. In addition, the wear rate and galling resistance are poorer than those of chromium plating (Ref 1).

One advantage of EN is that the deposit follows all of the contours of the substrate without the excessive buildup at the edges and corners that is common with chromium plating. Sharp edges and blind holes receive the same plating thickness. The process bath, however, is more sensitive to impurities than the chromium plating bath, and it must be closely monitored to maintain the proper concentrations and balance of the metal ions and reducing agents. In addition, the bath life is finite and less than that of chromium plating, which means that periodically it must be "dumped" and a fresh bath prepared. Deposition rate and coating properties are affected by temperature, pH, and metal ion/reducing agent concentration.

Electroless nickel plating can be used as a chromium plating alternative in limited applications, such as for very well lubricated conditions. It cannot be cost-effectively plated as thick as chromium, but because it plates more evenly, the need for substantial overplating can often be eliminated. The main drawback with EN is that the coating is not as hard as chromium plate. However, a postplating heat-treatment step can improve its hardness significantly. Although EN does not wear as well as chromium plating and is more susceptible to galling wear, on a positive note, it imparts greater corrosion protection than chromium plate and should not result in significant fatigue life debit.

**Nickel-Tungsten Composite Electroplating.** Two separate nickel-tungsten composite electroplating processes are available as potential alternatives to chromium plating: nickel-tungsten-boron (Ni-W-B) composite electroplate (Ref 2) and nickel-tungsten-silicon carbide (Ni-W-SiC) composite electroplate (Ref 3, 4). The two processes are similar in that they are both electrolytic and deposit a composite of nickel and tungsten onto the substrate. Both have been developed relatively recently and are not yet widely used. Each coating exhibits many of the desirable properties of chromium plating, but additional testing is required before the processes can be widely used in critical applications. The processes use less energy than chromium plating, so the platings are more uniform than chromium and can result in cost savings by allowing greater throughput and a minimal amount of overplating. In addition, the applications are tank-based, which makes a transition from chromium plating relatively straightforward.

Ni-W-B composite electroplating deposits a coating that is approximately 59.5% Ni, 39.5% W, and 1% B (Ref 2). The coating has a bright silver-white, highly lustrous appearance at thicknesses of up to 0.25 mm (10 mils), above which it becomes matte in appearance. The physical properties of the coating are listed in Table 1. The coating has favorable chemical and abrasion resistance, high ductility, a low coefficient of friction, and plates very uniformly and smoothly. However, as compared with chromium, Ni-W-B is less hard; postplating heat treatment raises the hardness significantly to a level that is equal to or slightly greater than that of chromium plate.

Ni-W-SiC composite plating is similar to Ni-W-B except that it uses silicon carbide interspersed in the matrix to relieve internal stresses and improve the coating hardness. The resulting deposit is roughly 46.3% Ni, 46.1% W, 4.3% Si, and 3.2% C (Ref 4). The appearance of the coating is similar to that of Ni-W-B, with the silicon carbide causing a nearly indiscernible darkening. The coating properties, which are also listed in Table 1, indicate favorable chemical resistance, abrasion resistance, and coefficient of friction. The hardness of the coating is somewhat greater than that of Ni-W-B, and with heat treatment it can exceed that of chromium plating.

The major disadvantages associated with these two nickel-tungsten processes are their lack of maturity, their potential increased costs over chromium, and, to a lesser extent, their reliance on nickel. Besides not having been scaled up to production, additional testing, which is ongoing at various locations, will be required to qualify these coatings for particular applications. The qualification process is not easy; engineers rightly err on the conservative side in approving such sweeping changes in potentially critical situations. Also, while no hard numbers exist, it has been estimated that these processes will cost considerably more than for chromium plating (Ref 5). However, these estimates do not consider the potential liability costs associated with the continued use of chromium. It is true that the use of nickel, and to a lesser extent the use of tungsten, may become more tightly regulated, but even so, there is much less nickel in these plating baths than there is chromium in a chromium bath, resulting in lower risk.

**Spray Coating Applications.** Several spray coating applications have shown promise as potential alternatives to chromium plating. Variations on this application include arc spray, flame spray, plasma spray, and high-velocity oxygen fuel (HVOF) spray. From a materials standpoint, the one having the best coating properties is HVOF spray, which is the type addressed in this section.

HVOF coatings are presently used in many industrial applications because they develop very hard, wear-resistant surfaces that have comparable performance requirements to those of chromium plating. HVOF spray is based on the detonation gun (D-gun) process developed by Union Carbide (Praxair). In HVOF coating application, an explosive gas mixture ignites in the barrel of the spray gun, which melts a powdered coating material and propels it (with a carrier gas) at supersonic speeds toward the substrate. The superior coating properties are a result of the high velocities that are reached in the process--the higher the velocity, the greater the force of impact at the substrate, resulting in fewer voids in the coating and more desirable properties.

There are presently numerous manufacturers of HVOF equipment and coating materials, each having a somewhat different design; the system and coating material selected contributes to the resulting coating properties. Table 2 lists the coating properties of some typical HVOF coatings that may be applicable to chromium plating elimination. Note that many HVOF coatings are chromium-base, so the use of the HVOF system would not necessarily result in chromium *elimination.* However, the HVOF process emits significantly less chromium than chromium plating, and recovered metal powders can be recycled.

**Table 2 Physical characteristics of high-velocity oxyfuel spray deposited coatings**

| Characteristic | Tungsten carbide- | Cobalt-chromium- | Nickel-chromium- | Chromium carbide- | Iron-nickel- |
|---|---|---|---|---|---|

| | **cobalt** | **nickel-tungsten** | **molybdenum** | **Nichrome** | **chromium** |
|---|---|---|---|---|---|
| Thickness buildup, mm (mils) | >1.3 (>50) | >1.3 (>50) | >2.5 (>100) | >0.6 mm (>25) | >1.5 (>60) max |
| Coating adhesion, MPa (psi) (ASTM C 633) | >90 (>13,000) | >70 (>10,000) | >70 (>10,000) | >88 (>12,000) | >75 (>11,000) |
| Hardness | 64-69 HRC | 53 HRC | 30-34 HRC | 65 HRC | 45 HRC |
| | 800-1650 DPH$_{300}$ | 550-700 DPH$_{300}$ | 350-450 DPH$_{300}$ | 800-850 DPH$_{300}$ | 550-650 DPH$_{300}$ |
| Machine finish, $\mu$m ($\mu$in.) (RHR rms as-sprayed)(a) | 4-6 (150-250) | 4-7.5 (200-300) | 4.3-6 (170-250) | 2.5-4.3 (100-170) | 6-9 (250-350) |
| Corrosion resistance, h (ASTM B 117) | >48(b) | >48(b) | >48(b) | >48(b) | >48(b) |
| Porosity, % | <1 | <1 | <1 | <1 | <1 |
| Abrasion resistance, mg (Taber CS-10, 1 kg, avg per 1000 to 6000 cycles) | <20 | <20 | <20 | <20 | <20 |
| Coefficient of friction | 0.18 | <0.20(b) | <0.20(b) | <0.20(b) | <0.20(b) |
| Falex wear rate | Excellent | Excellent(b) | Excellent(b) | Excellent(b) | Excellent(b) |
| Threshold galling wear | Excellent(b) | Excellent(b) | Excellent(b) | Excellent(b) | Excellent(b) |
| Chemical resistance | Excellent | Excellent | Excellent | Excellent | Excellent |
| Coating stripping ability | More difficult | More difficult | More difficult | More difficult | Difficult |
| Fatigue loss | Less than for chromium(b) | Less than for chromium(b) | Less than for chromium(b) | Less than for chromium(b) | Less than for chromium(b) |

(a) Ground machined finish is <0.2 μm (<8 μin.) for all coatings. RHR, roughness height rating.

(b) Significant uncertainty due to testing method or speculated effects based on metallurgical properties

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## Alternatives to Chromate Conversion Coating

Chromate conversion coating is a nonelectrolytic application to light metals, generally aluminum and its alloys, for the purpose of imparting corrosion protection and paint adhesion properties. The process is widely used in the aerospace industry and can be applied by brush, spray, wipe, or immersion. Chromate conversion coating offers numerous advantages over the potential alternatives:

- Greatly improved wet and dry paint adhesion
- Self-healing corrosion protection in case of scratched parts
- Simple application process and easy-to-maintain bath chemistry
- Mature process; in many applications has been the preferred coating for years

Presently, there are no drop-in substitutes to chromate conversion coating that adequately address each of its advantages.

The major disadvantage of chromate conversion coating is simply its use of hexavalent chromium. The tank-based process does not have the misting emission problem typical of chromium plating, but in applying the coating to entire aircraft, the subsequent rinse process can generate large quantities of chromium-containing wastes.

Several tests are routinely used to quantify the characteristics of conversion coatings. Paint adhesion can be measured using the wet tape adhesion method, scrape adhesion method, knife scribe test, crosshatch adhesion test, and others. Corrosion resistance is typically measured using the salt spray corrosion resistance test, ASTM B117, which is conducted on either unpainted or painted specimens. Examples of the performance of chromate conversion coatings in these tests are included in Table 3, which also shows the performance of alternatives.

**Table 3 Coating characteristics of chromate conversion coating and prospective alternative processes**

| **Characteristic** | **Chromate conversion coating** | **Cobalt/ molybdenum-base coating** | **Oxide layer growth coating** | **Sulfuric acid boric acid anodizing** |
|---|---|---|---|---|
| Salt spray testing, unpainted, h | >336 | >336 | >168 | >336 |
| $SO_2$/salt spray testing, unpainted, h | <168 | . . . | >168 | >168 |
| Salt spray testing, painted, h | >2,000 | >1,500 | >2,000 | >2,000 |
| | Pass | Pass | Pass | Pass |
| Paint adhesion, crosshatch test | Pass | Pass | Pass | Pass |

| | | | | |
|---|---|---|---|---|
| Paint adhesion, wet tape | Pass | Pass | Pass | Pass |
| Electrical resistance, MΩ | <5,000 | <5,000 | >5,000 | >5,000 |
| | <10,000 after salt spray | <10,000 after salt spray | >10,000 after salt spray | >10,000 after salt spray |

Potential alternatives to chromate conversion coating are discussed below. These include a proprietary cobalt and molybdenum-based process, a multistep process that grows a corrosion-resistant oxide layer, and various others.

**Cobalt/molybdenum-base conversion coating** is a project of a major aerospace company and a supplier of conversion coatings, Parker-Amchem. It is a developmental process that uses cobalt and molybdates rather than chromates. Laboratory tests have shown that the coating is capable of meeting the important corrosion resistance and paint adhesion characteristics (Table 3), but the process has not been scaled up to production levels.

The cobalt/molybdenum process requires one additional process tank and rinse step for sealing, which could have considerable cost impact. In addition, it requires heated baths, resulting in increased energy usage. This makes the estimated cost associated with the process about twice as much as that of chromate conversion coating (Ref 6), keeping in mind that liability costs, which could be significant, are not factored into the costs of chromate conversion coating. Although this is a significant increase, the cost is not as much as for the oxide layer growth process described below. Probably the greatest disadvantage of the cobalt/molybdenum-base process is that it is still developmental and has not been scaled up to production levels.

Advantages of this coating process are that it would be universally applicable to parts that are presently chromate conversion coated. It is still a tank-based process for immersion application (it is also being developed for spray, brush, and wipe applications), and it requires only slightly more time than the present coating process.

**Oxide layer growth in high-temperature deionized water** was developed and refined within the past decade (Ref 7, 8, 9), and this process is somewhat more mature than the cobalt/molybdenum process. Several variations are in different stages of development. This process uses a series of steps, including immersion in boiling distilled water, to build a corrosion-resistant paint base on aluminum. Following the growth of the corrosion-resistant oxide layer, several proprietary baths are used to seal and enhance the properties of the coating. The coating meets the corrosion protection and paint adhesion requirements of a conversion coating (see Table 2) and has been tested extensively by the Navy (Ref 10).

The major drawback of the oxide layer growth process is its cost. It requires many additional steps, involving numerous tanks of chemicals at various elevated temperatures. Consequently, the energy costs and processing times, as well as capital costs, increase substantially. In fact, it is estimated that the tank-based process may cost up to ten times as much as the present chromate conversion coating process (Ref 6).

A variation on the process involves spray application within a cabinet coater, a chamber large enough to handle the applicable parts. The various solutions are then applied sequentially using a steam generator. The concept is a joint venture of the developer of the process and another company, Electrosteam Generator Corporation. It saves on heating costs and reduces the volume of chemical required, but it is still in the developmental stage.

**Other chromate conversion coating alternatives** may prove to be of use in eliminating chromium from conversion coatings. These include sulfuric acid/boric acid anodizing (SBAA), various phosphate treatments, and other emergent technologies.

SBAA was developed by a major aerospace company to replace chromic acid anodizing (Ref 11). The process imparts exceptional paint adhesion and corrosion protection at a cost comparable to that of chromate conversion coating, and it may prove valuable as a replacement for chromate conversion coatings on some parts. However, SBAA is an anodic process, so it is not universally appropriate to all parts, especially parts with steel inserts or those having sharp edges, welds, crevices, and other areas that entrap fluids. This problem severely limits the applicability of SBAA as a chromate conversion coating alternative.

Phosphate coatings do not provide as high a quality of coating as the present process. However, in applications where the conversion coating/primer/topcoat is treated as a "system" for testing purposes (i.e., the *bare* salt spray corrosion resistance is not considered important), this type of coating could be an appropriate substitute. It is in use within the automotive industry, but it has the disadvantages of additional process steps, long process cycle time, and increased energy consumption.

Table 4 lists several experimental and developmental technologies that may lead to breakthroughs with respect to replacement of chromium in conversion coatings in some applications. Another developmental technology is the "no-rinse" conversion coating, which, although not a chromium-eliminating technology, has the capability to reduce the amount of chromium discharged. The Navy and Air Force have worked to develop a conversion coating that can be applied to an entire aircraft with no rinse step, which is where the majority of the chromium emissions occur during brush or wipe applications of the conversion coating.

**Table 4 Emergent alternative conversion coat technologies**

| **Process description** | **Status** |
|---|---|
| Trivalent chromium conversion coatings | Meets no corrosion in 500 h requirement (ASTM B 117 salt spray test) |
| | Still contains chromium |
| | Electrolytic process |
| Hydrated alumina coating | Poor paint adhesion |
| | Meets no corrosion in 500 h requirement (ASTM B 117 salt spray test) |
| Hydrated metal salt coating (Mg, Ni, Mn, Sn, Ti, Fe, Ba, Cu, Co, Ca) | Does not meet salt spray requirement |
| | Poor adhesion |
| Peroxide oxidant coating | Does not meet salt spray requirement |
| | Poor adhesion |
| | Unstable chemical baths |
| Oxyanion analogs (molybdates, tungstates, vanadates, and permanganates) | Moderate corrosion resistance |
| | Poor paint adhesion |
| | Molybdates with borate seem best |
| | Expensive |

| | |
|---|---|
| Potassium permanganate coating | Moderate corrosion protection (168 h) |
| | Poor wet tape adhesion |
| | Does not work well on 2024 or 7075 |
| | Requires boiling deionized water |
| | Multistep process, expensive |
| Rare earth metal salts (cerium) | Corrosion protection close to that of chromium |
| | Good paint adhesion |
| | Unstable chemical bath |
| | Expensive |
| | Has good future potential |
| Zirconium oxide/yttrium oxide in aqueous polymeric solution | Good paint adhesion |
| | Moderate salt spray protection (100 h) |
| | Commercially used for >10 years |
| | One step |
| | Expensive |
| Silanes or titanates | Good adhesion |
| | Moderate corrosion resistance |
| | Contain flammable solvents |
| | Thickness dependent, must be cured |
| | Difficult to dispose of |
| | Good corrosion protection on 1000-, 3000-, and 6000-series |

|  |  |
|---|---|
|  | alloys |
|  | Poor wet paint adhesion |
|  | Single process bath |
|  | Environmentally benign |
|  | Very promising |

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# Vapor Degreasing Alternatives

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## Introduction

VAPOR DEGREASING has been widely used for many years in the automotive, aerospace, and other manufacturing and processing industries to degrease and clean parts prior to chemical processing, bonding, painting, and other treatments. The chemicals traditionally used for this process are trichloroethylene (TCE) and perchloroethylene (PCE); however, these compounds have proven to be serious health and environmental hazards. Concern about these hazards led to the use of alternate chemicals: chlorofluorocarbons (CFC) and 1,1,1-trichloroethane (TCA). These compounds are less toxic and appeared, at least initially, to have no adverse effects on the environment.

Since the early 1980s, however, there has been mounting evidence that the ozone layer is being depleted, and the release into the atmosphere of CFC and TCA from their use in various industrial operations and consumer products has been identified as a contributor to this problem. CFC and TCA are classified by federal law as class 1 ozone depleting chemicals (ODC).

The traditional vapor degreasing process is described in the article "Solvent Cold Cleaning and Vapor Degreasing" in this Volume. This present article discusses the regulatory mandates that affect the use of industrial degreasing methods and describes several of the modified and alternative processes that are being used in place of traditional vapor degreasing.

## Regulatory Constraints

Industry has used vapor degreasing with either a volatile organic compound (VOC) or an ODC as the solvent for many years, and the process has gained widespread acceptance. However, many laws have been put into place to regulate or restrict the use of traditional vapor degreasing, and many new regulations are pending. As these laws come into effect, it becomes increasingly more expensive to operate and maintain these systems and to dispose of the waste they generate. Aqueous degreasing techniques (see the section "Aqueous Systems" in this article) have been developed that offer industry an attractive alternative because they are less expensive to operate and maintain, they allow for easier disposal of waste, and they are also subject to fewer regulations. This section addresses many of the regulations in the United States that affect traditional and alternative degreasing systems. Additional information is available in the article "Environmental Regulation of Surface Engineering" in this Volume.

**Environmental Protection Agency (EPA) Regulations.** In 1967, the U.S. Congress enacted the Clean Air Act, which made provisions for the attainment and maintenance of ambient air quality. The passage of the Clean Air Act, which is administered by the EPA, marked the start of major regulatory initiatives to control the emissions of VOC from industrial processes. In 1977, Congress passed the Clean Water Act to maintain and ensure the quality of water that is used for recreation and consumption. Both of these acts contain language that requires monitoring and control of emissions to the air and water. The Clean Air Act also requires the EPA to promulgate a National Emission Standard for Hazardous Air Pollutants (NESHAP). The NESHAP standard limits the amount of hazardous air pollutants that can be released to the environment and requires the use of the maximum achievable control technology (MACT) to control the emissions. Both TCE and TCA are included as pollutants on the NESHAP list.

Because of these regulations, TCE and PCE have become costly to use for vapor degreasing applications. The higher costs are due to the limits on emissions and the controls required to capture these emissions, plus the restrictions on the disposal of waste materials. In the face of these rising costs, many industries switched to using CFC and TCA as vapor degreasing solvents. However, in 1990 the EPA amended the Clean Air Act to adopt the Montreal Protocol, which calls for worldwide cessation of the production of ozone-depleting chemicals. This step had the effect of making CFC and TCA as costly to use as TCE and PCE, and eventually they will be unavailable for use.

The primary alternatives to ODC and VOC materials are aqueous degreasing systems. Because the components are solids and soluble in water, compliance with the Clean Air Act can be easily achieved. It is compliance with the Clean Water Act that is the key regulatory issue with aqueous degreasers. Users of these systems should select component materials with great care. Some materials that are currently considered to be essentially nonhazardous (such as phosphates and glycol ethers) could be restricted in the future.

**The Occupational Health and Safety Administration** (OSHA) is a U.S. government agency that provides guidelines to employers to ensure the workplace safety of their employees. Through a variety of tests by OSHA and other organizations, OSHA has established safe 8-h exposure levels of 50 ppm for TCE and 25 ppm for PCE. When CFC and TCA replaced TCE and PCE as vapor degreasing solvents, the permissible exposure limits for CFC and TCA were set at 350 ppm. In other words, the ODC are seen as being less toxic to workers than either TCE and PCE.

The new aqueous degreasing materials have exposure limits that are, for the most part, higher than those for the ODC or VOC materials. The routes of exposure for ODC and VOC materials are inhalation, ingestion, and adsorption. For aqueous materials, inhalation is generally not an issue, and thus the primary routes of entry are limited to ingestion and adsorption. For these reasons, the aqueous degreasers are generally considered to be safer to work with than the ODC and VOC materials.

**The Superfund Amendments and Reauthorization Act** (SARA), enacted in 1986, deals with communities' "right-to-know." The right-to-know encompasses everything from where a toxic waste site may be located to what type and how much of certain chemicals are being used and/or stored at manufacturing facilities in the area that could cause problems should they be released into the environment.

The ODC and VOC materials used for vapor degreasing are on the list of chemicals that must be reported to the state in order to comply with the right-to-know law. Most materials used for aqueous degreasing do not appear on this list and have no reporting requirements.

**The Resource Conservation and Recovery Act** (RCRA) of 1976 requires that hazardous waste be disposed of in a manner that will not cause any adverse environmental or health effects. The RCRA also established that industrial manufacturers and processors must have plans for hazardous waste and solid waste management. Recycling of materials plays an important part in these plans.

Aqueous degreasing techniques offer the potential for easier and less expensive recycling as compared to vapor degreasing. In addition, the waste generated by aqueous degreasing does not cause the adverse environmental and health effects associated with VOC and ODC waste.

## Aqueous Systems

Aqueous degreasing can be accomplished by hot tank or dip tank systems. Ultrasonic cleaning and spray cleaning are system options.

### *Hot Tank Systems*

Heated, aqueous degreasing systems have been designed to replace vapor degreasers of various capacities. The equipment and processes described in this section have successfully replaced vapor degreasers in many applications within the aerospace industry, primarily to remove forming lubricants from detail parts prior to heat treatment, inspection, or finishing operations.

**Advantages.** The main advantage to these aqueous systems is that they are in regulatory compliance for air emissions. These systems are generally safer to operate and maintain than those using vaporized chlorinated solvents. They can remove many hydrocarbon-based oils, salts, and water-based materials. Treatment of spent aqueous solutions and rinse water can also often be accomplished on site.

**Disadvantages.** These systems generally require wash, rinse, and dry stages as a minimum. This often means that additional floor space is required as a vapor degreaser provides a clean, dry part using a single tank. Some utilities costs may be higher because heat must be provided to at least two liquid tanks and sometimes to a forced-air drier. More attention must be paid to racking considerations in an aqueous process because more space for solution flow is needed around the part surface. Process cycle times for aqueous degreasing are several times longer than for vapor degreasing due to the multiple steps required.

**Equipment / Materials.** In general, at least two tanks will be required: one to contain the wash solution and at least one to contain the rinse water. Additional rinse stages will significantly reduce water usage, but this advantage must be weighed against the additional capital cost and floor space required. The preferred material of construction for these tanks is stainless steel. Cost, compatibility with the cleaning solution, and life expectancy of the tanks are considerations when specifying tank material. When retrofitting a vapor degreaser tank with sufficient freeboard, a fresh water spray rinse or mist above the immersion wash or rinse tanks can improve rinsing, reduce overall water usage, and compensate for evaporative losses from the immersion tank(s).

Agitation of the fresh and rinse solutions is required. The flow of fresh solution past the part surface aids in cleaning and rinsing. A solution-recirculation system powered by centrifugal pumps is commonly used. The pumps are protected by a strainer and followed by cartridge or bag filters. These pumps deliver solution to a manifold that feeds an array of nozzles located near the tank walls. These nozzles should be oriented to maximize solution flow past the parts. Air sparging is not acceptable with many aqueous solutions due to the potential for foaming. When air sparging is used on the first (dirty) rinse stage, unacceptable levels of foaming may also be observed. This is due to carryover of soap solution. If agitation is vigorous, cleaning can also be enhanced by the mechanical scrubbing effect of the impinging fluid. This is often difficult to achieve in large tanks. Ultrasonic agitation also may be impractical on these larger systems, although the feasibility of using ultrasonic equipment ultimately depends on part geometry, economic factors, and other application requirements. Controllers should be used to maintain a constant temperature within the tank to ensure uniform cleaning.

Level controllers can be used in both the wash and rinse stages to add fresh water automatically to make up for evaporative losses. A conductivity meter can also be used to determine when the rinse needs to be freshened due to soap carryover. If the cleaning solution will foam, the pipe providing this make-up water should feed into the tank at a point below the surface to prevent foaming due to air entrainment and splashing. This should also be considered in the plumbing layout of the wash tank drainage system. A free fall of degreasing solution into a waste holding tank can quickly fill the tank with foam and create a severe maintenance problem. Electrically isolating the parts or basket from the tank walls may be required to prevent galvanic corrosion resulting from the formation of an electrolytic cell within the wash tank.

If parts must be dry and ambient evaporation rates are unacceptable, a forced-air drier may be required. High volumes of heated air are used. Flow rates and temperatures can be as high as practical while preventing part damage. The material handling system will probably have to disengage from the parts basket to allow for an airtight seal to improve drying and to minimize humidity in the shop area. High-pressure air (air knives) can be used to blow the water off the parts. These are most useful if the part and basket geometry allows the air knife apertures to get consistently within a few inches of the parts. The noise generated by these air knives should be considered if their use is intended.

**Process Description.** Parts are washed, rinsed, and dried conventionally. First, the parts must be placed in the basket or rack that supports and moves the work through the various processing stages. More spacing between parts is often required when racking for an aqueous process than with a vapor degreaser due to the greater reliance on liquid flow past the part surface. More consideration must also be given to part movement and/or part flotation when racking, due to the large increase in density of the cleaning medium. Special racking schemes or agitation systems may also be required for parts with hidden surfaces such as tubing. Tumblers or rotating baskets sometimes improve cleaning for small parts. When the load is racked for processing, the cleaning cycle is initiated. An automated material-handling system can be incorporated to move the basket through the wash, rinse, and dry stages, thus allowing the operator to perform other activities such as loading or unloading another basket.

The primary variables affecting cleaning performance in the wash stage are the solution temperature and concentration, the immersion time, the thickness and composition of the soil layer to be removed, and the level of agitation. Agitation is an especially important factor.

Higher temperatures generally result in better cleaning. Sometimes the bulk melting point of a paste or grease must be achieved for good cleaning. Temperatures above 65 to 70 °C (150 to 160 °F) can cause excessive wear of equipment, however, and increase the possibility of drying the soap solution onto the parts while transferring to the rinse stage(s).

The chemical supplier recommendations and engineering requirements developed through testing will help determine the concentration of soap required in the wash stage. This can vary between 3 and 20% by volume. Although higher concentration may improve cleaning, it will also result in more burden on the rinse stage and on waste treatment. Titration methods are often used to determine the soap concentration, and incremental additions of concentrated soap are often used to maintain the bath at its concentration set point. Eventually (after 3 to 12 mo), spent baths must be dumped and replaced with fresh solutions due to the buildup of emulsified oils and general degradation of the bath effectiveness. Cleaning performance of previous baths under similar conditions is often the best indicator for predicting bath life.

Immersion times of 15 to 30 min in the wash stage are standard. Increasing the wash stage time beyond this adds little in terms of cleaning benefits and often results in a cleaning cycle that is too long.

Agitation levels are usually fixed once the equipment is installed but should be designed to achieve solution flow rates as high as practical while considering issues such as equipment and utility costs, solution foaming, and part damage.

An often overlooked factor in improving cleaning performance is the soil that must be removed. Parts are sometimes grossly overcontaminated during prior operations and improved performance can often be achieved by reducing the amount of soil to be removed. In some cases, it is possible to eliminate a superfluous cleaning step entirely. Replacement of a hard-to-clean lubricant is another approach. The use of specific forming lubricants in many shops has evolved over the years in part because of the presence of the vapor degreaser. Lubricants that were compatible with the vapor degreaser solvents were preferred over water-based products that would not clean or that promoted acid formation within the solvent. For many applications, an aqueous cleanable lubricant can be just as successful in the upstream operation as the vapor degreasable one was.

After washing is complete, the basket is moved to the rinse stage(s). If soap drying onto the parts is a problem, a fine mist of warm fresh water or rinse water directed at the parts above the wash stage may be helpful. The parts are immersed in the rinse stage(s) for at least 5 min. Multiple rinse stages help conserve water but require more floor space and utilities. If a final spray rinse of fresh water is available above the immersion rinse stage, this should also be utilized. Temperatures above 65 °C (150 °F) can cause excessive wear on equipment and can produce mineral deposits on the tank walls.

After rinsing is complete, the basket is moved to the forced-air drier. Drying time will depend on the design of the system and the amount of parts and water going in. Parts with geometries that trap solution may need to be tilted or blown off with air knives to dry. Fifteen minutes is a reasonable length of time for a drying cycle.

Parts are generally unracked after the wash, rinse, and dry steps are complete. If parts are to be re-racked for the next operation (i.e., heat treatment), consideration may be given to a common rack that could be used by both operations. This could allow the elimination of a racking and unracking step.

**Regeneration** of aqueous cleaners is performed by removing the soils or contaminants (oils) from the cleaning solution. Oils that float to the surface of a wash tank can often be removed by manual or automatic skimming. Parts being pulled up through a floating oil or foam patch run the risk of having the soil redeposited. Agitation systems can be designed to create a surface flow that propels these floaters over a knife-edged weir. The weir can feed a more sophisticated device such as a coalescer, centrifuge, or ultrafilter to effect a more complete separation. The oil can be captured and the cleaner returned to the bath. Pumps used in conjunction with these systems should be of a low shear type design (i.e., diaphragm pumps) to minimize mixing of the oil and cleaner. Emulsifying-type cleaners are more difficult to regenerate using equipment than surfactant-type cleaners. Aqueous cleaners that strongly emulsify the soils often require nothing more elaborate than the cartridge filtration mentioned in the "Equipment/Materials" section above. When the bath becomes saturated with soils, cleaning performance will become unacceptable and dumping the spent bath and replacing it with fresh solution will be required.

**Maintenance.** Equipment should be designed with maintainability in mind. Pumps should be protected by strainers. They should have valves on either side for isolating. Pumps and motors should be easy to access and replace. Seals, pumps, piping, and other components should be compatible with the temperatures and chemistries of the solutions. Heat exchangers should also be accessible for replacement in the event of failure. Temperature, level, and conductivity sensors should be located in the body of the tank and should be easily accessible. Regeneration equipment should be easy to maintain, or it runs the risk of being turned off.

**Example.** A 1,1,1-trichloroethane vapor degreaser was being used to degrease detail aluminum aircraft parts prior to air furnace heat treatment. These parts are contaminated with forming lubricants from blanking and brake press operations. The original tank was 8 m (27 ft) long, 1.5 m (5 ft) wide, and 8 m (27 ft) deep. Very few of the parts going through this system were more than 3.5 m (12 ft) long, and other larger degreasing systems were available within the same building. To retrofit this vapor degreaser to an aqueous system, the tank was modified with the addition of a dividing wall down the center. This structural wall created two 4 m (13.5 ft) long, 1.5 m (5 ft) wide by 8 m (27 ft) deep tanks. Tanks were also modified by adding recirculating agitation systems as described above. Additional heating capacity was required, which was added via steam heat exchangers in the recirculation system. Heat transfer through the dividing wall was found to limit the maximum temperature difference achievable between these two tanks to about -12 °C (10 °F).

A steam-heated, forced-air drier was placed at the factory-floor level adjacent to the tanks and within reach of the overhead crane. A drying cart was used to allow the parts basket to be side loaded into the dryer after being disengaged from the crane. The parts basket and overhead crane system was modified for the smaller working envelope. Multiple-parts baskets and racks are available that are compatible with the adjacent heat-treat furnace material handling system. One load can be processed through the wash and rinse stages, while another is in the drier.

### *Dip Tank Systems*

Dip tank cleaning systems are effective for many applications. Part configuration is a factor: the shape of the part must allow excess cleaning fluid and rinse water to drain away when the parts are removed from the tank. If these fluids do not drain away properly, it could lead to corrosion of ferrous metals and excessive depletion of the cleaning chemical from the wash tank. The proper racking of parts will help to eliminate this possibility.

Arrangement of parts in the dip basket is very important. The parts should not overlap and there should be space between each part to allow the cleaning solution to circulate. The most common reason for unsatisfactory results is failing to follow these requirements.

**Ultrasonic dip tank methods** are mostly used for small parts on a relatively small scale because the equipment is very expensive. This method is able to remove much heavier contamination than a simple dip tank can accomplish. Ultrasonic cleaning is also effective where partially hidden recesses (i.e., blind holes) are present in the part configuration.

It must be pointed out that an ultrasonic tank that has been configured for solvent cleaning is not suitable for aqueous cleaning. The sonic frequencies need to be changed from 25 to 40 kHz or higher for aqueous cleaning. Once the frequency (transducer) modification has been made, meaningful cleaning evaluations can proceed. Additional information on ultrasonic cleaning and equipment is available in the article "Ultrasonic Cleaning" in this Volume.

**Spray washer methods** are recommended when production requires very high throughput, or when parts have irregular surfaces. This method will remove very heavy oils and greases and other contaminants.

**Contaminant Removal.** After being removed from the parts, some oil and grease will end up floating (because they are lighter than water) in the wash tank. These contaminants must be removed from the wash tank so that they do not interfere with the efficiency of the cleaning solution.

***Skimming*** is the most practical method for removing these contaminants. Devices for this purpose are readily available from industrial supply companies. They feature an oil attractive surface that rejects water; the oil is removed from the skimming surface by wiper blades and is collected for disposal.

***Ultrafiltration*** may be a viable option for large tank systems. A great deal of experimentation has taken place involving ultrafiltration of aqueous cleaning chemicals. It has been found that with either polymeric or ceramic membranes, a filter pore size of 0.3 to 0.5 μm with a 500,000 molecular weight cutoff is the most efficient at removing oil, grease, and other contaminants while still allowing the cleaning chemical and the water to pass through. Ultrafiltration equipment is very expensive, but it can be cost effective in situations where waste disposal is severely restricted.

**Cleaning tank maintenance** is an important consideration. It must be remembered that the major losses from the cleaning tank will be water due to evaporation. Actual cleaning chemical losses will depend on part configurations and their effect on dragout (process chemical loss).

With all aqueous cleaning methods, maintenance of recommended solution concentrations is very important. The manufacturer of the process chemical is best able to provide the methods for maintaining process chemical concentrations.

**Rinse Water Quality.** The quality of the rinse water has a significant impact on the cleanliness of the part. Tap water will effectively rinse a surface but often will leave a residue that has nothing to do with the cleaner used. The type of rinse water that should be used depends on the cleanliness requirements of the part. Those with strict requirements should be rinsed with the highest quality water, namely distilled water. Next cleanest is deionized water, then soft water (water treated with Zeolite resin), and finally tap water.

## Converting an Existing Vapor Degreaser

Converting an existing vapor degreaser to an aqueous cleaning system can enhance the cleaning process and costs less than purchasing entirely new equipment. Figure 1 is a schematic drawing of a vapor degreasing system converted for aqueous cleaning; see the article "Solvent Cold Cleaning and Vapor Degreasing" in this Volume for schematics of conventional vapor degreasers. In some cases, only minimal modifications are needed. Depending on thickness of tank walls, reinforcement may be required to accommodate the increased weight and volume of cleaner in the tank. The refrigerant freeboard coils can be disconnected because they will no longer be required.

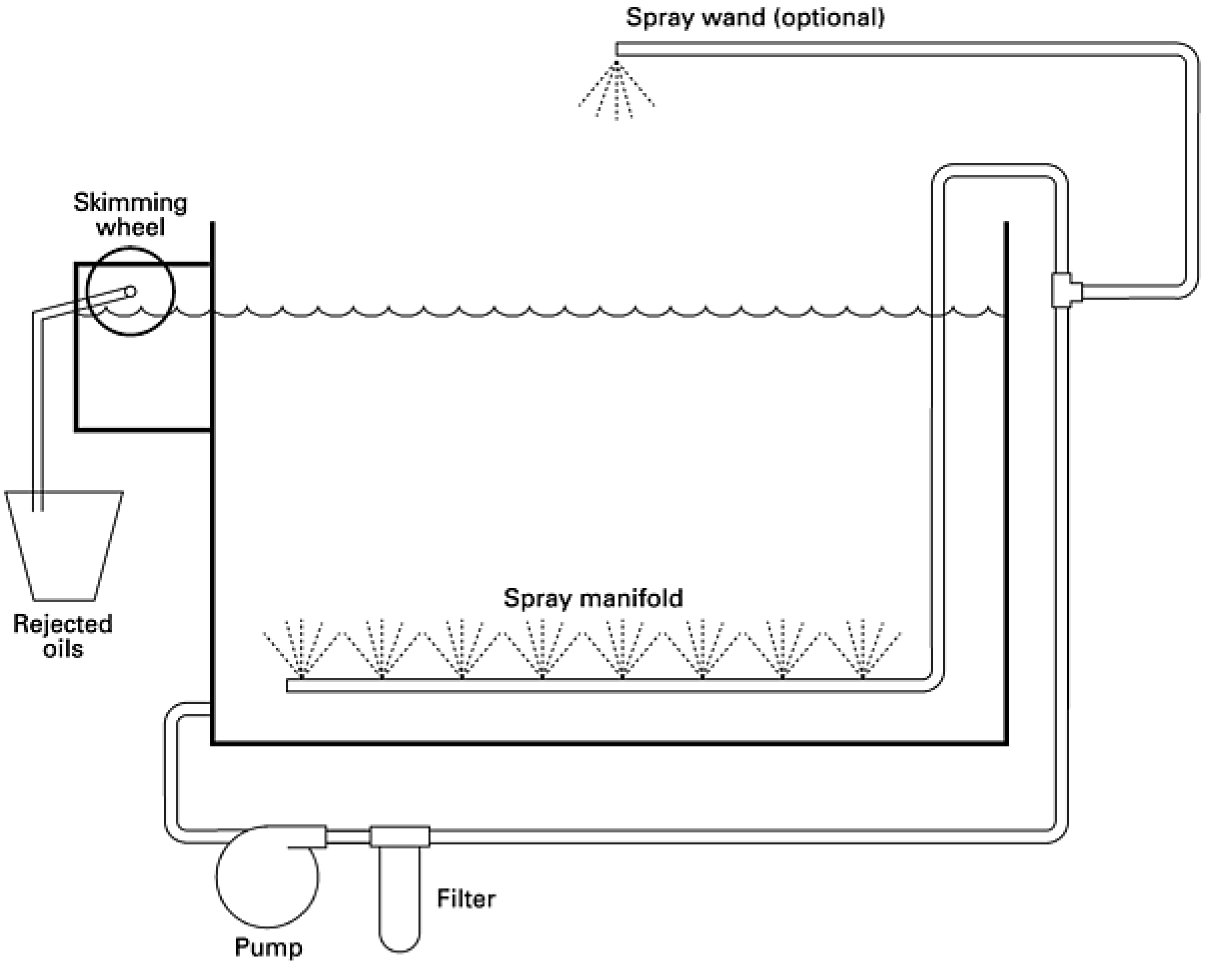

**Fig. 1 Schematic of a vapor degreasing system converted for aqueous cleaning**

A circulation system will be needed for effective aqueous cleaning. This can consist of a circulation pump and spray manifolds (under solution level), a "lightening" tank mixer, air sparging (not recommended for some alkaline cleaners, which can foam), and even ultrasonic agitation. If the degreaser has a hand spray wand, this can still be used for more aggressive cleaning (again, this would not be recommended for some alkaline cleaners, which can foam).

For alkaline cleaners that reject oils (as opposed to emulsification-type cleaners), some type of oil removal device will be necessary. There are several options available to accomplish this. Skimming devices such as belts or wheels work well. Coalescers, separation tanks, and microfiltration are also effective at removing oils.

Filtering is another option for prolonging the life of the cleaner. Filter media such as fabric and paper cartridges, bags, or ceramic can be used. Selection of proper filter size depends on the molecular size of the contaminants and the molecular size of the cleaning agent ingredients.

A series of rinse tanks to remove the cleaner will need to be added to the cleaning area as well as some type of drying device to remove the rinse water from the workpieces.

## Advanced Vapor Degreasing Systems

Another option to traditional vapor degreasing is the so-called advanced vapor degreasing system (Fig. 2). This system is quite different from a conventional vapor degreaser. Instead of using a single vapor degreasing step, the advanced vapor degreaser is a three-stage system involving the use of a solvating chemical (aliphatic esters), a rinsing agent (perfluoro hexane), and a vapor rinse.

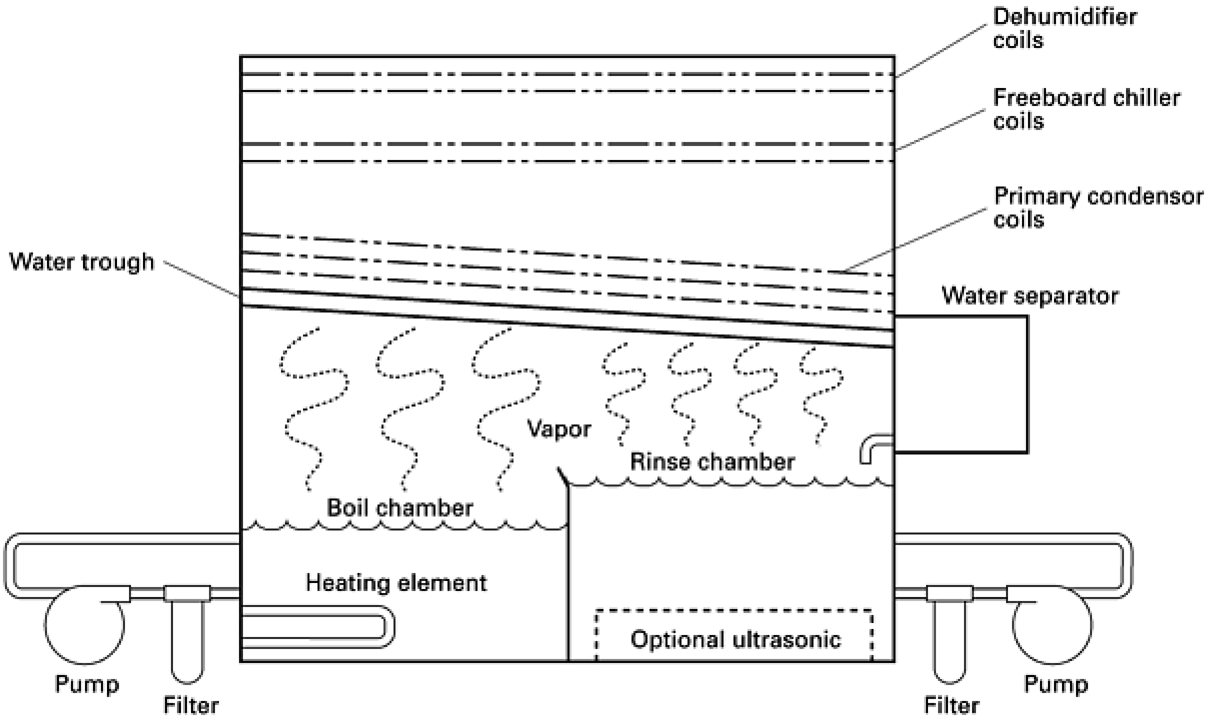

**Fig. 2** Schematic of an advanced vapor degreasing system

Equipment for an advanced vapor degreasing system consists of a boil chamber containing a solvating chemical, a rinse chamber containing the rinsing agent, a pump and filter system for both chambers, primary condenser coils, freeboard chiller coils, dehumidifier coils, a water separator, and a freon compressor. Some systems include an optional ultrasonic unit.

The boil chamber generates vapors that rise to the point where the primary condenser coils suppress the vapor column. Distillate generated from this vapor rinse is collected through a trough system and then funneled into a water separator and finally into the rinse chamber. The added rinse solution from this process overflows into the boil chamber (which is already combined with the solvating agent), completing the process cycle.

Parts to be cleaned are first immersed into the boiling solvating chemical/rinse agent mixture. They are then immersed into the rinse agent, which displaces the remaining solvating chemical; the use of an ultrasonic unit at this stage enhances the removal of solvating chemical. Finally, the parts are raised into the vapor column where they are rinsed with condensate vapor and then dried.

## Compliant Organic Coatings

**Thomas E. Kearney, Courtaulds Aerospace**

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## Introduction

THE FEDERAL CLEAN AIR ACT requires the Environmental Protection Agency (EPA) to establish a set of health-related standards for air pollutants. One of these pollutants is ozone, which is the primary component of the condition known as smog. Because smog is caused in part by the photochemical oxidation of solvent vapors from coating application sources, this regulation has had a profound impact on how coatings are formulated and applied. A whole new class of products has been developed, compliant coatings, that contain lower amounts of organic solvents. This article discusses the compliant coating products available for use in the aerospace industry, including their characteristics and their limitations compared to conventional noncompliant materials.

As of this writing, the use of compliant coatings is not universally required. The National Ambient Air Quality Standard defines the maximum amount of ozone that can be present in an area in order to maintain the air quality required. States with nonattainment regions (regions where the amount of ozone exceeds the maximum) are required to develop a state implementation plan (SIP) that demonstrates how the state will achieve the standard. A SIP usually requires the use of compliant coatings. In attainment areas (regions that meet the air quality standard), compliant coatings are not required. However, the EPA is currently developing control technique guidelines for the aerospace industry that will standardize these organic emission regulations across regions.

## Rule 1124

The most stringent regulations within the United States have been implemented by California because of its severe air quality problems. The South Coast Air Quality Management District (SCAQMD) has issued a regulation, Rule 1124, that generally has been the bellwether document for the aerospace industry. As a result, coatings suppliers have concentrated on developing products to meet this rule. Its method of control is to designate the maximum allowable specific weight of volatile organic compounds (VOCs) per unit volume of material. In Rule 1124 the limits are expressed in grams per liter; other regulations may use pounds per gallon. Following are the definitions used in this rule:

- *Primer* is applied directly to an aerospace component for the purposes of corrosion prevention, protection from the environment, functional fluid resistance, and/or adhesion of subsequent coatings.
- *Topcoat* is applied over a primer for purposes such as improved appearance, identification, or maximum corrosion protection of exterior surfaces.
- *Flight test coating* is applied to an aircraft or missile prior to flight testing to protect the aircraft from corrosion and provide required marking during flight test evaluation.
- *Impact-resistant coating* protects aerospace components such as aircraft landing gear, landing gear components, and other surfaces subject to erosion, abrasion, or impact from runway debris.
- *Maskant for chemical milling* is applied directly to an aerospace component during chemical milling of that component.
- *Fuel tank coating* is applied to the interior of integral fuel cells of an aircraft to protect it from corrosion and/or bacterial growth.

Table 1 presents the Rule 1124 requirements in condensed form. It includes the products that require, or will require in the near future, substantially reduced VOC contents. The bulk of VOC emissions from the aerospace industry are from primers, topcoats, and chemical milling maskants. This paper addresses the methods most commonly used to bring these products into compliance: waterborne coatings, exempt-solvent-based coatings, high-solids coatings, powder coating, and electrodeposition, along with the application equipment used.

**Table 1 Maximum allowable volatile organic compound contents**

| **Coating** | **Pre-1985** | **Current** | **As of 1 Jan 1996** |
|---|---|---|---|
| Primer | 650 | 350 | 350 |
| Topcoat | 600 | 420 | 420 |
| Flight test coating used on missiles or single-use aircraft | 840 | 420 | 420 |
| Impact-resistant coating | 600 | 420 | 420 |
| Maskant for chemical milling | 1200 | 250 | 250 |

|  |  |  |  |
|---|---|---|---|
| Fuel tank coating | 720 | 720 | 420 |

Note: All values are given in grams per liter of coating.

## Waterborne Coatings

Water can be used in organic coatings to form either emulsions or solutions. However, polymers that can be solubilized in water usually form films with poor moisture resistance, which makes them unsuitable for aerospace environments. The most successful approach has been to use emulsions in which water is the major carrier but is not a solvent for the resins in the coating. These materials are not free from VOC, however. Some organic solvents must be included to control evaporation and flow and to provide film coalescence.

The VOC content in waterborne coatings is determined on a basis that excludes water from the calculation:

$$g/L = \frac{W_s - W_w}{V_m - V_w}$$

where g/L is the grams of VOC per liter of coating, $W_s$ is the weight of VOC in grams, $W_w$ is the weight of water in grams, $V_m$ is the volume of material in liters, and $V_w$ is the volume of water in liters.

**Waterborne Primers.** The compliant waterborne primers used in the aerospace industry have been based on epoxy resins and polyamine or polyamide curing agents. There are two approaches to formulating these primers. One is to supply the product as an emulsion that can be mixed and applied in a manner similar to that used for solvent-based primers. The second method is to provide a very-high-solids material that can be dispersed in water to form an emulsion just prior to application. A pre-emulsified product is easier for the user to handle, but the water-reducible high-solids material may be preferred for its shipping and storage properties.

Following are some of the characteristics of waterborne primers:

- These products require a scrupulously clean substrate for proper adhesion. They are not forgiving of imperfect surface preparation.
- Drying time can be substantially slower when humidity is high. Drying can be assisted by increasing the air flow across the wet primer.
- Surfactants and water-miscible cosolvents may cause water sensitivity if the primer is exposed to harsh environments before it is completely cured.
- When a waterborne primer is supplied as an emulsion, viscosity may be substantially higher than with a solvent-based primer. However, this is a false body and the applied film will be smooth and uniform.
- The higher density of water, compared to that in most organic solvents, results in less overspray and improves transfer efficiency. (Transfer efficiency is discussed in the section "Application Equipment" in this article.)

Primers supplied for military and commercial applications differ in that the latter must be resistant to the phosphate ester hydraulic fluid used in these aircraft. The densely cross-linked surface that is usually required for resistance to phosphate esters is difficult to achieve with an emulsion, so these products have been primarily used for military aircraft. The specification for military aircraft primers is MIL-P-85582. However, products have recently been developed that will meet some commercial requirements for phosphate ester resistance. Boeing Aircraft Company has qualified a waterborne product to their specification BMS10-11 for commercial use, which requires phosphate ester resistance.

Implementation of waterborne epoxy primers has been successful. In general, their adhesion properties, corrosion protection, and service life have been comparable to those of conventional solvent-based materials.

**Waterborne Topcoats.** To date, waterborne topcoats have been limited to single-package emulsions, which are most often used as replacements for solvent-based lacquers. However, one manufacturer has developed a two-package aliphatic urethane resin system that shows promise. Coatings made with this material are now under evaluation.

**Waterborne Chemical Milling Maskant.** In chemical milling, metal is removed by chemical etching rather than by mechanical methods. The maskant is a coating of any kind that defines which areas on the part are to remain unetched (it protects those areas from the action of the etchant). Chemical mill masking has historically been the largest contributor of VOC emissions in the aerospace industry. The solvents used have been toluene, a combination of aromatic solvents, and more recently perchloroethylene. Perchloroethylene is attractive because it has been classified as an exempt solvent in many states. However, it is being considered for reclassification as an air toxin, which would restrict its use.

Prior to July 1993, the VOC emissions limit for chemical milling maskant in Rule 1124 was 1200 g/L (10 lb/gal). The current regulation is 250 g/L (2 lb/gal). This VOC reduction can be achieved by collecting solvent emissions with air pollution control equipment, such as carbon absorption beds, or by using water-based products.

Water-based chemical milling maskants have been available for several years. Two approaches have been used.

***The anode dipping process*** takes its name from the fact that the emulsified particles are attracted to the part to be masked in much the same way that metallic ions are attracted to the anode in electroplating. It is similar to the method used to produce rubber latex gloves. The part to be masked is immersed in a solution of a multivalent salt. After flashoff, the part is dipped into a bath of a latex rubber. The salt on the surface causes the latex to coagulate on the part to an even film thickness of 200 to 250 μm (8 to 10 mils). This must be cured at a low bake (85 to 90 °C, or 190 to 200 °F) for about 1 h. As the water leaves the film, some porosity may remain, and usually a third dip in a seal coat is required. This process provides excellent edge protection and an even film over the part. It also lends itself very well to automation because all parts, regardless of size, can be handled in the same manner. The disadvantage is that it is a three-tank process that requires extra floor space and substantial expenditure on capital equipment.

***The single tank method*** uses a chemically resistant emulsion polymer, formulated with fillers and additives to control the film thickness and adhesion properties. Multiple dips are usually required to achieve the necessary film thickness. The parts are rotated between dips to eliminate variation in film thickness from top to bottom ("wedging"). A bake between coats and after completion is required. The single-tank process can usually be installed in the existing facility, and shop personnel may adapt to it more easily because it more closely approximates the procedure for solvent-based material. The disadvantages are that it may be difficult to achieve coverage on edges and complex parts, and that a longer force-dry at lower temperatures is usually required to avoid entrapment of water.

In both processes, the emulsion bath should be closely monitored to control tank stability. The viscosity and pH should be checked at least weekly.

## Exempt-Solvent-Based Coatings

Exempt solvents are a class of organic materials that are nonphotochemically reactive and therefore are not precursors to the formation of ozone. Chemically, these are chlorinated hydrocarbons and chlorofluorocarbons (CFCs). The exempt solvents that have been most commonly used in coating formulations are 1,1,1-trichloroethane (TCA, also known as methyl chloroform) and methylene chloride.

Although these compounds are not smog producers, they have been shown to deplete the ozone layer in the upper atmosphere. Therefore, their use will be restricted in the future. The SCAQMD has established a policy to phase out CFCs on or before December 31, 1995. The Montreal protocol, to which the United States is a signatory, is an international agreement that requires the use of ozone-depleting compounds to be discontinued by the year 2000. However, because these products are still widely used in compliant coating formulations, they may be used for a year or two more, and they are included in this discussion.

The calculation for determining the VOC content of exempt-solvent-based materials is similar to that used for waterborne coatings:

$$g / L(VOC \text{ less exempt}) = \frac{W_s - W_{es}}{V_m - V_{es}}$$

where g/L (VOC less exempt) is the grams of VOC per liter of coating, less exempt compounds, $W_s$ is the weight of the nonexempt volatile compound in grams, $W_{es}$ is the weight of the exempt compound in grams, $V_m$ is the volume of material in liters, and $V_{es}$ is the volume of the exempt compound in liters.

**Exempt-Solvent-Based Primers.** TCA is the exempt solvent that is most generally used in primers. It is compatible with most organic resins, but it has a lower solubility parameter and a faster evaporation rate than other solvents used in formulating aerospace materials. TCA has been successfully used to formulate epoxy primers for both the military and commercial markets. The military specification is MIL-P-23377F, Class 3. The commercial specifications include Boeing Aircraft BMS10-11; McDonnell Douglas DMS2104, Composition B; and Gulfstream GMS5004. TCA has been popular because it requires no modification of existing procedures or equipment.

Following are some characteristics of exempt-solvent-based primers:

- These products have a tendency to dry spray because of the fast evaporation rate. Additional TCA may be required to ensure a sufficiently wet film.
- The commercially available TCA usually contains 3 to 5% of a stabilizer to prevent the formation of corrosive chloride compounds. This stabilizer is classified as a VOC.
- Because of the high density of chlorinated solvents, there tends to be less overspray than with conventional primers.
- Care must be taken to avoid the use of aluminum pressure vessels with these primers. A violent reaction with aluminum can occur under some circumstances.

**Exempt-Solvent-Based Topcoats.** There are no exempt-solvent-based topcoats currently in use in the aerospace industry. Until recently, Grumman Aerospace had a specification in use (GM4209) that was based on this technology, but this material has been discontinued because of the restrictions on the use of chlorinated solvents.

## High-Solids Coatings

Coatings may be made compliant simply by reducing the amount of organic solvent in the formula. However, to produce the high-performance epoxies and urethanes required for the aerospace industry at a sprayable viscosity, suppliers must use much lower-molecular-weight resins and curing agents than in the past. These are typically liquid resins, and the drying time is strongly dependent on the cross-linking rate and the buildup in molecular weight. The result is a much longer tack-free time than with conventional noncompliant materials. In addition, this reaction causes the molecular weight to increase, which increases the viscosity and shortens the usable work life. In spite of these difficulties, coating suppliers have been able to produce materials that meet the needs of the industry.

**High-Solids Primers.** High-solids primers have proven to be a viable alternative to waterborne primers and exempt-solvent-based primers for achieving VOC compliance. They are usually low-molecular-weight epoxies reacted with low-viscosity polyamides or polyamines. These primers have a VOC content of 340 g/L or less.

Following are some of the characteristics of high-solids primers:

- These products normally require up to 4 h of drying before topcoating and 12 h or more to dry hard.
- The usable pot life is 4 h or less because of the comparatively rapid buildup in viscosity.
- Care must be taken to avoid applying a wet film that is overly heavy. Higher solids cause the film thickness to increase very quickly.

Compared to waterborne primers, high-solids primers offer:

- Better chemical and fluid resistance
- Less sensitivity to surface contamination
- Better compatibility with high-solids topcoats

The military specification for high-solids aerospace primers is MIL-P-23377F, Class 2. Commercial high-solids primer candidates are now in the qualification phase.

**High-Solids Urethane Topcoats.** High-solids has been the method most often selected for meeting the VOC requirements for topcoats. Development in this area has been concentrated primarily on aliphatic urethanes. Coatings formulated with these materials have the desirable properties of weatherability, durability, and flexibility. Low-molecular-weight polyesters and acrylics have become generally available that can be cross-linked with aliphatic isocyanate prepolymers to form urethanes. For instances where the use of isocyanates is limited, or greater chemical or fluid resistance is required, topcoats have been formulated with an epoxy resin base.

The low-molecular-weight components necessary to achieve a sprayable viscosity present difficulties similar to those experienced with high-solids primers. The drying time is again related to the increase in molecular weight, and there is a tradeoff between drying time and usable work life. Formulators attempt to balance these properties by using catalysts for the isocyanate-hydroxyl reaction. Increasing the amount of catalyst shortens the tack-free time but also results in a more rapid increase in viscosity. Conversely, less catalyst means a longer drying time and a longer pot life. Depending on the needs of the user, a satisfactory compromise of properties usually can be achieved.

Following are some of the characteristics of high-solids urethanes:

- Complete drying may require 8 to 12 h or more. However, a second coat, if required, can be applied after the film takes on an initial set, and most of the solvent is released in about 2 h.
- The usable pot life is typically 4 h or less.
- Hot humid weather may result in blistering or "solvent pop" if the film thickness is not properly controlled. Under colder conditions there may be a greater tendency to sag or run.

The specification covering high-solids urethanes for military applications is MIL-C-85285. Type I is 420 g/L (3.5 lb/gal) for aircraft applications, and type II is 340 g/L (2.8 lb/gal) for ground support equipment. An example of a commercial high-solids specification is BMS10-60 TY II, Grade B, which has a maximum VOC content of 420 g/L (3.5 lb/gal).

**High-Solids Self-Priming Urethane Topcoat.** The self-priming topcoat was developed by the Naval Air Warfare Center. The specification is TT-P-2756. The self-priming topcoat combines the functions of a primer and those of a topcoat into a single product that is environmentally compliant. In addition, the corrosion inhibitors incorporated in the formula are chromate-free. This product, commonly known as Unicoat, has been in use for several years at Navy and Air Force depots. In general, its performance has been satisfactory; it works best when applied over a chromated conversion coating such as MIL-C-5541. The use of self-priming topcoats should be avoided if the aircraft will be exposed to harsh environmental conditions over a long period of time.

**High-Solids Epoxy Topcoats.** The use of epoxy topcoats is indicated when exposure to ultraviolet light is not a factor and good fluid resistance is required, as in the interior of commercial aircraft. Sample specifications are Boeing Aircraft BMS10-11, type II or McDonnell Douglas DPM110. These products have a VOC content of 420 g/L (3.5 lb/gal). The Navy has issued a specification MIL-C-22750E for a high-solids epoxy that can be used where the use of urethanes is restricted, as on shipboard. This specification requires a VOC content of 340 g/L (2.8 lb/gal). These epoxy topcoats have the short pot life and longer drying time of most high-solids materials.

## Powder Coatings

Powder coatings are not yet in general use in the aerospace industry, but there is a great deal of interest because of the benefits they offer in terms of VOC content reduction and efficiency of application. Further development may overcome some of the limitations of these coatings. As the name implies, these coatings are applied as powder to a given surface. The solid ingredients, resin pigments, extenders, and so forth are melted together to produce a completely homogenous plastic mass. This is cooled to room temperature and ground to a powder.

The powders that have been considered for use in the aerospace industry are thermoset, meaning that the components react at elevated temperatures to form a cured film. The powder is applied electrostatically (i.e., the electrically charged particles are sprayed on the part to be coated, which is grounded) and is held in place by electrostatic attraction. The coating is then fused together and cured at temperatures from 135 to 200 °C (275 to 400 °F). The types of thermoset powders available fall into the general categories of epoxies, polyesters, polyurethanes, and acrylics. Many of the aerospace applications are on aluminum or aluminum-alloy substrates, which are sensitive to changes in strength properties when exposed to high temperatures. For this reason the principal types used have been epoxy-resin-based materials that can be cured at temperatures as low as 120 °C (250 °F). Powders based on other polymers usually require temperatures of 175 to 200 °C (350 to 400 °F) to achieve optimum properties.

The advantages of powder coatings are that no VOCs are present, up to 98% of the powder can be deposited on the part, application is easy, and minimal rework is required. The disadvantages for aerospace applications are that powder coatings cannot be used on assemblies or aircraft exteriors that cannot be heated, and that epoxy-resin-based products have poor ultraviolet stability and so cannot be used on exterior surfaces.

## Electrodeposition

Electrodeposition (electrocoating) is similar to electroplating but deposits organic materials rather than metal ions. It uses the principle of *electrophoresis*, the movement of charged suspended particles under the influence of an applied voltage. This process may be either *anodic*, in which the anode is the coated part, or *cathodic*, in which the organic coating is deposited on the cathode (Fig. 1). Because of problems associated with coating-substrate interaction in anodic systems, the cathodic process is chosen for aerospace applications. The types of materials deposited by electrocoating are epoxies, acrylics, or polyesters cross-linked with melamines or blocked isocyanates. A bake of 135 to 230 °C (275 to 450 °F) is required to cure the deposited film.

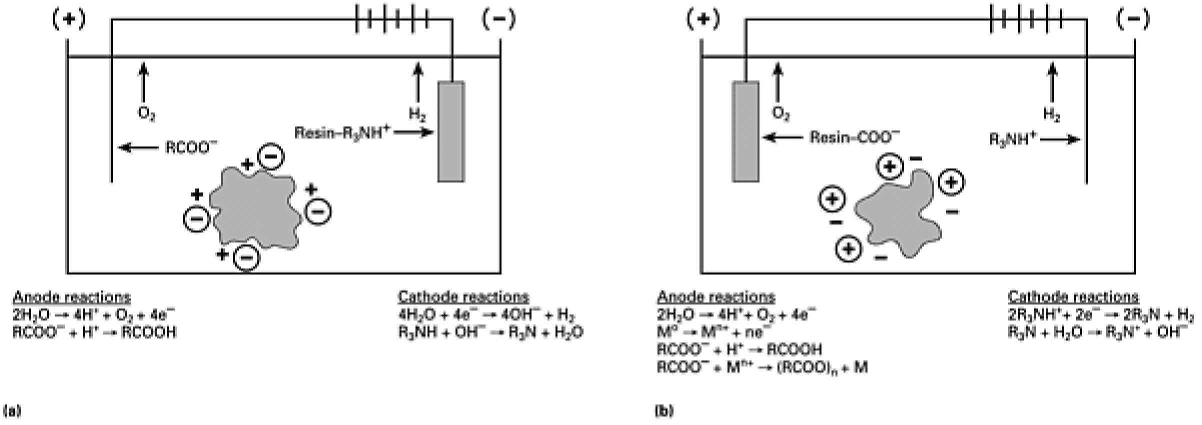

**Fig. 1 Electrodeposition process. (a) Cathodic deposition (resin deposits on the negative electrode). (b) Anodic deposition**

The advantages of electrodeposition are that:

- The process emits very low levels of VOC.
- The coating film is deposited at a uniform thickness so that the total film weight can be controlled.
- The deposited film has superior adhesion and film density.

The disadvantages of electrodeposition in the aerospace industry are that:

- The initial equipment cost is high.
- The large variation in the sizes of parts to be coated makes it difficult to determine an optimum bath size.
- Electrocoat baths are sensitive to degradation, so turnover at fairly frequent intervals is important. If the bath components are not depleted and replenished at a sufficient rate, it may be necessary to discard the aged product and recharge with fresh material.
- The heat required for curing can affect the temper of aluminum alloys. Careful monitoring of the time

and temperature of the bake is necessary.

Electrodeposition seems to have enough advantages to ensure that it will be used in many applications in the aerospace industry, such as the coating of small parts.

## Application Equipment

The regulations for VOC compliance often dictate the transfer efficiency of the spray equipment used to apply the coatings. Transfer efficiency is defined as the percentage of material actually applied to the object out of the total nonvolatile material sprayed. Rule 1124 requires that the transfer efficiency be a minimum of 65% or that the excess overspray be collected by air pollution control equipment. The types of spray equipment commonly used are described below.

**Air-atomized spray equipment** is the conventional equipment that has been in use for many years. The coating is broken into very fine particles by an air flow at a pressure of 200 to 480 kPa (30 to 70 psi). This method usually results in the best appearance because of the excellent breakup. However, air-atomized spray equipment has a transfer efficiency of only 20 to 30%.

**Airless spray equipment** forces the coating through a small orifice (diameter of 0.22 to 0.53 mm, or 0.009 to 0.021 in.) under high pressure (6200 to 11,700 kPa, or 900 to 1700 psi). This atomizes the liquid paint into fine particles, but even so the particles are much larger than those produced by air atomization. The transfer efficiency is better than that of air atomization, about 45%, but because of the comparatively large particle size it is difficult to achieve a satisfactory film appearance.

**Air-assisted airless spray equipment** is similar to airless spray equipment, except that compressed air under low pressure is introduced at the top and the bottom of the fan pattern to break up the tails of the large particles. This produces a better appearance than airless spray. In addition, because lower hydraulic pressures are used (700 to 2750 kPa, or 100 to 400 psi), the transfer efficiency is somewhat better.

**High-volume, low-pressure spray equipment** is similar to that used for conventional air atomization. The difference is that the guns are constructed with special air and fluid nozzles that allow the coating to be atomized at low air pressures and velocities. This creates a soft spray effect that produces higher transfer efficiencies, usually 60 to 70%.

**Electrostatic spray equipment** charges the atomized particles so that they are electrically attracted to the grounded metallic part. The resulting "wrap effect" greatly reduces overspray and improves transfer efficiency to 60 to 90%. This technique is effective only if the resistivity of the liquid coating is at least 0.05 MΩ · m. The more highly polar solvents used in aerospace coatings, such as methyl ethyl ketone, are very conductive and result in low resistivities. Some solvents with high resistivity, such as aromatics or esters, must be included in the formula to achieve the desired transfer efficiency.

### Compliant Wipe Solvent Cleaners

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## Introduction

WIPE SOLVENTS are used to remove contaminants from a workpiece before it undergoes manufacturing operations that require clean surfaces, such as bonding, sealing, painting, welding, plating, specialized surface treatment procedures, and others. Traditional wipe solvent cleaners include:

- Methyl ethyl ketone
- Methyl isobutyl ketone
- Trichloroethene (trichloroethylene)
- Tetrachloroethylene (perchloroethylene)

- 1,1,1-trichloroethane (methyl chloroform)
- Acetone
- Toluene
- Dichloromethane (methylene chloride)
- Tetrachloromethane (carbon tetrachloride)
- Benzene
- Xylene
- Ethylene glycol ethers
- Diethylene glycol ethers
- 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113)
- Combinations of these materials

The U.S. Environmental Protection Agency (EPA) has classified these materials as being either hazardous air pollutants or ozone layer depleting substances. Some relevant regulations are identified in Table 1, along with a curtailment schedule that will either limit or prohibit the use of certain materials in the future. The article "Solvent Cold Cleaning and Vapor Degreasing" in this Volume provides additional information about these cleaners.

**Table 1 U.S. regulations related to curtailment in the use of solvent materials**

| U.S. Regulation | Material | Curtailment schedule |
|---|---|---|
| Clean Air Act Amendments of 1990, Hazardous Air Pollutants | 190 chemicals, including benzene, chloroform, methyl ethyl ketone, methyl isobutyl ketone, toluene, xylene, trichloroethylene, ethylene glycol ethers, and diethylene glycol ethers | Discontinue use by late 1997 |
| EPA Industrial Toxics (33/50) Program (voluntary) | 17 toxic chemicals,including benzene,carbon tetrachloride, chloroform, methyl ethyl ketone, methyl isobutyl ketone, toluene, 1,1,1-trichloroethane, trichloroethylene, and xylene | 33% reduction of use by end of 1992; 50% reduction by end of 1995 (from 1988 levels) |
| Presidential Directive to Accelerate Phase-Out of Ozone Layer Depleting Substances, Feb 1992 | Chlorofluorocarbons, halons, 1,1,1-trichloroethane, and carbon tetrachloride | Production phase-out: 50% beginning Jan 1993, 100% by Jan 1996. (Air Force will ban purchases after April 1994) |

## Alternate Materials

Innovative methods will be required to develop wipe solvent materials that will meet EPA requirements for the emission of volatile organic compounds, the reduction or elimination of hazardous air pollutants, and the elimination of ozone layer depleting substances. Besides meeting EPA requirements, the alternate wipe solvents must be effective in their required applications.

Frequently, the contaminating materials that need to be removed from a surface are actually a combination of materials, and therefore the use of mixed solvents is required to remove them. For example, one of the most widely used wipe solvent cleaners is the MIL-C-38736 formulation (Ref 1), which contains solvents that remove oil-and water-soluble contaminants (Table 2). Particulate materials that are insoluble are removed by the wiping action during cleaning. Some of the solvents in this formulation are classified as hazardous air pollutants. This cleaner also has a very high vapor pressure, which contributes to volatile organic compound emissions, and a low flash point, which warrants it a classification as a flammable material.

**Table 2 Compositions of MIL-C-38736 wipe solvent cleaners**

| Solvent | Concentration,% |
|---|---|
| **Type I** | |
| Aromatic naphtha | 50 |
| Ethyl acetate | 20 |
| Methyl ethyl ketone | 20 |
| Isopropyl alcohol | 10 |
| **Type II (nonphotochemically reactive)[a]** | |
| Toluene | 18.5 |
| Ethyl acetate | 35.5 |
| Methyl ethyl ketone | 36 |
| Isopropyl alcohol | 10 |

(a) A nonphotochemically reactive solvent is any solvent or solvent combination with an aggregate of less than 20% of its total volume composed of the chemical compounds listed in (1),(2), or (3) below and which does not exceed the individual volume percentage composition limitations. (1) A combination of hydrocarbons, alcohols, aldehydes, esters, ethers, or ketones having an olefinic or cycloolefinic type unsaturation, not to exceed 5% of the total volume. (2) A combination of aromatic compounds with eight or more carbon atoms to the molecule, except ethylbenzene, not to exceed 8% of the total volume. (3) A combination of ethylbenzene, ketones having branched hydrocarbon structures, trichloroethylene, or toluene, not to exceed 20% of the total volume.

Alternate nonhazardous air pollutants and higher vapor pressure materials that can be used to formulate a cleaner that is as efficient as the MIL-C-38736 formulation are available. A series of naphtha-type hydrocarbon materials with a variety of flash points and vapor pressures is available from one manufacturer, whereas naphtha-type hydrocarbons and blends of them that contain dibasic esters are produced by another producer (Table 3). In many cases, glycol ethers (carbon chain >8) can be substituted for methyl ethyl ketone, because they are not classified as hazardous air pollutants and can be selected with low vapor pressures and high flash points.

**Table 3 Characteristics of isoparaffins**

| Commercial name[a] | Flash point | | Distillation range | | Evaporation rate[b] | Vapor pressure[c] | |
|---|---|---|---|---|---|---|---|
| | °C | °F | °C | °F | | kPa | mm Hg |
| Isopar C | -7.2 | 19 | 97-103 | 207-217 | 560 | 13.1 | 98 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Isopar E | 7.2 | 45 | 117-137 | 243-279 | 155 | 6.9 | 52 |
| Isopar G | 41.1 | 106 | 160-174 | 320-345 | 27 | 1.9 | 14 |
| Isopar H | 53.3 | 128 | 179-189 | 354-372 | 9 | 0.83 | 6.2 |
| Isopar K | 52.7 | 127 | 177-197 | 351-387 | 8 | 0.76 | 5.7 |
| Isopar L | 62.2 | 144 | 191-201 | 376-405 | 4 | 0.69 | 5.2 |
| Isopar M | 88.9 | 192 | 223-251 | 433-484 | 0.5 | 0.41 | 3.1 |
| Isopar V | 136.1 | 277 | 273-317 | 523-592 | <0.1 | 0.03 | 0.26 |
| Axarel 9100 | 93.3 | 200 | . . . | . . . | <0.1 | <0.01 | <0.1 |

(a) Isopar is a registered tradename of Exxon Chemical Co.; Axarel is a registered tradename of DuPont Chemical Co.

(b) Based on butyl acetate = 1.

(c) Vapor pressure determined at 25 °C (77 °F).

Another solvent to consider is ethyl lactate, which is completely miscible with water and most organic solvents. This material, which has a flash point higher than 37.8 °C (100 °F), is reported to be an excellent wipe solvent cleaner for many applications. It is approved by the U.S. Federal Drug Administration for use as a food additive and, therefore, is considered relatively nontoxic.

The terpene hydrocarbon materials also can be used as alternate solvent materials. They include naturally occurring organic compounds, such as *d*-limonene, dipentene, α-terpinene, terpinolene, α-terpineol, and other proprietary terpene hydrocarbons. A major objection to these materials is their odor, which can become overwhelming with prolonged use. Other objections include their instability (auto-oxidation and decomposition), their reactivity with certain polymers and elastomers, and the presence of nonvolatile residue upon evaporation. However, a new class of these materials with low odor and flash points higher than 93.3 °C (200 °F) have been developed (Ref 2). These newer formulations also claim to be low in nonvolatile residue content.

A nonflammable, noncombustible material that is widely used as a wipe solvent cleaner is 1,1,1-trichloroethane (methyl chloroform). Because it is classified as a Class I ozone layer depleting substance, its manufacture will be discontinued in 1994. Reported substitutes listed in the EPA Significant New Alternatives Program (SNAP) are tetrachloroethylene (perchloroethylene), trichloroethene (trichloroethylene), and dichloromethane (methylene chloride), which are all highly toxic materials, and some of the fluorochlorohydrocarbons, which are classified as Class II ozone layer depleting substances. The use of the latter materials will be severely limited by the EPA after 1994. It should be noted, however, that the SNAP alternatives are for vapor degreasing and cold cleaning operations, rather than wipe solvent cleaning operations.

One company manufactures a series of perfluorocarbons that are nonflammable, noncombustible solvents (Table 4). However, the cleaning efficiency of these materials is very poor, and they are only being considered at this time as rinsing and drying agents in new degreasing systems, in combination with either isopropyl alcohol or terpene hydrocarbons. It is also likely that the EPA will ban their use in the near future.

**Table 4 Characteristics of perfluorocarbons**

| Commercial name[a] | Chemical name | Flash point | Boiling point |  | Vapor pressure[b] |  |
|---|---|---|---|---|---|---|
|  |  |  | °C | °F | kPa | mm Hg |
| PF-5050 | Perfluoropentane | None | 29 | 84 | 81.3 | 610 |
| PF-5052 | Perfluoro-*N*-methyl morpholine | None | 50 | 122 | 36.5 | 274 |
| PF-5060 | Perfluorohexane | None | 56 | 133 | 30.9 | 232 |
| PF-5070 | Perfluoroheptane | None | 82 | 180 | 10.5 | 79 |
| PF-5080 | Perfluorooctane | None | 101 | 214 | 3.9 | 29 |

(a) Products of 3M Co.

(b) Vapor pressure determined at 25 °C (77 °F).

Aqueous cleaners, including the newer enzyme cleaning materials, are another class of materials that should be considered as wipe solvent cleaner candidates. These materials have been used previously in wipe solvent cleaning operations and are currently replacing the use of vapor degreasing operations in many manufacturing facilities. Objections to using these materials in wipe solvent cleaning operations include a slow evaporation rate, an unacceptable amount of residue, an inability to remove uncured polymers, such as fuel tank sealant materials encountered in manufacturing operations and carbonaceous soils encountered in the exterior cleaning of aircraft and support equipment during operation and maintenance.

Water-soluble, oil-soluble, and insoluble materials are all encountered in production operations. Wipe solvent cleaners have been developed that combine several of the solvents already discussed (Table 5). These cleaners have low vapor pressures and flash points higher than 37.8 °C (100 °F), which means they are classified as nonflammable. Evaluation tests have shown that these wipe solvent cleaners are very efficient in general-purpose wipe solvent cleaning operations.

**Table 5 Combination wipe solvent cleaners**

| Formulation[a] | Flash point |  | Evaporation rate[b] | Vapor pressure[c] |  |
|---|---|---|---|---|---|
|  | °C | °F |  | kPa | mm Hg |

| | | | | | |
|---|---|---|---|---|---|
| Propylene glycol propyl ether, isoparaffins, and ethyl lactate | 46.1 | 115 | 20 | 0.23 | 1.7 |

(a) Developed by Lockhead Fort Worth Co.

(b) Based on butyl acetate = 1.

(c) Vapor pressure determined at 25 °C (77 °F).

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## References cited in this section

1. "Cleaning Compound, Solvent Mixtures," MIL-C-38736, U.S. Military Specification
2. A. Richard Koetzle, "High Temperature Flash Point, Stable Cleaning Composition," U.S. Patent 5,112,516, 12 May 1992

## Evaluation of Wipe Solvent Cleaners

The specific procedure for using wipe solvent cleaners involves wetting a clean cloth with the solvent, wiping the surface to be cleaned, and removing the residual solvent from the surface with a clean, dry cloth. The wipe solvent must either dissolve the contaminants or keep them in suspension until they can be removed from the surface with the clean, dry cloth. If the solvent evaporates too quickly, then the contaminants are merely redeposited on the surface. Because a wipe solvent cleaner is likely to be used as a general-purpose cleaner in production operations, it would need to clean all types of surfaces, such as metals, including those that have been chemically treated, anodized, or plated; primers; paints; coatings; rubbers; plastics, and others. It is actually unlikely that a single wipe solvent cleaner would be suitable for all cleaning operations. It is also obvious that extensive evaluations would be required to ensure the applicability of the wipe solvent cleaner to the cleaning processes under consideration.

An initial evaluation should include a literature review to determine the properties of the selected wipe solvent cleaner materials, such as toxicity, flash point, vapor pressure, and corrosion potential. Consultation with an industrial hygienist and an environmental professional is also recommended to ensure the acceptability of the candidate material.

Laboratory screening tests can then be conducted to determine the general cleaning efficiency properties of the candidate material, as well as its compatibility with the surface materials to be cleaned. These tests can include a simple water-break test and adhesion tests using an adhesive material that is representative of those that will be applied in production operations. Compatibility tests can consist of exposing the materials to be cleaned to the wipe solvent cleaner and then observing deterioration and other deleterious effects that might occur.

**Evaluation Parameters by Property.** After selecting the potential candidates, based on screening test results, extensive evaluation tests must be conducted. For general-purpose wipe solvent cleaner operations, the properties summarized in Table 6 and described below should be determined.

**Table 6 Tests for wipe solvent cleaners**

| **Attribute** | **Test method** |
|---|---|
| Cleaning efficiency | Contaminate substrate with standard contaminant. Expose to 48.9 °C (120 °F) for 24 h. Clean with candidate cleaner. Perform mechanical property test simulating subsequent operations. |
| Compatibility | Expose substrates to candidate cleaners. Observe for deterioration of substrates. |

| | |
|---|---|
| Corrosion potential | Immersion corrosion, ASTM F 483; sandwich corrosion, ASTM F 1110; hydrogen embrittlement, ASTM F 519; and stress cracking, ASTM G 38 |
| Vapor pressure | Calculate using Eq 1 (described in text) |
| Volatile organic compounds | ASTM D 3960 |
| Flash point | ASTM D 3278 |
| Odor | ASTM D 1296 or subjective evaluation using operators performing cleaning operations in open and confined areas |
| Dry residue | Apply candidate cleaners to a cleaned reflective surface. Allow to evaporate. Observe for residue and/or streaking. |
| Composition | Chromatography, ASTM D 3545; infrared analysis, ASTM E 1252 |
| Water content | ASTM D 1364 |
| Acidity | ASTM D 1613 |
| Refractive index | ASTM D 1218 |
| Density | ASTM D 1475 |

***The cleaning efficiency*** property of the wipe solvent cleaner will determine if subsequent operations can be satisfactorily performed. The surfaces to be cleaned should be contaminated with a solution such as that described in AMS 3166 (Ref 3) and shown in Table 7, followed by cleaning with the candidate wipe solvent cleaner. After the contaminating material is applied to the test substrate, it should be exposed to a temperature of 48.9 °C (120 °F) for 24 h, in order to ensure that crevices and imperfections in the substrate are sufficiently contaminated. Next, the test substrate should be cleaned with the proposed wipe solvent material. Because the laboratory tests listed in Table 6 do not guarantee that the wipe solvent will in fact be suitable for use in actual manufacturing operations, physical property tests, such as sealant adhesion, adhesive strength, paint and primer application and adhesion, and subsequent chemical surface treatments and processing should be conducted to determine if the wipe solvent is effective in removing the contaminant. It is also important to ensure that subsequent manufacturing operations will not be compromised.

**Table 7 Standard contaminant for testing the cleaning efficiency of wipe solvent cleaners**

| Ingredient | Parts by weight |
|---|---|
| Glycerol monostearate | 3.0 |
| Glycerol trioleate | 9.0 |

| | |
|---|---|
| Caprylic acid | 3.0 |
| Lauryl alcohol | 1.3 |
| Cholesterol | 1.2 |
| Mineral oil | 2.7 |
| Petrolatum | 3.0 |
| Lecithin | 0.3 |
| Water | 70.0 |

Heat and blend and add 0.5 wt% lamp black. Do not heat above 93.3 °C (200 °F).

It should be noted that new compliant wipe solvent cleaner formulations may not be as efficient in preparing some substrates as the wipe solvent cleaner formulations that are currently used. Therefore, it may be necessary to use additional techniques to obtain a satisfactory surface for the intended purpose. For example, evaluation tests have revealed that some substrates cleaned with the wipe solvent cleaners listed in Table 5 required the application of an adhesion promoter to ensure the adhesion of fuel tank sealants.

***Compatibility*** tests will determine the effects of the wipe solvent cleaner on the substrates being cleaned and adjacent materials that the cleaner may contact. The materials should be exposed to the wipe solvent cleaner for a typical time period. After exposure, the materials should be observed for etching, staining, and oxidation in metals; deterioration, softening, and swelling in elastomers; cracking or crazing in plastics; and loss of adhesion for any coated surfaces. Whether these changes are permanent or transitory should also be determined. These test results should indicate which substrates will require different wipe solvent cleaners.

Compatibility tests that were conducted on the formulations given in Table 5 indicated that these cleaners were satisfactory for use on most of the substrates investigated. However, they could not be used in cleaning operations involving most elastomers (specifically, the silicone, natural, neoprene, butyl, and nitrile rubbers) and some plastic materials, such as acrylics, polycarbonates, polystyrene, and polyurethane. Alternate cleaners, such as diluted isopropyl alcohol and, in some cases, acetone, were required for the wipe solvent cleaning of these substrates.

***The corrosion potential*** of the wipe solvent cleaner is an extremely important property that must be determined for metal-cleaning operations. In some cases, the wipe solvent cleaner contacts the metals for a short period of time, whereas in cases such as assembly cleaning, it can become trapped in the faying surfaces of joints, which would allow long-term contact with metal surfaces. Numerous corrosion tests are available to indicate potential problems in these applications.

The most simple test is the total immersion corrosion test, described in ASTM F 483. In applications where entrapment of the wipe solvent cleaner may occur, the sandwich corrosion test described in ASTM F 1110 is satisfactory. If the metals being cleaned are subject to hydrogen embrittlement or stress-corrosion cracking, then corrosion tests such as these described in ASTM F 519 and ASTM G 38 should be conducted. Other corrosion tests are available and should be selected if they better simulate the requirements of the wipe solvent cleaner operation in question.

***Vapor pressure*** is directly related to evaporation rate for a given solvent type, such as alcohols or ketones. Generally, the lower the vapor pressure, the lower the evaporation rate. Because the EPA tends to require a maximum pressure of 6 kPa (45 mm Hg) for wipe solvent cleaners, it is obvious that the evaporation rate of new wipe solvent cleaners will be much slower than that experienced traditionally. This is beneficial in that less cleaner will be required for a given cleaning operation. A potential hazard, however, is that there is a greater chance of the wipe solvent cleaner being trapped in the faying surfaces of manufactured assemblies. In addition, areas that are hard to reach will be more difficult to wipe dry during wipe cleaning operations. The vapor pressure of candidate wipe solvent cleaners can be calculated using Eq 1:

$$VP = \sum\nolimits_j^i \frac{(VP)_i (W)_i/(MW)_i}{\sum_i \left[ (W)_i/(MW)_i + \sum_j \left[ (W)_j/(MW)_j \right] \right]} \qquad \textbf{(Eq 1)}$$

where $VP$ is the composite vapor pressure of the volatile organic compound in the solvent cleaner, $(VP)_i$ is the vapor pressure at 20 °C (68 °F) of the "$i$"th component in the solvent cleaner, $(W)_{i \text{ or } j}$ is the weight in grams of the "$i$"th (or "$j$"th) component in the solvent cleaner, $(MW)_{i \text{ or } j}$ is the molecular weight of the "$i$"th (or "$j$"th) component in the solvent cleaner, $i$ is the volatile organic compound component(s) in the solvent cleaner, and $j$ is the exempt component(s) in the solvent cleaner, as defined by appropriate federal, state, and local regulations.

***Volatile organic compounds*** are contained in many of the new wipe solvent cleaners. The emission of these compounds must be minimized to meet most established clean-air requirements. Because wipe solvent cleaners are normally used in all areas of production operations, unique methods must be developed to conform to these emission requirements.

To control the emissions from the solvents listed in Table 5, which have very low vapor pressures that result in reduced evaporation rates, one company immediately places the used wiping cloths that are wet with wipe solvent into an aluminum-coated plastic bag. The bags are then collected at the end of each shift and compacted into sealed drums for later disposal. This method reduces volatile organic compound emissions by approximately 75%. The drums of compacted cloths can be used as high-energy, supplemental fuel in cement manufacturing and incinerated in permitted hazardous waste incinerators. Volatile organic compound content is determined using the test method described in ASTM D 3960.

***Flash Points.*** Wipe solvent cleaners with flash points higher than 37.8 °C (100 °F) are classified by the Occupational Safety and Health Administration (OSHA) as combustible materials, whereas those cleaners with flash points below that temperature are classified as flammable materials. The former type of cleaner is preferred because of safety concerns. In cases where nonflammable, noncombustible materials are required, only a limited number of compliant materials are available, and their cleaning efficiency may not suffice for the specific operation. If this is the case, alternate cleaning procedures, such as providing an inert atmosphere or establishing cleaning areas where ignition sources can be eliminated, should be investigated. Flash point is determined using the procedure described in ASTM D 3278.

***Odor*** is a rather subjective property of wipe solvent cleaners. In addition to conducting a standard test, as defined in ASTM D 1295, other tests should be conducted under the conditions of actual production environments. These environments should include open-area cleaning, as well as confined-space cleaning. A number of different operators should be used to obtain a general consensus on the odor of the wipe solvent cleaner. This odor should be mild and not objectionable to personnel engaged in the cleaning operations. Methods of minimizing odor include an increase in ventilation and the use of respirators.

***Dry Residue.*** The wipe solvent cleaner must evaporate without leaving residue on the surface that could interfere with subsequent manufacturing operations. This property can be determined by applying the candidate cleaner to a test substrate, allowing it to evaporate, and then observing the resulting surface for evidence of residue and streaking. Optimally, the test substrate should be a cleaned, reflective surface.

***Other properties*** to evaluate include composition, water content, acidity, refractive index, and density. It is useful to determine these properties by conducting receiving inspection-type tests to ensure that the wipe solvent cleaner has the same composition as when evaluated. These tests will also indicate if accidental contamination of the cleaner has occurred. The relevant test methods are identified in Table 6.

Industrial hygiene and safety is another important aspect of the wipe solvent cleaner that must be evaluated. The cleaner should not contain components listed by OSHA as being hazardous materials, which are toxic under use conditions. It is also important to not exceed threshold limit value, which is typically a minimum of 150 parts per million for a wipe solvent cleaner, although lower values may be satisfactory if suitable protection techniques are incorporated. To determine the protection methods required to limit the exposure of cleaning personnel to the wipe solvent cleaners, monitoring tests should be conducted on the air near those personnel. Depending on the cleaning operation (open or confined areas) and area ventilation, it may be necessary to use respirators while conducting cleaning activities. Eye and skin protection should also be investigated and the necessary devices made available to personnel.

### Reference cited in this section

3. "Solvents, Cleaning, for Cleaning Prior to Application of Sealing Compounds," AMS 3166, Society of Automotive Engineers

- **A**
- **abrasion**
  - (1) A process in which hard particles or protuberances are forced against and moved along a solid surface. (2) A roughening or scratching of a surface due to abrasive wear . (3) The process of grinding or wearing away a surface through the use of abrasives.
- **abrasive**
  - (1) A hard substance used for grinding , honing , lapping , superfinishing , polishing, pressure blasting, or barrel finishing . Abrasives in common use are alumina, silicon carbide, boron carbide, diamond, cubic boron nitride, garnet, and quartz. (2) Hard particles, such as rocks, sand, or fragments of certain hard metals, that wear away a surface when they move across it under pressure. See also superabrasives .
- **abrasive blasting**
  - A process for cleaning or finishing by means of an abrasive directed at high velocity against the workpiece. Abrasive blasting methods include grit blasting , sandblasting , and shotblasting .
- **abrasive disk**
  - (1) A grinding wheel that is mounted on a steel plate, with the exposed flat side being used for grinding. (2) A disk-shaped, coated abrasive product.
- **abrasive flow machining**
  - Removal of material by a viscous abrasive media flowing under pressure through or across a workpiece.
- **abrasive jet machining**
  - Material removal from a workpiece by impingement of fine abrasive particles that are entrained in a focused, high-velocity gas stream.
- **abrasive machining**
  - A machining process in which the points of abrasive particles are used as machining tools. Grinding is a typical abrasive machining process.
- **abrasive wear**
  - The removal of material from a surface when hard particles slide or roll across the surface under pressure. The particles may be loose or may be part of another surface in contact with the surface being abraded. Compare with adhesive wear .
- **abrasive wheel**
  - A grinding wheel composed of an abrasive grit and a bonding agent.
- **abrasivity**
  - The extent to which a surface, particle, or collection of particles will tend to cause abrasive wear when forced against a solid surface under relative motion and under prescribed conditions.
- **accelerated aging**
  - A process by which the effects of aging are accelerated under extreme and/or cycling temperature and humidity conditions. The process is meant to duplicate long-time environmental conditions in a relatively short space of time.
- **acicular ferrite**
  - A highly substructured nonequiaxed ferrite formed upon continuous cooling by a mixed diffusion and shear mode of transformation that begins at a temperature slightly higher than the transformation temperature range for upper bainite. It is distinguished from bainite in that it has a limited amount of carbon available; thus, there is only a small amount of carbide present.
- **acicular ferrite steels**
  - Ultralow carbon (<0.08%) steels having a microstructure consisting of either acicular ferrite or a mixture of acicular and equiaxed ferrite .
- **acid cleaning**
  - Process in which a solution of mineral acid, organic acid, or acid salt, in combination with a wetting agent and detergent, is used to remove oxide, shop soil, oil, grease, and other contaminants from metal surfaces, with or without the use of heat.
- **acrylic**
  - A coating based on a polymer containing short-chain esters of acrylic and methacrylic acid. Their physical properties can be controlled in part by the choice of the alcohol used to make the ester.

- **activation**
  - (1) The changing of a passive surface of a metal to a chemically active state. Contrast with passivation . (2) The (usually) chemical process of making a surface more receptive to bonding with a coating or an encapsulating material.
- **active**
  - The negative direction of electrode potential . Also used to describe corrosion and its associated potential range when an electrode potential is more negative than an adjacent depressed corrosion rate (passive) range.
- **active metal**
  - A metal ready to corrode, or being corroded.
- **actual contact area**
  - In tribology, the total area of contact formed by summing the localized asperity contact areas within the apparent area of contact . Also known as real area of contact.
- **addition agent**
  - See additive .
- **additive**
  - (1) A material added in small quantities to a solution to modify its characteristics. For example, additives may be added to a plating solution to modify the character of the deposit. (2) In lubrication, a material added to a lubricant for the purpose of imparting new properties or of enhancing existing properties. Main classes of additives include anticorrosive, antifoam, antioxidant , antiwear, detergent , dispersant , extreme-pressure lubricant , and VI improver additives. (3) In polymer engineering, a substance added to another substance, usually to improve properties, such as plasticizers , initiators, light stabilizers, and flame retardants.
- **adherend**
  - A body held to another body by an adhesive. See also substrate .
- **adhesion**
  - The attractive force that exists between a deposit and its substrate that can be measured as the force required to separate a deposit and its substrate. Contrast with cohesion .
- **adhesion promoter**
  - A coating applied to a substrate , before it is coated with an adhesive, to improve the adhesion of the substrate. Also called primer .
- **adhesive**
  - A substance capable of holding materials together by surface attachment. Adhesive is a general term and includes, among others, cement, glue, mucilage, and paste. These terms are loosely used interchangeably. Various descriptive adjectives are applied to the term adhesive to indicate certain physical characteristics: hot-melt adhesives, pressure-sensitive adhesives, structural adhesives, ultraviolet/electron-beam cured adhesives, and water-based adhesives.
- **adhesive bond**
  - Attractive forces, generally physical in character, between an adhesive and the base materials. Two principal interactions that contribute to the adhesion are van der Waals bonds and dipole bonds.
- **adhesive film**
  - A synthetic resin adhesive, with or without a film carrier fabric, usually of the thermosetting type, in the form of a thin film of resin, used under heat and pressure as an interleaf in the production of bonded structures.
- **adhesive strength**
  - The strength of the bond between an adhesive and an adherend .
- **adhesive wear**
  - (1) Wear by transference of material from one surface to another during relative motion due to a process of solid-phase welding. Particles that are removed from one surface are either permanently or temporarily attached to the other surface. (2) Wear due to localized bonding between contacting solid surfaces leading to material transfer between the two surfaces or loss from either surface. Compare with abrasive wear .
- **adsorption**
  - The adhesion of the molecules of gases, dissolved substances, or liquids to the surfaces of solids or liquids with which they are in contact.
- **aerated bath nitriding**

  - A type of liquid nitriding in which air is pumped through the molten bath creating agitation and increased chemical activity.
- **AFS 50-70 test sand**
  - A rounded quartz sand specified for use as an abrasive in the dry sand-rubber wheel test (ASTM G 65). Using the U.S. Sieve Series, none of this sand will be retained on Sieve No. 40, 5% maximum will be retained on Sieve No. 50, 95% minimum will be retained on Sieve No. 70, and none will pass Sieve No. 100. This places all the particle diameters between 425 and 150 μm. See also sieve analysis .
- **age hardening**
  - (1) Hardening by aging (heat treatment) usually after rapid cooling or cold working. (2) (of grease). The increasing consistency of a lubricating grease with time of storage.
- **age softening**
  - Spontaneous decrease of strength and hardness that takes place at room temperature in certain strain hardened alloys, especially those of aluminum.
- **agglomerate**
  - The clustering together of a few or many particles, whiskers, or fibers, or a combination thereof, into a larger solid mass.
- **aging**
  - (1) The storage of porcelain enamel slips or powders before use. (2) The change occurring in porcelain enamel slips or powders with the lapse of time. (3) In heat treatment, a change in the properties of certain metals and alloys that occurs at ambient or moderately elevated temperatures after hot working or a heat treatment (quench aging in ferrous alloys, natural or artificial aging in ferrous and nonferrous alloys) or after cold working (strain aging). The change in properties is often, but not always, due to a phase change (precipitation ), but never involves a change in chemical composition of the metal or alloy.
- **air cap**
  - A device for forming, shaping, and directing an air pattern for the atomization of wire or ceramic rod.
- **air feed**
  - A thermal spraying process variation in which an air stream carries the powdered material to be sprayed through the gun and into the heat source.
- **air gap**
  - In extrusion coating, the distance from the die opening to the nip formed by the pressure roll and the chill roll.
- **air hole**
  - A hole in a casting caused by air or gas trapped in the metal during solidification.
- **air setting**
  - The characteristic of some materials, such as refractory cements, core pastes, binders , and plastics, to take permanent set at normal air temperatures.
- **alclad**
  - Composite wrought product comprised of an aluminum alloy core having one or both surfaces a metallurgically bonded aluminum or aluminum alloy coating that is anodic to the core and thus electrochemically protects the core against corrosion .
- **aliphatic solvent**
  - A type of solvent comprised mainly of straight-chain hydrocarbons. Examples are gasoline, kerosene, hexane, and naphtha.
- **alkaline cleaner**
  - A material blended from alkali hydroxides and such alkaline salts as borates, carbonates, phosphates, or silicates. The cleaning action may be enhanced by the addition of surface-active agents and special solvents.
- **alkyd**
  - A coating based on a polyester binder . The polyester binders are chemical combinations of molecules that contain more than one acid or alcohol group. Alkyds are widely used in water-based house paints and automotive primers.
- **alligatoring**
  - (1) Pronounced wide cracking over the entire surface of a coating having the appearance of alligator hide. (2) The longitudinal splitting of flat slabs in a plane parallel to the rolled surface. Also called fishmouthing.

- **allowance**
  - (1) The specified difference in limiting sizes (minimum clearance or maximum interference) between mating parts, as computed arithmetically from the specified dimensions and tolerances of each part. (2) In a foundry, the specified clearance. The difference in limiting sizes, such as minimum clearance or maximum interferences between mating parts, as computed arithmetically. See also tolerance .
- **aluminizing**
  - Forming of an aluminum or aluminum alloy coating on a metal by hot dipping, hot spraying, or diffusion .
- **amorphous**
  - Not having a crystal structure; noncrystalline.
- **Amsler wear machine**
  - A wear and traction-testing machine consisting of two disk-shaped specimens oriented such that their axes are parallel and whose circumferential, cylindrical surfaces are caused to roll or roll and slide against one another. The rotation rates of each disk may be varied so as to produce varying degrees of sliding and rolling motion.
- **anchorite**
  - A zinc-iron phosphate coating for iron and steel.
- **anchor pattern**
  - A pattern made by blast cleaning abrasives on an adherend surface in preparation for adhesive application prior to bonding. Pattern is examined in profile.
- **angle of attack**
  - In tribology, the angle between the direction of motion of an impinging liquid or solid particle and the tangent to the surface at the point of impact.
- **angle of incidence**
  - In tribology, the angle between the direction of motion of an impinging liquid or solid particle stream and the plane of the surface.
- **angle-ply laminate**
  - A laminate having fibers of adjacent plies, oriented at alternating angles.
- **anion**
  - A negatively charged ion.
- **anionic detergent**
  - A detergent that produces aggregates of negatively charged ions with colloidal properties.
- **anneal to temper**
  - A final partial anneal that softens a cold-worked nonferrous alloy to a specified level of hardness or tensile strength.
- **anode**
  - The electrode in electrolysis at which negative ions are discharged, positive ions are formed, or other oxidizing reactions occur. Contrast with cathode .
- **anode corrosion**
  - The dissolution of a metal acting as an anode .
- **anode film**
  - (1) The layer of solution in contact with the anode that differs in composition from that of the bulk of the solution. (2) The outer layer of the anode itself consisting of oxidation or reaction products of the anode metal.
- **anodic cleaning**
  - Electrolytic cleaning in which the work is the anode . Also called reverse-current cleaning.
- **anodic coating**
  - A protective, decorative, or functional coating, formed by conversion of the surface of a metal in an electrolytic oxidation process.
- **anodic etching**
  - Method of revealing microstructure by selective dissolution of the polished surface under application of a direct current. Variation with layer formation: anodizing.
- **anodic inhibitor**
  - A chemical substance or mixture that prevents or reduces the rate of the anodic or oxidation reaction. See also inhibitor .
- **anodic pickling**
  - Electrolytic pickling in which the work is the anode.

- **anodic protection**
    - (1) A technique to reduce the corrosion rate of a metal by polarizing it into its passive region, where dissolution rates are low. (2) Imposing an external electrical potential to protect a metal from corrosive attack. (Applicable only to metals that show active-passive behavior.) Contrast with cathodic protection .
- **anodic reaction**
    - Electrode reaction equivalent to a transfer of positive charge from the electronic to the ionic conductor. An anodic reaction is an oxidation process. An example common in corrosion is Me $\mathrm{Me}^{n+} + ne^{-}$
- **anodizing**
    - An electrolytic oxidation process in which the surface of a metal, when anodic, is converted to a coating having desirable protective, decorative, or functional properties.
- **anolyte**
    - The portion of electrolyte in the vicinity of the anode; in a divided cell, the portion of electrolyte on the anode side of the diagram.
- **antioxidant**
    - Any additive for the purpose of reducing the rate of oxidation and subsequent deterioration of a material.
- **antipitting agent**
    - An additive for electroplating solutions to prevent the formation of pits or large pores in the electrodeposit.
- **antiskinning agents**
    - Chemicals added to a paint to help prevent the formation of a surface film on the paint.
- **apparent area of contact**
    - In tribology, the area of contact between two solid surfaces defined by the boundaries of their macroscopic interface.
- **arc of contact**
    - The portion of the circumference of a grinding wheel or cutter touching the work being processed.
- **aromatic**
    - A type of solvent based on benzene ring molecules. Aromatics are often used as diluents in acrylic lacquers. Typical examples are benzene, xylol, and toluol.
- **asperity**
    - In tribology, a protuberance in the small-scale topographical irregularities of a solid surface.
- **atmospheric corrosion**
    - The gradual degradation or alteration of a material by contact with substances present in the atmosphere, such as oxygen, carbon dioxide, water vapor, and sulfur and chlorine compounds.
- **atomic replica**
    - A thin replica devoid of structure on the molecular level. It is prepared by the vacuum or hydrolytic deposition of metals or simple compounds of low molecular weight. See also replica .
- **atomization**
    - In thermal spraying, the division of molten material at the end of the wire or rod into fine particles.
- **attack-polishing**
    - Simultaneous etching and mechanical polishing.
- **attrition**
    - Removal of small fragments of surface material during sliding contact.
- **attritor**
    - A high-intensity ball mill whose drum is stationary and whose balls are agitated by rotating baffles, paddles, or rods at right angle to the drum axis.
- **attritor grinding**
    - The intensive grinding or alloying in an attritor. Examples: milling of carbides and binder metal powders and mechanical alloying of hard dispersoid particles with softer metal or alloy powders.
- **austempering**
    - A heat treatment for ferrous alloys in which a part is quenched from the austenitizing temperature at a rate fast enough to avoid formation of ferrite or pearlite and then held at a temperature just above $M_s$, the martensite start temperature, until transformation to bainite is complete. Although designated as bainite in both austempered steel and austempered ductile iron (ADI), austempered

  steel consists of two-phase mixtures containing ferrite and carbide, while austempered ductile iron consists of two-phase mixtures containing ferrite and austenite .
- **austenite**
  - A solid solution of one or more elements in face-centered cubic iron (gamma iron). Unless otherwise designated (such as nickel austenite), the solute is generally assumed to be carbon.
- **austenitizing**
  - Forming austenite by heating a ferrous alloy into the transformation range (partial austenitizing) or above the transformation range (complete austenitizing). When used without qualification, the term implies complete austenitizing.
- **autocatalytic plating**
  - Deposition of a metal coating by a controlled chemical reduction, catalyzed by the metal or alloy being deposited.
- **average grain diameter**
  - The mean diameter of an equiaxed grain section whose size represents all the grain sections in the aggregate being measured. See also grain size .
- **B**
- **babbitting**
  - The process by which a babbitt metal is mechanically or chemically bonded to a shell or stiffener, which supports the weight and torsion of a rotating, oscillating, or sliding shaft. The babbitt metal, being softer than the support and having excellent antifrictional properties, prevents galling and/or scoring of the shaft over long periods of use.
- **babbitt metal**
  - A nonferrous bearing alloy originated by Isaac Babbitt in 1839. Currently, the term includes several tin-base alloys consisting mainly of various amounts of copper, antimony, tin, and lead. Lead-base babbitt metals are also used.
- **back emission**
  - The electrical breakdown of air resulting from an excessive charge buildup in porcelain enamel powder film during powder application. This reaction is due to the self-limiting characteristic of electrostatic powders. Also known as back ionization.
- **backing**
  - (1) In grinding, the material (paper, cloth, or fiber) that serves as the base for coated abrasives . (2) In welding, a material placed under or behind a joint to enhance the quality of the weld at the root. It may be a metal backing ring or strip; a pass of weld metal; or a nonmetal such as carbon, granular flux or a protective gas atmosphere . (3) In plain bearings, that part of the bearing to which the bearing alloy is attached, normally by a metallurgical bond .
- **backing film**
  - A film used as auxiliary support for the thin replica or specimen-supporting film.
- **back ionization**
  - See back emission .
- **bainite**
  - A metastable aggregate of ferrite and cementite resulting from the transformation of austenite at temperatures below the pearlite range but above $M_s$, the martensite start temperature. Upper bainite is an aggregate that contains parallel lath-shape units of ferrite, produces the so-called "feathery" appearance in optical microscopy, and is formed above approximately 350 °C (660 °F). Lower bainite, which has an acicular appearance similar to tempered martensite , is formed below approximately 350 °C (660 °F).
- **bainitic hardening**
  - Quench-hardening treatment resulting principally in the formation of bainite .
- **Bakelite**
  - A proprietary name for a phenolic thermosetting resin used as a plastic mounting material for metallographic samples.
- **ball milling**
  - In porcelain enameling, a method of grinding and mixing ceramic materials, with or without liquid, in a dense, ceramic-lined rotating cylinder or conical mill partially filled with grinding media such as pebbles or porcelain balls.
- **bark**
  - The decarburized layer just beneath the scale that results from heating steel in an oxidizing atmosphere.

- **barrel burnishing**
  - The smoothing of surfaces by means of tumbling the work in rotating barrels in the presence of metallic or ceramic shot, and in the absence of abrasive. In ball burnishing, the shot consists of hardened steel balls.
- **barrel finishing**
  - Improving the surface finish of workpieces by processing them in rotating equipment along with abrasive particles that may be suspended in a liquid. The barrel is normally loaded about 60% full with a mixture of parts, media, compound, and water. See also tumbling .
- **barrel plating**
  - (or cleaning). Plating articles in a rotating container, usually a perforated cylinder that operates at least partially submerged in a solution.
- **barrier coat**
  - An exterior coating applied to a composite filament-wound structure to provide protection. In fuel tanks, a coating applied to the inside of the tank to prevent fuel from permeating the side wall.
- **barrier film**
  - The layer of film used during cure to permit removal of air and volatiles from a reinforced plastic or a composite lay-up while minimizing resin loss.
- **barrier layer**
  - In anodizing aluminum, the thin, pore-free, semiconducting aluminum oxide region nearest the metal surface and distinct from the main anodic oxide coating, which has a pore structure.
- **base metal**
  - (1) The original metal to which one or more coatings are applied. Also known as basis metal. (2) The metal present in the largest proportion in an alloy; brass, for example, is a copper-base alloy. (3) A metal that readily oxidizes, or that dissolves to form ions. Contrast with noble metal .
- **basis metal**
  - See base metal .
- **beads**
  - Defects in porcelain enamel caused by coarse enamel particles, spitting of guns, or falloff of accumulation on guns. Also known as lumps.
- **Beilby layer**
  - The altered surface layer formed on a crystalline solid during a wear process or by mechanical polishing that, according to a theory by Sir George Beilby, consists of a material in an amorphous state. It is now generally accepted that an amorphous layer is not formed at a surface except possibly in some special cases; however, the term is still used to denote a surface altered by wear, without any implication as to its actual structure.
- **bending**
  - The straining of material, usually flat sheet or strip metal, by moving it around a straight axis lying in the neutral plane. Metal flow takes place within the plastic range of the metal, so that the bent part retains a permanent set after removal of the applied stress. The cross section of the bend inward from the neutral plane is in compression; the rest of the bend is in tension.
- **bend test**
  - A test for determining relative ductility of metal that is to be formed (usually sheet, strip, plate, or wire) and for determining soundness and toughness of metal (after welding, for example). The specimen is usually bent over a specified diameter through a specified angle for a specified number of cycles. There are four general types of bend test, named according to the manner in which the forces are applied to the specimen to make the bend: free bend, guided bend, semiguided bend, and wrap-around bend. Bend tests can also be used to test the adhesion of metallic or organic coatings.
- **beta rays**
  - Beams of electrons that can be used to cure certain kinds of paints.
- **binder**
  - The paint material that forms the film, so called because it binds the pigment and any additives present into a solid durable film. Also referred to as the resin.
- **bisque**
  - A coating of wet process porcelain enamel that has been dried, but not fired.
- **black annealing**
  - Box annealing or pot annealing ferrous alloy sheet, strip, or wire impart a black color to the oxidized surface. See also box annealing .

- **black carburizing**
  - Simulating the carburizing operation without introducing carbon. This is usually accomplished by using an inert material in place of the carburizing agent, or by applying a suitable protective coating to the ferrous alloy.
- **black oxide**
  - A black finish on a metal produced by immersing it in hot oxidizing salts or salt solutions.
- **black specking**
  - Same as specking .
- **blank nitriding**
  - Simulating the nitriding operation without introducing nitrogen. This is usually accomplished by using an inert material in place of the nitriding agent or by applying a suitable protective coating to the ferrous alloy.
- **blasting or blast cleaning**
  - A process for cleaning or finishing metal objects with an air blast or centrifugal wheel that throws abrasive particles against the surface of the workpiece. Small, irregular particles of metal are used as the abrasive in grit blasting ; sand, in sandblasting ; and steel, in shotblasting .
- **blister**
  - (1) A raised area, often dome shaped, resulting from loss of adhesion between a coating or deposit and the base metal . (2) In porcelain enamel , a defect caused by gas evolution, consisting of a bubble that forms during fusion and remains when the porcelain enamel solidifies. (3) A casting defect, on or near the surface of the metal, resulting from the expansion of gas in a subsurface zone. It is characterized by a smooth bump on the surface of the casting and a hole inside the casting directly below the bump.
- **blistering**
  - The development during firing of enclosed or broken macroscopic vesicles or bubbles in a body, or in a glaze or other coating.
- **bloom**
  - (1) A visible exudation or efflorescence on the surface of an electroplating bath. (2) A bluish fluorescent cast to a painted surface caused by deposition of a thin film of smoke, dust, or oil. (3) A loose, flowerlike corrosion product that forms when certain metals are exposed to a moist environment.
- **blow hole**
  - A void produced by the outgassing of trapped air during cure. (2) A void in a solder connection caused by outgassing or a void in a fired dielectric.
- **blue annealing**
  - Heating hot-rolled ferrous sheet in an open furnace to a temperature within the transformation range, then cooling in air to soften the metal. A bluish oxide surface layer forms.
- **blue brittleness**
  - Brittleness exhibited by some steels after being heated to some temperature within the range of about 205 to 370 °C (400 to 700 °F), particularly if the steel is worked at the elevated temperature. Killed steels are virtually free of this kind of brittleness.
- **blue dip**
  - A solution containing a mercury compound, once widely used to deposit mercury on a metal by immersion, usually prior to silver plating .
- **blue enamel**
  - (1) In dry-process enameling , an area of enamel coating so thin that it appears blue in color. (2) In wet-process enameling , a cover coat applied too thinly to hide the substrate.
- **bluing**
  - (or blueing). Subjecting the scale-free surface of a ferrous alloy to the action of air, steam, or other agents at a suitable temperature, thus forming a thin blue film of oxide and improving the appearance and resistance to corrosion. This term is ordinarily applied to sheet, strip, or finished parts. It is used also to denote the heating of springs after fabrication to improve their properties.
- **blushing**
  - (1) Whitening and loss of gloss of a usually organic coating caused by moisture. Also called blooming. (2) The condensation of atmospheric moisture at the adhesive bond line interface.
- **bobbing compound**
  - A compound used for heavy buffing that usually contains some form of coarse silica such as flint or quartz. Considerably more abrasive than tripoli compound .

- **boiling**
    - A defect visible in fired porcelain enamel that is caused by gas evolution and that results in the formation of blisters , pinholes , specking , dimples , or a spongy surface.
- **bond**
    - (1) In grinding wheels and other relatively rigid abrasive products, the material that holds the abrasive grains together. (2) In an adhesive bonded or diffusion bonded joint, the line along which the faying surfaces are joined together. (3) In thermal spraying, the junction between the material deposited and the substrate , or its strength. See also adhesive bond , mechanical bond , and metallic bond .
- **bond coat**
    - In thermal spraying, a preliminary (or prime) coat of material which improves adherence of the subsequent thermal spray deposit.
- **boriding**
    - Thermochemical treatment involving the enrichment of the surface layer of an object with borides. This surface-hardening process is performed below the $Ac_1$ temperature (the temperature at which austenite begins to form during heating). Also referred to as boronizing.
- **box annealing**
    - Annealing a metal or alloy in a sealed container under conditions that minimize oxidation. In box annealing a ferrous alloy, the charge is usually heated slowly to a temperature below the transformation range, but sometimes is above or within it, and is then cooled slowly; this process is also called close annealing or pot annealing. See also black annealing .
- **breakout**
    - Fiber separation or break on surface plies at drilled or machined composite material edges.
- **bright annealing**
    - Annealing in a protective medium to prevent discoloration of the bright surface.
- **bright dip**
    - A solution that produces, through chemical action, a bright surface on an immersed metal.
- **brightener**
    - An agent or combination of agents added to an electroplating bath to produce a lustrous deposit.
- **bright finish**
    - A high-quality finish produced on ground and polished rolls. Suitable for electroplating.
- **bright nitriding**
    - Nitriding in a protective medium to prevent discoloration of the bright surface. Compare with blank nitriding .
- **bright plate**
    - An electrodeposit that is lustrous in the as-plated condition.
- **bright-throwing power**
    - The measure of the ability of a plating solution or a specified set of plating conditions to deposit uniformly bright electroplate on an irregularly shaped cathode .
- **Brinelling**
    - (1) Indentation of the surface of a solid body by repeated local impact or impacts, or static overload. Brinelling may occur especially in a rolling-element bearing. (2) Damage to a solid bearing surface characterized by one or more plastically formed indentations brought about by overload. See also false Brinelling .
- **brittle**
    - Permitting little or no plastic deformation prior to fracture.
- **brittle erosion behavior**
    - Erosion behavior having characteristic properties (e.g., little or no plastic flow, the formation of cracks) that can be associated with brittle fracture of the exposed surface. The maximum volume removal occurs at an angle near 90°, in contrast to approximately 25° for ductile erosion behavior .
- **brittle fracture**
    - Separation of a solid accompanied by little or no macroscopic plastic deformation . Typically, brittle fracture occurs by rapid crack propagation with less expenditure of energy than for ductile fracture . Brittle tensile fractures have a bright, granular appearance and exhibit little or no necking. A chevron pattern may be present on the fracture surface, pointing toward the origin of the crack, especially in brittle fractures in flat platelike components. Examples of brittle fracture include transgranular cracking and intergranular cracking .

- **brittleness**
  - The tendency of a material to fracture without first undergoing significant plastic deformation . Contrast with ductility .
- **broaching**
  - Cutting with a tool that consists of a bar having a single edge or a series of cutting edges (teeth) on its surface. The cutting edges of multiple-tooth, or successive single-tooth, broaches increase in size and/or change in shape. The broach cuts in a straight line or axial direction when relative motion is produced in relation to the workpiece, which may also be rotating. The entire cut is made in single or multiple passes over the workpiece to shape the required surface contour.
- **bronzing**
  - (1) Applying a chemical finish to copper or copper-alloy surfaces to alter the color. (2) Plating a copper-tin alloy on various materials.
- **brush plating**
  - A method of plating in which the plating solution is applied with a pad or brush, within which is an anode that is moved over the cathode to be plated. Also called selective plating.
- **brush polishing (electrolytic)**
  - A method of electropolishing in which the electrolyte is applied with a pad or brush in contact with the part to be polished.
- **bubble structure**
  - Size and spatial distribution of voids within fired porcelain enamel .
- **buckle**
  - (1) Bulging of a large, flat face of a casting; in investment casting, caused by dip coat peeling from the pattern. (2) An indentation in a casting, resulting from expansion of the sand, can be termed the start of an expansion defect. (3) A local waviness in metal bar or sheet, usually transverse to the direction of rolling.
- **buffer**
  - A compound or mixture that, when contained in solution, causes the solution to resist change in pH. Each buffer has a characteristic limited range of pH over which it is effective.
- **buffing**
  - Developing a lustrous surface by contacting the work with a rotating buffing wheel .
- **buffing wheel**
  - Buff sections assembled to the required face width for use on a rotating shaft between flanges. Sometimes called a buff.
- **buff sections**
  - Fabric, paper, or leather disks with concentric center holes held together by various types of sewing to provide degrees of flexibility or hardness. These sections are assembled to make wheels for polishing or buffing .
- **building up**
  - Electroplating for the purpose of increasing the dimensions of a workpiece.
- **built-up edge**
  - (1) Chip material adhering to the tool face adjacent to the cutting edge during cutting. (2) Material from the workpiece, especially in machining, which is stationary with respect to the tool. See also wedge formation .
- **bull's-eye structure**
  - The microstructure of malleable or ductile cast iron when graphite nodules are surrounded by a ferrite layer in a pearlitic matrix.
- **burned-in sand**
  - A defect consisting of a mixture of sand and metal cohering to the surface of a casting.
- **burned-on sand**
  - A misnomer usually indicating metal penetration into sand, resulting in a mixture of sand and cast metal adhering to the surface of a casting.
- **burning**
  - (1) Permanently damaging a metal or alloy by heating to cause either incipient melting or intergranular oxidation. (2) During subcritical annealing, particularly in continuous annealing, production of a severely decarburized and grain-coarsened surface layer that results from excessively prolonged heating to an excessively high temperature. (3) In grinding, getting the work hot enough to cause discoloration or to change the microstructure by tempering or

hardening. (4) In sliding contacts, the oxidation of a surface due to local heating in an oxidizing environment. See also metallurgical burn .

- **burnishing**
  - Finish sizing and smooth finishing of surfaces (previously machined or ground) by displacement, rather than removal, of minute surface irregularities with smooth point or line-contact, fixed or rotating tools.
- **burnoff**
  - (1) The unintentional removal of an autocatalytic deposit from a nonconducting substrate, during subsequent electroplating operations, owing to the application of excessive current or a poor contact area. (2) In porcelain enamel , a condition caused by thin application resulting in a black or yellow-green color. The enamel layer may appear transparent. Lack of bubble structure and shinier scale may be associated with this condition.
- **burnt deposit**
  - A rough, noncoherent or otherwise unsatisfactory deposit produced by the application of an excessive current density and usually containing oxides or other inclusions.
- **burr**
  - An undesirable projection of material that results from a cutting, forming, blanking, or shearing operation, especially a rough edge left on sheet steel after stamping or punching.
- **burr hardness**
  - Hardness of the burr in the vicinity of the base of the burr .
- **burr height**
  - The distance a burr projects above the surface of the workpiece.
- **burring**
  - (1) The process of removing burrs (preferred word is deburring ). (2) The intentional production of a small flange around holes in a pressworking operation (preferred word is flanging). (3) The act of burr formation.
- **bus (bus bar)**
  - A rigid conducting section, for carrying current to the anode and cathode bars.
- **butler finish**
  - A semilustrous metal finish composed of fine, uniformly distributed parallel lines, usually produced with a soft abrasive buffing wheel ; similar in appearance to the traditional hand-rubbed finish on silver.
- **buttering**
  - A form of surfacing in which one or more layers of weld metal are deposited on the groove face of one member (for example, a high-alloy weld deposit on steel base metal that is to be welded to a dissimilar base metal). The buttering provides a suitable transition weld deposit for subsequent completion of the butt weld (joint).
- **C**
- **calcareous coating or deposit**
  - A layer consisting of a mixture of calcium carbonate and magnesium hydroxide deposited on surfaces being cathodically protected against corrosion , because of the increased pH adjacent to the protected surface.
- **calender**
  - The passing of plastic sheet material between sets of pressure rollers to produce a smooth finish and a desired thickness.
- **calomel half cell (calomel electrode)**
  - A half cell containing a mercury electrode in contact with a solution of potassium chloride of specified concentration that is saturated with mercurous chloride (calomel).
- **calorizing**
  - Imparting resistance to oxidation to an iron or steel surface by heating in aluminum powder at 800 to 1000 °C (1470 to 1830 °F).
- **canning**
  - (1) A dished distortion in a flat or nearly flat sheet metal surface, sometimes referred to as oil canning. (2) Enclosing a highly reactive metal within a relatively inert material for the purpose of hot working without undue oxidation of the active metal.
- **capillary attraction**

  - (1) The combined force of adhesion and cohesion that causes liquids, including molten metals, to flow between very closely spaced and solid surfaces, even against gravity. (2) In powder metallurgy, the driving force for the infiltration of the pores of a sintered compact by a liquid.
- **carbide tools**
  - Cutting or forming tools, usually made from tungsten, titanium, tantalum, or niobium carbides, or a combination of them, in a matrix of cobalt, nickel, or other metals. Carbide tools are characterized by high hardnesses and compressive strengths and may be coated to improve wear resistance.
- **carbon edges**
  - Carbonaceous deposits in a wavy pattern along the edges of a steel sheet or strip; also known as snaky edges.
- **carbonitriding**
  - A case hardening process in which a suitable ferrous material is heated above the lower transformation temperature in a gaseous atmosphere of such composition as to cause simultaneous absorption of carbon and nitrogen by the surface and, by diffusion, create a concentration gradient. The heat-treating process is completed by cooling at a rate that produces the desired properties in the workpiece.
- **carbon restoration**
  - Replacing the carbon lost in the surface layer from previous processing of a steel by carburizing this layer to substantially the original carbon level. Sometimes called recarburizing.
- **carburizing**
  - Absorption and diffusion of carbon into solid ferrous alloys by heating, to a temperature usually above $Ac_3$, in contact with a suitable carbonaceous material. A form of case hardening that produces a carbon gradient extending inward from the surface, enabling the surface layer to be hardened either by quenching directly from the carburizing temperature or by cooling to room temperature, then reaustenitizing and quenching.
- **carrier gas**
  - In thermal spraying, the gas used to carry the powdered materials from the powder feeder or hopper to the gun.
- **case**
  - In heat treating, that portion of a ferrous alloy, extending inward from the surface, whose composition has been altered during case hardening . Typically considered to be the portion of an alloy (a) whose composition has been measurably altered from the original composition, (b) that appears light when etched, or (c) that has a higher hardness value than the core.
- **case hardening**
  - A generic term covering several processes applicable to steel that change the chemical composition of the surface layer by absorption of carbon, nitrogen, or a mixture of the two and, by diffusion, create a concentration gradient. The processes commonly used are carburizing and quench hardening , cyaniding , nitriding , and carbonitriding . The use of the applicable specific process name is preferred.
- **cast film**
  - A film made by depositing a layer of liquid plastic onto a surface and stabilizing this form by the evaporation of solvent, by fusing after deposition, or by allowing a melt to cool. Cast films are usually made from solutions or dispersions .
- **cast replica**
  - In metallography, a reproduction of a surface in plastic made by the evaporation of the solvent from a solution of the plastic or by polymerization of a monomer on the surface. See also replica .
- **catalyst**
  - A chemical used to change the rate of a chemical reaction. Differs from a curing agent in that the catalyst is not itself chemically consumed in the reaction, while a curing agent is. Technically, catalysts that increase reaction rates are called accelerators; those that decrease reaction rates are called inhibitors or retarders.
- **catastrophic wear**
  - Sudden surface damage, deterioration, or change of shape caused by wear to such an extent that the life of the part is appreciably shortened or action is impaired.
- **cathode**

  - The electrode in electrolysis at which positive ions are discharged, negative ions are formed, or other reducing actions occur. Contrast with anode .
- **cathode film**
  - The layer of solution in contact with the cathode that differs in composition from that of the bulk of the solution.
- **cathodic cleaning**
  - Electrolytic cleaning in which the work is the cathode . Also called direct-current cleaning.
- **cathodic corrosion**
  - Corrosion resulting from a cathodic condition of a structure usually caused by the reaction of an amphoteric metal with the alkaline products of electrolysis .
- **cathodic disbondment**
  - The destruction of adhesion between a coating and its substrate by products of a cathodic reaction .
- **cathodic pickling**
  - Electrolytic pickling in which the work is the cathode .
- **cathodic protection**
  - The prevention of corrosion of a metal by electrically connecting it to a sacrificial anode . The anode is itself decomposed, and the object of interest is protected. The sacrificial anode must be replaced periodically. Contrast with anodic protection .
- **cathodic reaction**
  - Electrode reaction equivalent to a transfer of negative charge from the electronic to the ionic conductor. A cathodic reaction is a reduction process. An example common in corrosion is: $\mathrm{Ni}^{2+} + 2e^{-} \quad \mathrm{Ni}$.
- **catholyte**
  - The portion of the electrolyte in the vicinity of the cathode ; in a divided cell the portion of the cathode side of the diaphragm.
- **cation**
  - A positively charged ion that migrates through the electrolyte toward the cathode under the influence of a potential gradient. See also anion and ion .
- **cationic detergent**
  - A detergent that produces aggregates of positively charged ions with colloidal properties.
- **caul**
  - In adhesive bonding, a sheet of material employed singly or in pairs in the hot or cold pressing of assemblies being bonded. A caul is used to protect either the faces of the assembly or the press platens, or both, against marring and staining in order to prevent sticking, facilitate press loading, impart a desired surface texture or finish, and provide uniform pressure distribution. A caul may be made of any suitable material such as aluminum, stainless steel, hardboard, fiberboard, or plastic, the length and width dimensions generally being the same as those of the plates of the press where it is used.
- **caustic dip**
  - A strongly alkaline solution into which metal is immersed for etching, for neutralizing acid, or for removing organic materials such as greases or paints.
- **cavitation**
  - The formation and collapse, within a liquid, of cavities or bubbles that contain vapor or gas or both. In general, cavitation originates from a decrease in the static pressure in the liquid. It is distinguished in this way from boiling, which originates from an increase in the liquid temperature. There are certain situations where it may be difficult to make a clear distinction between cavitation and boiling, and the more general definition that is given here is therefore to be preferred. In order to erode a solid surface by cavitation, it is necessary for the cavitation bubbles to collapse on or close to that surface.
- **cavitation corrosion**
  - A process involving conjoint corrosion and cavitation .
- **cavitation erosion**
  - Progressive loss of original material from a solid surface due to continuing exposure to cavitation .
- **cell**
  - Electrochemical system consisting of an anode and a cathode immersed in an electrolyte . The anode and cathode may be separate metals or dissimilar areas on the same metal. The cell

includes the external circuit, which permits the flow of electrons from the anode toward the cathode.

- **cementite**
  - A hard ( 800 HV), brittle compound of iron and carbon, known chemically as iron carbide and having the approximate chemical formula $Fe_3C$. It is characterized by an orthorhombic crystal structure. When it occurs as a phase in steel, the chemical composition will be altered by the presence of manganese and other carbide-forming elements. The highest cementite contents are observed in white cast irons, which are used in applications where high wear resistance is required.
- **centerless grinding**
  - Grinding the outside or inside diameter of a cylindrical piece that is supported on a work support blade instead of being held between centers and that is rotated by a so-called regulating or feed wheel.
- **ceramic-metal coating**
  - A mixture of one or more ceramic materials in combination with a metallic phase applied to a metallic substrate that may or may not require heat treatment prior to service. This term may also be used for coatings applied to nonmetallic substrates, for example, graphite.
- **ceramic process**
  - The production of articles or coatings from essentially inorganic, nonmetallic materials, the article or coating being made permanent and suitable for utilitarian and decorative purposes by the action of heat at temperatures sufficient to cause sintering, solid-state reactions, bonding, or conversion partially or wholly to the glassy state.
- **chafing**
  - Repeated rubbing between two solid bodies that can result in surface damage and/or wear.
- **chafing fatigue**
  - Fatigue initiated in a surface damaged by rubbing against another body. See also fretting .
- **Charpy test**
  - An impact test in which a V-notched, keyhole-notched, or U-notched specimen, supported at both ends, is struck behind the notch by a striker mounted at the lower end of a bar that can swing as a pendulum. The energy that is absorbed in fracture is calculated from the height to which the striker would have risen had there been no specimen and the height to which it actually rises after fracture of the specimen. Contrast with Izod test .
- **chatter marks**
  - Surface imperfections on the work being ground, usually caused by vibrations transferred from the wheel-work interface during grinding.
- **checking**
  - The development of slight breaks in a coating that do not penetrate to the underlying surface. See also craze cracking .
- **chelating agent**
  - (1) An organic compound in which atoms form more than one coordinate bond with metals in solution. (2) A substance used in metal finishing to control or eliminate certain metallic ions present in undesirable quantities.
- **chemical conversion coating**
  - A protective or decorative nonmetallic coating produced in situ by chemical reaction of a metal with a chosen environment. It is often used to prepare the surface prior to the application of an organic coating and to provide some corrosion protection.
- **chemical deposition**
  - The precipitation or plating-out of a metal from solutions of its salts through the introduction of another metal or reagent to the solution.
- **chemical etching**
  - The dissolution of the material of a surface by subjecting it to the corrosive action of an acid or an alkali.
- **chemical milling**
  - A process for the selective and controlled removal of metal from a surface through the use of chemical etchants.
- **chemical polishing**
  - The improvement in surface smoothness of a metal by simple immersion in a suitable solution.
- **chemical vapor deposition (CVD)**

    - (1) A coating process, similar to gas carburizing and carbonitriding, whereby a reactant atmosphere gas is fed into a processing chamber where it decomposes at the surface of the workpiece, liberating one material for either absorption by, or accumulation on, the workpiece. A second material is liberated in gas form and is removed from the processing chamber, along with excess atmosphere gas. (2) Process used in manufacture of several composite reinforcements, especially boron and silicon carbide, in which desired reinforcement material is deposited from vapor phase onto a continuous core, for example, boron on tungsten wire (core).
- **chevron pattern**
    - A fractographic pattern of radial marks (shear ledges) that look like nested letters "V;" sometimes called a herringbone pattern. Chevron patterns are typically found on brittle fracture surfaces in parts whose widths are considerably greater than their thicknesses. The points of the chevrons can be traced back to the fracture origin.
- **chipping**
    - Fracturing and breaking away of fragments of a porcelain enamel surface.
- **chips**
    - Pieces of material removed from a workpiece by cutting tools or by an abrasive medium.
- **chlorinated lubricant**
    - A lubricant containing a chlorine compound that reacts with a rubbing surface at elevated temperatures to protect it from sliding damage. See also extreme-pressure lubricant , sulfochlorinated lubricant , and sulfurized lubricant .
- **chlorinated solvent**
    - A liquid organic compound of carbon, hydrogen, and chlorine such as methylene chloride, perchloroethylene, 1,1,1-trichloroethane, and trichloroethylene. These solvents are very effective for degreasing with a minimum fire hazard, but their use is heavily regulated due to their classification as ozone-depleting chemicals.
- **chromadizing**
    - Improving paint adhesion on aluminum or aluminum alloys, mainly aircraft skins, by treatment with a solution of chromic acid. Also called chromidizing or chromatizing. Not to be confused with chromating or chromizing .
- **chromate treatment**
    - A treatment of metal in a solution of a hexavalent chromium compound to produce a conversion coating consisting of trivalent and hexavalent chromium compounds.
- **chromating**
    - The process for producing a conversion coating containing chromium compounds.
- **chromium buffing compound**
    - A buffing compound consisting of fine unfused alumina. Originally developed to color buff chromium-plated parts that had been stained or frosted in the electroplating process.
- **chromium plating**
    - Electrodeposition of chromium on a substrate.
- **chromizing**
    - A surface treatment at elevated temperature, generally carried out in pack, vapor, or salt baths, in which an alloy is formed by the inward diffusion of chromium into the base metal .
- **cladding**
    - (1) A layer of material, usually metallic, that is mechanically or metallurgically bonded to a substrate . Cladding may be bonded to the substrate by any of several processes, such as roll-cladding and explosive forming. (2) A relatively thick layer (>1 mm, or 0.04 in.) of material applied by surfacing for the purpose of improved corrosion resistance or other properties. See also coating , surfacing , and hardfacing .
- **clad metal**
    - A composite metal containing two or more layers that have been bonded together. The bonding may have been accomplished by co-rolling, co-extrusion, welding, diffusion bonding, casting, heavy chemical deposition, or heavy electroplating.
- **cleaning**
    - The removal of grease, oxides, or other foreign material from a surface. See also types of cleaning: alkaline , anodic , cathodic , diphase , electrolytic , emulsion , immersion , soak , solvent , spray , ultrasonic .
- **cleaning-emulsifiable solvent**

  - Two-stage cleaning system wherein a concentrate containing organic solvents and surface-active agents is applied to a surface, subsequently emulsified, and removed along with the soil , by water rinsing.
- **clean surface**
  - A surface that is free of foreign material, both visible and invisible.
- **coarse grains**
  - Grains larger than normal for the particular wrought metal or alloy or of a size that produces a surface roughening known as orange peel or alligator skin.
- **coated abrasive**
  - An abrasive product (sandpaper, for example) in which a layer of abrasive particles is firmly attached to a paper, cloth, or fiber backing by means of glue or synthetic-resin adhesive.
- **coating**
  - A relatively thin layer (<1 mm, or 0.04 in.) of material applied by various processes for the purpose of corrosion prevention, resistance to high-temperature scaling, wear resistance, lubrication, or other purposes.
- **coating strength**
  - A measure of the cohesive bond within a coating, as opposed to coating-to-coating substrate bond; the tensile strength of a coating.
- **coating stress**
  - The stresses in a coating resulting, for example, from rapid cooling of molten or semimolten particles as they impact the substrate or from differential thermal expansion.
- **cocoa**
  - In fretting wear , a powdery form of debris, usually consisting of iron oxides, that is expelled from a ferrous metal joint near the location where fretting wear is occurring. Also known as red mud.
- **coefficient of friction**
  - The dimensionless ratio of the friction force ($F$) between two bodies to the normal force ($N$) pressing these bodies together: (or $f$) = ($F/N$).
- **cohesion**
  - (1) The state in which the particles of a single substance are held together by primary or secondary valence forces. As used in the adhesive field, the state in which the particles of the adhesive (or adherend) are held together. (2) Force of attraction between the molecules (or atoms) within a single phase. Contrast with adhesion .
- **coil breaks**
  - Creases or ridges in sheet or strip that appear as parallel lines across the direction of rolling and that generally extend the full width of the sheet or strip. Most commonly seen in as-annealed carbon steels.
- **cold etching**
  - Etching to reveal microstructure conducted at room temperature and below.
- **cold lap**
  - Wrinkled markings on the surface of an ingot or casting from incipient freezing of the surface and too low a casting temperature.
- **cold rolled sheets**
  - A metal mill product produced from a hot rolled pickled coil that has been given substantial cold reduction at room temperature. The resulting product is usually annealed and temper rolled to make it suitable for most common applications. The usual end product is characterized by improved surface, greater uniformity in thickness, and improved mechanical properties compared with hot rolled sheet.
- **cold shut**
  - (1) A discontinuity that appears on the surface of cast metal as a result of two streams of liquid meeting and failing to unite. (2) A lap on the surface of a forging or billet that was closed without fusion during deformation. (3)Freezing of the top surface of an ingot before the mold is full.
- **cold treatment**
  - Exposing steel to suitable sub-zero temperatures (-85 °C, or -120 °F) for the purpose of obtaining desired conditions or properties such as dimensional or microstructural stability. When the treatment involves the transformation of retained austenite, it is usually followed by tempering.
- **cold-worked structure**

    - A microstructure resulting from plastic deformation of a metal or alloy below its recrystallization temperature.
- **collodion replica**
    - In metallography, a replica of a surface cast in nitrocellulose.
- **colloidal particle**
    - An electrically charged particle, generally smaller in size than 200 μm, dispersed in a second continuous phase.
- **colloids**
    - Aggregates of molecules in solution (dispersion ) resulting in particles having dimensions in the 0.001 millimicron to 1000 micron range.
- **colonial finish**
    - A surface finish achieved by selectively buffing an oxidized surface, thereby producing lustrous highlights against the oxidized background.
- **color anodizing**
    - In anodizing of aluminum, formation of a colored coating on aluminum where the colored compound, pigment, or dye is incorporated after the coating has been formed and prior to sealing.
- **color buffing**
    - Producing a final high luster by buffing . Sometimes called coloring .
- **color etching**
    - Same as staining and tint etching .
- **coloring**
    - The production of desired colors on metal surfaces by appropriate chemical or electrochemical action. See also color buffing .
- **color oxide**
    - A material used to impart color to a porcelain enamel .
- **columnar structure**
    - A coarse structure of parallel elongated grains formed by unidirectional growth, most often observed in castings, but sometimes seen in structures resulting from diffusional growth accompanied by a solid-state transformation.
- **comet tails (on a polished surface)**
    - A group of comparatively deep unidirectional scratches that form adjacent to a microstructural discontinuity during mechanical polishing. They have the general shape of a comet tail. Comet tails form only when a unidirectional motion is maintained between the surface being polished and the polishing cloth.
- **complex ion**
    - An ion composed of two or more ions or radicals, both of which are capable or independent existence, for example, cuprocyanide $(Cu(CN)_3)^{2-}$.
- **composite coating**
    - A coating on a metal or non-metal that consists of two or more components, one of which is often particulate in form. Example: a cermet composite coating on a cemented carbide cutting tool. Also known as multilayer coating.
- **composite plate**
    - An electrodeposit consisting of layers of at least two different compositions.
- **compound zone**
    - The surface layer of diffusion-treated steels, which is made up of intermetallic compounds such as nitrides or carbides.
- **compressive burr**
    - The burr produced in blanking or piercing operations in which the slug separates from the stock in a compressive stress field. Burrs produced in this manner initially begin as tensile burrs and are typically identified as tensile-plus-compressive burrs .
- **conditioning**
    - The conversion of a surface on a plastic substrate to a suitable state for successful treatment in succeeding steps.
- **conductance**
    - The capacity of a medium, usually expressed in mhos, for transmitting electric current. The reciprocal of resistance.
- **conducting salt**
    - A salt added to the solution in order to increase its conductivity.

- **conformal coating**
    - A coating that covers and exactly fits the shape of the coated object.
- **contact plating**
    - A metal plating process wherein the plating current is provided by galvanic action between the work metal and a second metal, without the use of an external source of current.
- **contact potential**
    - In corrosion technology, the potential difference at the junction of two dissimilar substances.
- **continuity of coating**
    - The degree to which a porcelain enamel or ceramic coating is free of defects , such as bare spots, boiling , blisters , or copperheads , that could reduce its protective properties.
- **controlled cooling**
    - Cooling a metal or alloy from an elevated temperature in a predetermined manner to avoid hardening, cracking, or internal damage, or to produce desired microstructure or mechanical properties.
- **controlled etching**
    - Electrolytic etching with selection of suitable etchant and voltage resulting in a balance between current and dissolved metal ions.
- **controlled rolling**
    - A hot-rolling process in which the temperature of the steel is closely controlled, particularly during the final rolling passes, to produce a fine-grain microstructure.
- **conversion coating**
    - A coating consisting of a compound of the surface metal, produced by chemical or electrochemical treatments of the metal. Examples include chromate coatings on zinc, cadmium, magnesium, and aluminum, and oxide and phosphate coatings on steel. See also chromate treatment and phosphating .
- **copper-accelerated salt-spray (CASS) test**
    - An accelerated corrosion test for some electrodeposits and for anodic coatings on aluminum.
- **copperhead**
    - A reddish spot in a porcelain enamel coating caused by iron pickup during enameling, iron oxide left on poorly cleaned base metal , or burrs on iron or steel base metal that protrude through the coating and are oxidized during firing. Also called pull through.
- **coring**
    - (1) A condition of variable composition between the center and surface of a unit of microstructure (such as a dendrite, grain, carbide particle); results from nonequilibrium solidification, which occurs over a range of temperature. (2) A central cavity at the butt end of a rod extrusion, sometimes called extrusion pipe.
- **Corrodkote test**
    - An accelerated corrosion test for electrodeposits.
- **corrosion**
    - The chemical or electrochemical reaction between a material, usually a metal, and its environment that produces a deterioration of the material and its properties.
- **corrosion embrittlement**
    - The severe loss of ductility of a metal resulting from corrosive attack, usually intergranular corrosion and often not visually apparent.
- **corrosion fatigue**
    - The process in which a metal fractures prematurely under conditions of simultaneous corrosion and repeated cyclic loading at lower stress levels or fewer cycles than would be required in the absence of the corrosive environment.
- **corrosion protection**
    - Modification of a corrosion system so that corrosion damage is mitigated.
- **corrosion rate**
    - Corrosion effect on a metal per unit of time. The type of corrosion rate used depends on the technical system and on the type of corrosion effect. Thus, corrosion rate may be expressed as an increase in corrosion depth per unit of time (penetration rate, for example, mm/yr) or the mass of metal turned into corrosion products per unit area of surface per unit of time (weight loss, for example, $g/m^2/yr$). The corrosion effect may vary with time and may not be the same at all points of the corroding surface. Therefore, reports of corrosion rates should be accompanied by information on the type, time dependency, and location of the corrosion effect.

- **corrosion resistance**
  - The ability of a material to withstand contact with ambient natural factors or those of a particular, artificially created atmosphere, without degradation or change in properties. For metals, this could be pitting or rusting; for organic materials, it could be crazing .
- **corrosive wear**
  - Wear in which chemical or electrochemical reaction with the environment is significant. See also oxidative wear .
- **corrugations**
  - In metal forming, transverse ripples caused by a variation in strip shape during hot or cold reduction.
- **corundum**
  - A naturally occurring fused aluminum oxide ($Al_2O_3$) used as an abrasive.
- **coulomb**
  - The quantity of electricity that is transmitted through an electric circuit in 1 s when the current in the circuit is 1 A. The quantity of electricity that will deposit 0.0011180 g of silver.
- **cover coat**
  - A porcelain enamel finish applied to and then fused over a ground coat or applied directly to the metal substrate and then fused.
- **covering power**
  - (1) The ability of a solution to give satisfactory plating at very low current densities, a condition that exists in recesses and pits. This term suggests an ability to cover, but not necessarily to build up, a uniform coating, whereas throwing power suggests the ability to obtain a coating of uniform thickness on an irregularly shaped object. (2) The degree to which a porcelain enamel coating obscures the underlying surface. (3) The ability of a glaze to uniformly and completely cover the surface of the fired ceramic ware.
- **crack**
  - (1) A fracture type discontinuity characterized by a sharp tip and high ratio of length and width to opening displacement. (2) A line of fracture without complete separation.
- **cratering**
  - Depressions on coated surfaces caused by excess lubricant. Cratering results when paint is too thin and later ruptures, leaving pinholes and other voids. Use of less thinner in the coating can reduce or eliminate cratering, as can the use of less lubricant on the part.
- **crater wear**
  - The wear that occurs on the rake face of a cutting tool due to contact with the material in the chip that is sliding along that face.
- **crawling**
  - In porcelain enamel , a condition similar to tearing that occurs when firing a sprayed enamel coating over another coating already fired. It is characterized by the aggregation of the topcoat into balls or irregularly shaped islands during firing, thus exposing the base coat layer.
- **craze cracking**
  - Irregular surface cracking of a metal associated with thermal cycling. This term is used more in the United Kingdom than in the United States, where the term checking is used instead.
- **crazing**
  - (1) A network of fine hairline cracks in a coating. (2) Cracking that occurs in fired glazes or other ceramic coatings due to critical tensile stresses. (3) In porcelain enamel , almost-invisible lines in the finished surface that extend down to the base metal.
- **creep-feed grinding**
  - A subset of surface grinding , creep-feed grinding produces deeper (full) depths of cut at slow traverse rates.
- **crevice corrosion**
  - Localized corrosion of a metal surface at, or immediately adjacent to, an area that is shielded from full exposure to the environment because of close proximity between the metal and the surface of another material.
- **critical current density**
  - In an electrolytic process, a current density at which an abrupt change occurs in an operating variable or in the nature of an electrodeposit or electrode film.
- **critical pigment volume concentration (CPVC)**

  - The volume percent of pigment in a coating in which the pigment particles are surrounded by resin so that no free surface pigment exists.
- **cross rolling**
  - Rolling of metal or sheet or plate so that the direction of rolling is about 90° from the direction of a previous rolling.
- **cure**
  - The process by which paint is converted from the liquid to the solid state.
- **current density**
  - The current flowing to or from a unit area of an electrode surface.
- **current efficiency**
  - (1) The ratio of the electrochemical equivalent current density for a specific reaction to the total applied current density . (2) The proportion of current used in a given process to accomplish a desired result; in electroplating, the proportion used in depositing or dissolving metal.
- **curing temperature**
  - The temperature to which a paint film or adhesive is subjected to cure the paint or adhesive.
- **curtain coating**
  - A method of coating that may be employed with low-viscosity resins or solutions, suspensions, or emulsions of resins in which the substrate to be coated is passed through and perpendicular to a freely falling liquid curtain (or waterfall). The flow rate of the falling liquid and the linear speed of the substrate passing through the curtain are coordinated in accordance with the thickness of coating desired.
- **cutting down**
  - Polishing or buffing for the purpose of removing roughness or irregularities.
- **cutting fluid**
  - A fluid used in metal cutting to improve finish, tool life, or dimensional accuracy. On being flowed over the tool and work, the fluid reduces friction, the heat generated, and tool wear, and prevents galling . It conducts the heat away from the point of generation and also serves to wash the chips away.
- **cutoff burr**
  - A projection of material left when the workpiece falls from the stock before the separating cut has been completed.
- **cut wire blasting**
  - Blasting with short, cut lengths of metal wire. See also abrasive blasting .
- **cyaniding**
  - A case-hardening process in which a ferrous material is heated above the lower transformation temperature range in a molten salt containing cyanide to cause simultaneous absorption of carbon and nitrogen at the surface and, by diffusion, create a concentration gradient. Quench hardening completes the process.
- **cylindrical grinding**
  - Grinding the outer cylindrical surface of a rotating part.
- **D**
- **dealloying**
  - The selective corrosion of one or more components of a solid solution alloy. Also called parting or selective leaching . See also decarburization , decobaltification , denickelification , dezincification , and graphitic corrosion .
- **deburring**
  - The removal of burrs, sharp edges, or fins by mechanical, chemical or electrochemical means.
- **decalescence**
  - A phenomenon, associated with the transformation of alpha iron to gamma iron on the heating (superheating) of iron or steel, revealed by the darkening of the metal surface owing to the sudden decrease in temperature caused by the fast absorption of the latent heat of transformation. Contrast with recalescence .
- **decarburization**
  - Loss of carbon from the surface layer of a carbon-containing alloy due to reaction with one or more chemical substances in a medium that contacts the surface. See also dealloying .
- **decobaltification**
  - Corrosion in which cobalt is selectively leached from cobalt-base alloys, such as Stellite, or from cemented carbides. See also dealloying and selective leaching .

- **deep etching**
    - In metallography, macroetching , especially for steels, to determine the overall character of the material, that is, the presence of imperfections, such as seams, forging bursts, shrinkage-void remnants, cracks, and coring.
- **defect**
    - (1) A discontinuity whose size, shape, orientation, or location makes it detrimental to the useful service of the part in which it occurs. (2) A discontinuity or discontinuities which by nature or accumulated effect (for example, total crack length) render a part or product unable to meet minimum applicable acceptance standards or specifications. This term designates rejectability.
- **deflocculating**
    - Thinning the consistency of a slip by adding a suitable electrolyte .
- **degreasing**
    - The removal of grease and oils from a surface. Can be accomplished by immersion in liquid organic solvent, by solvent vapors condensing on the parts being cleaned (vapor degreasing), or by spraying the parts with solvent.
- **delayed fishscaling**
    - See fishscale .
- **delta iron**
    - Solid phase of pure iron that is stable from 1400 to 1539 °C (2550 to 2800 °F) and possesses the body-centered cubic lattice.
- **denickelification**
    - Corrosion in which nickel is selectively leached from nickel-containing alloys. Most commonly observed in copper-nickel alloys after extended service in fresh water. See also dealloying and selective leaching .
- **depletion**
    - Selective removal of one component of an alloy, usually from the surface or preferentially from grain-boundary regions. See also dealloying .
- **deposit corrosion**
    - Corrosion occurring under or around a discontinuous deposit on a metallic surface. Also called poultice corrosion.
- **deposition efficiency**
    - In thermal spraying, the ratio, usually expressed in percent, of the weight of spray deposit to the weight of the material sprayed.
- **deposition rate**
    - In thermal spraying, the weight of material deposited in a unit of time. It is usually expressed as kilograms per hour (kg/h) or pounds per hour (lb/h).
- **descaling**
    - A chemical or mechanical process for removing the thick layer of oxides formed on some metals at elevated temperatures.
- **detergent**
    - A surface active agent that possesses the ability to clean soiled surfaces. See also types of detergents: anionic , cationic , and nonionic .
- **detergent additive**
    - In lubrication technology, a surface-active additive that helps to keep solid particles suspended in an oil.
- **devitrification**
    - In porcelain enamel , a surface defect caused by crystallization of the enamel due to overfiring or contamination, resulting in the loss of the glassy, vitreous appearance of the surface.
- **dezincification**
    - Corrosion in which zinc is selectively leached from zinc-containing alloys leaving a relatively weak layer of copper and copper oxide. Most commonly found in copper-zinc alloys containing less than 85% copper after extended service in water containing dissolved oxygen. See also dealloying and selective leaching .
- **diamond**
    - A highly transparent mineral composed entirely of carbon (allotropic form of carbon) having a cubic structure. The hardest material known, it is used as a gemstone and as an abrasive in cutting and grinding applications. Natural diamonds are produced deep within the earth's crust at extremely high pressures and temperatures. Synthetic diamonds are synthesized by subjecting

carbon, in the form of graphite, to high temperatures and pressures using large special-purpose presses. See also superabrasives .

- **diamondlike film**
  - A hard, noncrystalline carbon film, usually grown by chemical vapor deposition or related techniques, that contains predominantly $sp^2$ carbon-carbon bonds.
- **diamond wheels**
  - A grinding wheel in which crushed and sized industrial diamonds are held in a resinoid, metal, or vitrified bond.
- **diaphragm**
  - A porous or permeable membrane separating anode and cathode compartments of an electrolytic cell from each other or from an intermediate compartment.
- **dichromate treatment**
  - A chromate conversion coating produced on magnesium alloys in a boiling solution of sodium dichromate.
- **dielectric shield**
  - In a cathodic protection system, an electrically nonconductive material, such as a coating, plastic sheet, or pipe, that is placed between an anode and an adjacent cathode to avoid current wastage and to improve current distribution, usually on the cathode.
- **die lines**
  - Lines or markings on formed, drawn, or extruded metal parts caused by imperfections in the surface of the die.
- **differential coating**
  - A coated product having a specified coating on one surface and a significantly lighter coating on the other surface (such as a hot dip galvanized product or electrolytic tin plate).
- **diffusion**
  - (1) Spreading of a constituent in a gas, liquid, or solid, tending to make the composition of all parts uniform. (2) The spontaneous movement of atoms or molecules to new sites within a material. (3) The movement of a material, such as a gas or liquid, in the body of a plastic. If the gas or liquid is absorbed on one side of a piece of plastic and given off on the other side, the phenomenon is called permeability. Diffusion and permeability are not due to holes or pores in the plastic but are caused by chemical mechanisms.
- **diffusion coating**
  - An alloy coating produced by applying heat to one or more coatings deposited on a base metal .
- **diluent**
  - A usually liquid inert substance added to some other substance or solution so that the volume of the latter substance is increased and its concentration per unit volume is decreased.
- **dimple**
  - In porcelain enamel , a cone-like depression defect in the fired enamel surface, somewhat larger than a pinhole . Also called flux pit.
- **dimpling**
  - (1) The stretching of a relatively small, shallow indentation into sheet metal. (2) In aircraft, the stretching of metal into a conical flange for a countersunk head rivet.
- **dip coating**
  - Applying a plastic coating by dipping the article to be coated into a tank of melted resin or plastisol , then chilling the adhering metal.
- **diphase cleaning**
  - Cleaning by means of solutions that contain a solvent layer and an aqueous layer. Cleaning is effected by both solvent and emulsifying action.
- **dipping**
  - In porcelain enameling, the process of coating a metal shape by immersion in slip, removal, and draining. In dry process enameling, the method of coating by immersing the heated metal shape for a short time in powdered frit .
- **dip plating**
  - Same as immersion coating .
- **direct cleaning**
  - Same as cathodic cleaning .
- **direct fire**

  - A method of maturing porcelain enamel so that the products of combustion come in contact with the ware.
- **disbondment**
  - The destruction of adhesion between a coating and the surface coated.
- **disk grinding**
  - Grinding with the flat side of an abrasive disk or segmented wheel. Also called vertical-spindle surface grinding.
- **dispersant additive**
  - In lubrication technology, an additive capable of dispersing cold oil sludge.
- **dispersing agent**
  - A material that increases the stability of a suspension of particles in a liquid medium.
- **dispersion**
  - To break big particles into small particles and suspend them in water so that they can be removed by rinsing. Alkaline silicates and phosphates are beneficial for dispersion.
- **dissolution etching**
  - Development of microstructure by surface removal.
- **divided cell**
  - A cell containing a diaphragm or other means for physically separating the anolyte from the catholyte .
- **double etching**
  - In metallography, use of two etching solutions in sequence. The second etchant emphasizes a particular microstructural feature.
- **drag-in**
  - The water or solution that adheres to the objects introduced into a bath.
- **drag-out**
  - The solution that adheres to the objects removed from a bath.
- **draining**
  - Part of the dipping or flow coating process during which the excess slip flows from suitably positioned ware.
- **drain time**
  - The time required for porcelain enamel slip applied by dipping, slushing, or flow coating to complete movement across the surfaces of a coated part.
- **dredge**
  - The sieve used to apply powdered porcelain enamel frit to the ware during dredging .
- **dredging**
  - In dry process enameling , the application of dry, powdered frit to hot ware by sifting.
- **dressing**
  - The process of eroding the bond matrix in a grinding wheel surface after truing or grinding in order to expose the abrasive grains and thereby improve grinding efficiency.
- **drier**
  - A catalyst added to speed the cure of oil-based paints. Driers are often metal salts of carboxylic acids.
- **drop etching**
  - In metallography, placing of a drop of etchant on the polished surface.
- **droplet erosion**
  - Erosive wear caused by the impingement of liquid droplets on a solid surface. See also erosion .
- **dross**
  - The scum that forms on the surface of molten metal largely because of oxidation but sometimes because of the rising of impurities to the surface.
- **dry etching**
  - In metallography, development of microstructure under the influence of gases.
- **drying cracks**
  - Irregular cracks in dry, unfired porcelain enamel caused by uneven or too rapid drying of the ware. The cracks may or may not heal over during the firing operation.
- **drying oil**
  - A water-insoluble liquid, usually obtained from a plant source, that reacts with oxygen (from the air) to form a cross-linked polymeric film.

- **dry process enameling**
    - A porcelain enameling process in which the metal article is heated to a temperature above the maturing temperature of the coating, usually 870 to 955 °C (1600 to 1750 °F). The coating materials are applied to the hot metal as a dry powder and fired.
- **dry-sand rubber wheel test**
    - In wear testing, a term used to describe a standard abrasive wear testing method in which a stream of dry quartz sand is passed between a rotating rubber wheel and a stationary test coupon that is held against it under specified normal force.
- **dry sliding wear**
    - Sliding wear in which there is no intentional lubricant or moisture introduced into the contact area. See also unlubricated sliding .
- **dry weight**
    - The weight per unit area of bisque .
- **ductile erosion behavior**
    - Erosion behavior having characteristic properties (i.e., considerable plastic deformation ) that can be associated with ductile fracture of the exposed solid surface. A characteristic ripple pattern forms on the exposed surface at low values of angle of attack. Contrast with brittle erosion behavior .
- **ductile fracture**
    - Fracture characterized by tearing of metal accompanied by appreciable gross plastic deformation and expenditure of considerable energy. Contrast with brittle fracture .
- **ductility**
    - The ability of a material to deform plastically without fracturing.
- **dummy (or dummy cathode)**
    - A cathode in a plating solution that is not to be made use of after plating. Often used for removal or decomposition of impurities.
- **duplex microstructure**
    - A two-phase structure.
- **dynamic electrode force**
    - The electrode potential measured when current is passing between the electrode and the electrolyte .
- **E**
- **edge strain**
    - Transverse strain lines or Lüders lines ranging from 25 to 300 mm (1 to 12 in.) in from the edges of cold rolled steel sheet or strip. See also Lüders lines .
- **electrical discharge grinding**
    - Grinding by spark discharges between a negative electrode grinding wheel and a positive workpiece separated by a small gap containing a dielectric fluid such as petroleum oil.
- **electrical discharge machining (EDM)**
    - Metal removal by a rapid spark discharge between different polarity electrodes, one on the workpiece and the other the tool, separated by a gap distance of 0.013 to 0.9 mm (0.0005 to 0.035 in.). The gap is filled with dielectrical fluid and metal particles, which are melted, in part vaporized, and expelled from the gap.
- **electrical pitting**
    - The formation of surface cavities by removal of metal as a result of an electrical discharge across an interface.
- **electric arc spraying**
    - A thermal spraying process using as a heat source an electric arc between two consumable electrodes of a coating material and a compressed gas which is used to atomize and propel the material to the substrate.
- **electrochemical cell**
    - An electrochemical system consisting of an anode and a cathode in metallic contact and immersed in an electrolyte . The anode and cathode may be different metals or dissimilar areas on the same metal surface.
- **electrochemical (chemical) etching**
    - General expression for all developments of microstructure through reduction and oxidation (redox reactions).
- **electrochemical corrosion**

  - Corrosion that is accompanied by a flow of electrons between cathodic and anodic areas on metallic surfaces.
- **electrochemical discharge machining**
  - Metal removal by a combination of the processes of electrochemical machining and electrical discharge machining . Most of the metal removal occurs via anodic dissolution (i.e., ECM action). Oxide films that form as a result of electrolytic action through an electrolytic fluid are removed by intermittent spark discharges (i.e., EDM action).
- **electrochemical machining (ECM)**
  - Controlled metal removal by anodic dissolution. Direct current passes through a flowing film of conductive solution that separates the workpiece from the electrode/tool. The workpiece is the anode , and the tool is the cathode .
- **electrochemical polishing**
  - An attack-polishing method in which the chemical action of the polishing fluid is enhanced or controlled by the application of an electric current between the specimen and the polishing wheel.
- **electrocorrosive wear**
  - Wear of a solid surface which is accelerated by the presence of a corrosion-inducing electrical potential across the contact interface. This process is usually associated with wear in the presence of a liquid electrolyte in the interface. However, moisture from the air can also facilitate this type of wear when a galvanic wear couple exists and the contacting materials are sufficiently reactive.
- **electrode**
  - A conductor through which current enters or leaves an electrolytic cell , at which there is a change from conduction by electrons to conduction by dry particles of matter, or vice versa.
- **electrodeposition**
  - (1) The deposition of a conductive material from a plating solution by the application of electric current. (2) The deposition of a substance on an electrode by passing electric current through an electrolyte. Electrochemical plating, electroforming , electrorefining , and electrowinning result from electrodeposition.
- **electrode potential**
  - The difference in potential between an electrode and the immediately adjacent electrolyte referred to some standard electrode potential as zero. See also various types of electrode potentials: dynamic , equilibrium , static , and standard .
- **electroforming**
  - The production or reproduction of articles by electrodeposition upon a mandrel or mold that is subsequently separated from the deposit.
- **electrogalvanizing**
  - The electroplating of zinc upon iron or steel.
- **electroless plating**
  - Deposition of a metallic coating by a controlled chemical reduction that is catalyzed by the metal or alloy being deposited.
- **electrolysis**
  - Production of chemical changes by the passage of current through an electrolyte .
- **electrolyte**
  - (1) A conducting medium in which the flow of current is accompanied by movement of matter. Most often an aqueous solution of acids, bases, or salts, but includes many other media, such as fused salts, ionized gases, some solids, and so on. (2) A substance that is capable of forming a conducting liquid medium when dissolved or melted.
- **electrolytic cell**
  - A unit apparatus in which electrochemical reactions are produced by applying electrical energy, or which supplies electrical energy as a result of chemical reactions and which includes two or more electrodes and one or more electrolytes contained in a suitable vessel.
- **electrolytic cleaning**
  - A process of removing soil , scale , or corrosion products from a metal surface by subjecting it as an electrode to an electric current in an electrolytic bath.
- **electrolytic corrosion**
  - Corrosion by means of electrochemical or mechanical action.
- **electrolytic grinding**
  - A combination of grinding and machining wherein a metal-bonded abrasive wheel, usually diamond, is the cathode in physical contact with the anodic workpiece, the contact being made

beneath the surface of a suitable electrolyte. The abrasive particles that produce grinding act as nonconducting spacers permitting simultaneous machining through electrolysis .

- **electrolytic pickling**
  - Pickling in which electric current is used, the work being one of the electrodes.
- **electrolytic polishing**
  - An electrochemical polishing process in which the metal to be polished is made the anode in an electrolytic cell where preferential dissolution at high points in the surface topography produces a specularly reflective surface. Also referred to as electropolishing .
- **electromotive series**
  - A table that lists in order the standard electrode potentials of specified electrochemical reactions.
- **electron-beam curing**
  - A system for curing paint films using the energy of an electron beam. The process lends itself to high-speed curing of paint on flat surfaces. Special paints must be used and personal shielding is required.
- **electron-beam radiation**
  - Radiation generated from high-energy electrons that is used in cross-linking coating systems.
- **electrophoresis**
  - The movement of colloidal particles produced by the application of an electric potential.
- **electroplating**
  - The application of a metallic coating on a surface by means of electrolytic action.
- **electropolishing**
  - A technique commonly used to prepare metallographic specimens, in which a high polish is produced making the specimen the anode in an electrolytic cell , where preferential dissolution at high points smooths the surface. Also referred to as electrolytic polishing .
- **electrorefining**
  - The process of anodically dissolving a metal from a pure anode and depositing it cathodically in a purer form.
- **electrostatic spray**
  - The process by which paint particles are electrically charged and attracted to a substrate bearing an opposite charge.
- **electrowinning**
  - The production of metals by electrolysis with insoluble anodes in solutions derived from ores or other materials.
- **elongated grain**
  - A grain with one principal axis slightly longer than either of the other two.
- **embeddability**
  - The ability of a bearing material to embed harmful foreign particles and reduce their tendency to cause scoring or abrasion.
- **embedded abrasive**
  - Fragments of abrasive particles forced into the surface of a workpiece during grinding , abrasion, or polishing.
- **embossing**
  - (1) Technique used to create depressions of a specific pattern in plastic film and sheeting. Such embossing in the form of surface patterns can be achieved on molded parts by the treatment of the mold surface with photoengraving or another process. (2) Raising a design in relief against a surface.
- **embrittlement**
  - The severe loss of ductility or toughness or both, of a material, usually a metal or alloy. Many forms of embrittlement can lead to brittle fracture . Many forms can occur during thermal treatment or elevated-temperature service (thermally induced embrittlement). In addition, steels and other metals and alloys can be embrittled by environmental conditions (environmentally assisted embrittlement).
- **emery**
  - Naturally occurring abrasive containing 57 to 75% aluminum oxide and a remainder of iron oxide and impurities.
- **emulsifying agent**
  - A substance that increases the stability of an emulsion .
- **emulsion**

  - A class of collodial dispersions containing two or more immiscible liquids such as oil in water. Emulsions are usually unstable and will separate into their components unless a stabilizing agent is present.
- **emulsion cleaning**
  - Cleaning by means of solutions containing organic solvents, water, and emulsifying agents .
- **enamel**
  - A broad classification of free-flowing clear or pigmented varnishes, treated oils, or other forms of organic coatings that usually dry to a hard, glossy or semiglossy finish.
- **end-quench hardenability test**
  - Same as Jominy test .
- **entrance burr**
  - Burr formed on the surface at which the cutting tool or its teeth enters the workpiece.
- **environmental cracking**
  - Brittle fracture of a normally ductile material in which the corrosive effect of the environment is a causative factor. Environmental cracking is a general term that includes corrosion fatigue , high-temperature hydrogen attack , hydrogen blistering, hydrogen embrittlement , liquid metal embrittlement, solid metal embrittlement, stress-corrosion cracking , and sulfide stress cracking . The following terms have been used in the past in connection with environmental cracking, but are becoming obsolete: caustic embrittlement, delayed fracture, season cracking, static fatigue, stepwise cracking, sulfide corrosion cracking, and sulfide stress-corrosion cracking. See also embrittlement .
- **equiaxed grain structure**
  - A structure in which the grains have approximately the same dimensions in all directions.
- **equilibrium electrode potential**
  - A static electrode potential when the electrode and the electrolyte are in equilibrium with respect to a specified electrochemical reaction.
- **erosion**
  - (1) Loss of material from a solid surface due to relative motion in contact with a fluid that contains solid particles. Erosion in which the relative motion of particles is nearly parallel to the solid surface is called abrasive erosion. Erosion in which the relative motion of the solid particles is nearly normal to the solid surface is called impingement erosion or impact erosion. (2) Progressive loss of original material from a solid surface due to mechanical interaction between that surface and a fluid, a multicomponent fluid, and impinging liquid, or solid particles. (3) Loss of material from the surface of an electrical contact due to an electrical discharge (arcing). See also cavitation erosion , electrical pitting , and erosion-corrosion .
- **erosion-corrosion**
  - A conjoint action involving corrosion and erosion in the presence of a moving corrosive fluid, leading to the accelerated loss of material.
- **erosion (erosive) wear**
  - See erosion .
- **etch**
  - (1) A roughened surface produced by chemical or electrochemical means. (2) To dissolve unevenly a part of the surface of a metal.
- **etchant**
  - (1) A chemical solution used to etch a metal to reveal structural details. (2) A solution used to remove, by chemical reaction, the unwanted portion of material from a printed circuit board. (3) Hydrofluoric acid or other agent used to attack the surface of glass for marking or decoration.
- **etch cleaning**
  - Removing soil by dissolving away some of the underlying metal.
- **etch cracks**
  - Shallow cracks in hardened steel containing high residual surface stresses, produced by etching in an embrittling acid.
- **etching (pitting)**
  - The localized attack of metal surfaces. Controlled etching of metals improves the adhesion of organic coatings. By contrast, uncontrolled etching of metals by an acid can cause damage by weakening the crystal structure.
- **etch rinsing**

  - Pouring etchant over a tilted surface until the desired degree of attack is achieved. Used for etchants with severe gas formation.
- **eutectoid**
  - (1) An isothermal reversible reaction in which a solid solution is converted into two or more intimately mixed solids on cooling, the number of solids formed being the same as the number of components in the system. (2) An alloy having the composition indicated by the eutectoid point on a phase diagram. (3) An alloy structure of intermixed solid constituents formed by a eutectoid reaction.
- **evaporative deposition**
  - The techniques of condensing a thin film of material on a substrate. The entire process takes place in a high vacuum. The source material may be radioactively heated by bombardment with electrons (electron-beam radiation ) or may be heated by thermal-conduction techniques.
- **exempt solvents**
  - Solvents that are not subject to air pollution legislation. Many alcohols, esters, some ketones, and mineral spirits are exempt. Aromatic and some ethylenic compounds are not exempt, and their use as solvents is therefore subject to regulation.
- **exit burr**
  - Burr formed on the surface at which the cutting tool or its teeth leaves the workpiece.
- **extreme-pressure lubricant**
  - A lubricant that imparts increased load-carrying capacity to rubbing surfaces under severe operating conditions. Extreme-pressure lubricants usually contain sulfur, halogens, or phosphorus. The term antiscuffing lubricant has been suggested as a replacement for extreme-pressure lubricant.
- **extrusion coating**
  - Using a resin to coat a substrate by extruding a thin film of molten resin and pressing it onto or into the substrate, or both, without the use of an adhesive.
- **extrusion pipe**
  - Same as coring (2).
- **F**
- **false Brinelling**
  - (1) Damage to a solid bearing surface characterized by indentations not caused by plastic deformation resulting from overload, but thought to be due to other causes such as fretting corrosion . (2) Local spots appearing when the protective film on a metal is broken continually by repeated impacts, usually in the presence of corrosive agents. The appearance is generally similar to that produced by Brinelling but corrosion products are usually visible. It may result from fretting corrosion. This term should be avoided when a more precise description is possible. False Brinelling (race fretting) can be distinguished from true Brinelling because in false Brinelling, surface material is removed so that original finishing marks are removed. The borders of a false Brinell mark are sharply defined, whereas a dent caused by a rolling element does not have sharp edges and the finishing marks are visible in the bottom of the dent.
- **fatigue**
  - The phenomenon leading to fracture under repeated or fluctuating stresses having a maximum value less than the ultimate tensile strength of the material.
- **fatigue striation**
  - Parallel lines frequently observed in electron microscope fractographs or fatigue fracture surfaces. The lines are transverse to the direction of local crack propagation; the distance between successive lines represents the advance of the crack front during the one cycle of stress variation.
- **fatigue wear**
  - (1) Removal of particles detached by fatigue arising from cyclic stress variations. (2) Wear of a solid surface caused by fracture arising from material fatigue. See also spalling .
- **feather burr**
  - A very fine or thin burr .
- **feather edge**
  - Same as feather burr except that feather edge can also refer to the ends of a lead-in or lead-out thread, which is a very thin machined ridge. Sometimes called a wire edge or whisker-type burr .
- **feed lines**
  - Linear marks on a machined or ground surface that are spaced at intervals equal to the feed per revolution or per stroke.

- **feed rate**
    - In thermal spraying, the rate at which material passes through the gun in a unit of time. A synonym for spray rate.
- **ferrite**
    - (1) A solid solution of one or more elements in body-centered cubic iron. Unless otherwise designated (for instance, as chromium ferrite), the solute is generally assumed to be carbon. On some equilibrium diagrams, there are two ferrite regions separated by an austenite area. The lower area is alpha ferrite; the upper, delta ferrite. If there is no designation, alpha ferrite is assumed. (2) An essentially carbon-free solid solution in which alpha iron is the solvent, and which is characterized by a body-centered cubic crystal structure. Fully ferritic steels are only obtained when the carbon content is quite low. The most obvious microstructural features in such metals are the ferrite grain boundaries.
- **ferrograph**
    - An instrument used to determine the size distribution of wear particles in lubricating oils of mechanical systems. The technique relies on the debris being capable of being attracted to a magnet.
- **filiform corrosion**
    - Corrosion that occurs under some coatings in the form of randomly distributed threadlike filaments.
- **film strength**
    - The relative resistance of a bisque to mechanical damage.
- **final polishing**
    - A polishing process in which the primary objective is to produce a final surface suitable for microscopic examination.
- **fine grinding**
    - See microgrinding .
- **fineness of enamel**
    - A measurement of the degree to which a frit has been milled in wet or dry form, usually expressed in grams residue retained on a certain type of mesh screen from a 50 $cm^3$ or a 100 g sample.
- **finish allowance**
    - (1) The amount of excess metal surrounding the intended final configuration of a formed part; sometimes called forging envelope, machining allowance, or cleanup allowance. (2) Amount of stock left on the surface of a casting for machining.
- **finish grinding**
    - The final grinding action on a workpiece, of which the objectives are surface finish and dimensional accuracy.
- **firing**
    - The controlled heat treatment of ceramic ware in a kiln or furnace to develop the desired final properties.
- **firing time**
    - The period during which the ware remains in the firing zone of the furnace to mature a ceramic or porcelain enamel coating.
- **fishscale**
    - A scaly appearance in a porcelain enamel coating in which the evolution of hydrogen from the base metal (iron or steel) causes loss of adhesion between the enamel and the base metal. Individual scales are usually small, but have been observed in sizes up to 25 mm (1 in.) or more in diameter. The scales are somewhat like blisters that have cracked part way around the perimeter but still remain attached to the coating around the rest of the perimeter. Delayed fishscaling occurs after the final porcelain enamel processing.
- **fixed-feed grinding**
    - Grinding in which the wheel is fed into the work, or vice versa, by given increments or at a given rate.
- **flaking**
    - (1) The removal of material from a surface in the form of flakes or scalelike particles. (2) A form of pitting resulting from fatigue. See also spalling .
- **flame cleaning**
    - Cleaning metal surfaces of scale , rust, dirt, and moisture by use of a gas flame.

- **flame hardening**
  - A process for hardening the surfaces of hardenable ferrous alloys in which an intense flame is used to heat the surface layers above the upper transformation temperature, whereupon the workpiece is immediately quenched.
- **flame spraying**
  - Thermal spraying in which a coating material is fed into an oxyfuel gas flame, where it is melted. Compressed gas may or may not be used to atomize the coating material and propel it onto the substrate. The sprayed material is originally in the form of wire or powder. Related terms are powder flame spraying and wire flame spraying . The term flame spraying is usually used when referring to a combustion-spraying process, as differentiated from plasma spraying .
- **flash coat**
  - A thin metallic coating usually less than 0.05 mm (0.002 in.) in thickness.
- **flash (or flash plate)**
  - A very thin electrodeposit, less than 2.5 μm (0.1 mil) thick. See also strike .
- **flash time**
  - The time between paint application and baking. Usually a considerable quantity of solvent is lost during this interval, and this solvent loss prevents popping problems in the oven.
- **flat honing**
  - A low-velocity abrading process, similar to honing , that uses a large, flat honing surface to simultaneously finish a large number of flat parts.
- **flocculate**
  - To aggregate into larger particles, to increase in size to the point where precipitation occurs.
- **flocculating**
  - In porcelain enameling, thickening the consistency of a slip by adding a suitable electrolyte .
- **flocking**
  - A method of coating by spraying finely dispersed textile powders or fibers.
- **floppers**
  - On metals, lines or ridges that are transverse to the direction of rolling and generally confined to the section midway between the edges of a coil as rolled.
- **flotation**
  - The rising of soil particles to the surface of cleaning baths for removal by skimming.
- **flow brightening**
  - (1) Melting of an electrodeposit, followed by solidification, especially of tin plate. See also reflowing . (2) Fusion (melting) of a chemically or mechanically deposited metallic coating on a substrate , particularly as it pertains to soldering.
- **flow coating**
  - The process of coating a metal shape by causing the slip to flow over its surface and then allowing the excess slip to drain.
- **flow lines**
  - (1) Texture showing the direction of metal flow during hot or cold working. Flow lines can often be revealed by etching the surface or a section of a metal part. (2) In mechanical metallurgy, paths followed by minute volumes of metal during deformation.
- **fluidized-bed coating**
  - A method of applying a thermoplastic or thermosetting resin coating to a heated article that is immersed in a dense-phase fluidized bed of powdered resin and thereafter heated in an oven to provide a smooth, pinhole -free coating.
- **fluorescent penetrant inspection**
  - Inspection using a fluorescent liquid that will penetrate any surface opening; after the surface has been wiped clean, the location of any surface flaws may be detected by the fluorescence, under ultraviolet light, of back-seepage of the fluid.
- **flux**
  - A substance that promotes fusion in a given ceramic mixture.
- **flux pit**
  - See dimple .
- **foam blanket**
  - An additive that forms a layer on the surface of electroplating baths that have poor anode /cathode efficiency and prevents any mist or spray from escaping.
- **foil**

    - Metal in sheet form less than 0.15 mm (0.006 in.) thick.
- **forged structure**
    - The macrostructure through a suitable section of a forging that reveals direction of working.
- **form grinding**
    - Grinding with a wheel having a contour on its cutting face that is a mating fit to the desired form.
- **Formvar replica**
    - A reproduction of a surface in a plastic Formvar film (used for the preparation of replicas or for specimen-supporting membranes).
- **free cyanide**
    - (1) True: The actual concentration of cyanide radical, or equivalent alkali cyanide, not combined in complex ions with metals in solution. (2) Calculated: The concentration of cyanide, or alkali cyanide, present in solution in excess of that calculated as necessary to form a specified complex ion with a metal or metals present in solution. (3) Analytical: The free cyanide content of a solution, as determined by a specified analytical method.
- **fretting**
    - A type of wear that occurs between tight-fitting surfaces subjected to cyclic relative motion of extremely small amplitude. Usually, fretting is accompanied by corrosion , especially of the very fine wear debris. Also referred to as fretting corrosion and false Brinelling (in rolling-element bearings).
- **fretting corrosion**
    - (1) The accelerated deterioration at the interface between contacting surfaces as the result of corrosion and slight oscillatory movement between the two surfaces. (2) A form of fretting in which chemical reaction predominates. Fretting corrosion is often characterized by the removal of particles and subsequent formation of oxides, which are often abrasive and so increase the wear. Fretting corrosion can involve other chemical reaction products, which may not be abrasive.
- **fretting wear**
    - Wear arising as a result of fretting .
- **friction**
    - The resisting force tangential to the common boundary between two bodies when, under the action of an external force, one body moves or tends to move relative to the surface of the other. The term friction is also used, incorrectly, to denote coefficient of friction . It is vague and imprecise unless accompanied by the appropriate modifiers, such as dry friction or kinetic friction. See also static coefficient of friction .
- **frit**
    - In porcelain enamel , the small friable particles produced by quenching a molten glassy material.
- **fused coating**
    - A metallic coating (usually tin or solder alloy) that has been melted and solidified, forming a metallurgical bond to the base metal .
- **fused spray deposit**
    - A self-fluxing spray deposit which is deposited by conventional thermal spraying and subsequently fused using either a heating torch or a furnace. The coatings are usually made of nickel and cobalt alloys to which hard particles, such as tungsten carbide, may be added for increased wear resistance.
- **fusing**
    - The melting of a metallic coating (usually electrodeposited) by means of a heat-transfer medium, followed by solidification.
- **fusion spray**
    - In thermal spraying, the process in which the coating is completely fused to the base metal , resulting in a metallurgically bonded, essentially void-free coating.
- **G**
- **galling**
    - (1) A condition whereby excessive friction between high spots results in localized welding with subsequent spalling and a further roughening of the rubbing surfaces of one or both of two mating parts. (2) A severe form of scuffing associated with gross damage to the surfaces or failure. Galling has been used in many ways; therefore, each time the term is encountered its meaning must be ascertained from the specific context of the usage. See also scoring and scuffing .

- **galvanic anode**
    - A metal which, because of its relative position in the galvanic series , provides sacrificial protection to metals that are more noble in the series, when coupled in an electrolyte . See also cathodic protection .
- **galvanic cell**
    - (1) An electrolytic cell capable of producing electrical energy by electrochemical action.
- **galvanic corrosion**
    - Corrosion associated with the current of a galvanic cell consisting of two dissimilar conductors in an electrolyte or two similar conductors in dissimilar electrolytes. Where the two dissimilar metals are in contact, the resulting reaction is referred to as couple action.
- **galvanic series**
    - A list of metals and alloys arranged according to their relative potentials in a given environment. Compare with electromotive series .
- **galvanizing**
    - Application of a coating of zinc to a metal surface using any of various processes.
- **galvanneal**
    - To produce a zinc-iron alloy coating on iron or steel by keeping the coating molten after hot-dip galvanizing until the zinc alloys completely with the base metal .
- **garnet**
    - A generic name for a related group of mineral silicates that have the general chemical formula $A_3B_2(\mathrm{SiO}_4)_3$, where $A$ can be calcium, magnesium, manganese, or ferrous iron, and $B$ can be aluminum, ferric iron, chromium, or titanium. Garnet is used for coating abrasive paper or cloth, for bearing pivots in watches, for electronics, and the finer specimens for gemstones. The hardness of garnet varies from Mohs 6 to 8 (1360 Knoop), the latter being used for abrasive applications.
- **gas atomization**
    - An atomization process whereby molten metal is broken up into particles by a rapidly moving inert gas stream. The resulting particles are nearly spherical with attached satellites.
- **gaseous corrosion**
    - Corrosion with gas as the only corrosive agent and without any aqueous phase on the surface of the metal. Also called dry corrosion. See also hot corrosion and sulfidation .
- **gas holes**
    - Holes in castings or welds that are formed by gas escaping from molten metal as it solidifies. Gas holes may occur individually, in clusters, or throughout the solidified metal.
- **gas lubrication**
    - A system of lubrication in which the shape and relative motion of the sliding surfaces cause the formation of a gas film having sufficient pressure to separate the surfaces.
- **gas porosity**
    - Fine holes or pores within a metal that are caused by entrapped gas or by the evolution of dissolved gas during solidification.
- **gassing**
    - The occurrence of surface defects such as poor gloss or blisters on fired enamel ware caused by bubbles from contamination or poor firing conditions.
- **gear (form) grinding**
    - Removal of material to obtain correct gear tooth form by grinding . This is one of the more exact methods of finishing gears.
- **gelatin replica**
    - A reproduction of a surface prepared in a film composed of gelatin. See also replica .
- **general corrosion**
    - (1) A form of deterioration that is distributed more or less uniformly over a surface. (2) Corrosion dominated by uniform thinning that proceeds without appreciable localized attack. See also uniform corrosion .
- **ghost lines**
    - Lines running parallel to the rolling direction that appear in a sheet metal panel when it is stretched. These lines may not be evident unless the panel has been sanded or painted. Not to be confused with leveler lines .
- **glass**
    - A term sometimes used for porcelain enamel or frit .

- **glass electrode**
  - A half cell in which the potential measurements are made through a glass membrane.
- **glaze**
  - (1) A ceramic coating matured to the glassy state on a formed ceramic article, or the material or mixture from which the coating is made. (2) In tribology, a ceramic or other hard, smooth surface film produced by sliding.
- **glazing**
  - Dulling the abrasive grains in the cutting face of a wheel during grinding .
- **gloss**
  - The shine or luster of a porcelain enamel or a painted surface.
- **gold filled**
  - Covered on one or more surfaces with a layer of gold alloy to form a clad or composite material. Gold-filled dental restorations are an example of such materials.
- **gouging abrasion**
  - A form of high-stress abrasion in which easily observable grooves or gouges are created on the surface. See also abrasion , and low-stress abrasion .
- **graded abrasive**
  - An abrasive powder in which the sizes of the individual particles are confined to certain specified limits. See also grit size .
- **graded coating**
  - A thermal spray coating consisting of several successive layers of different materials; for example, starting with 100% metal, followed by one or more layers of metal-ceramic mixtures, and finishing with 100% ceramic.
- **grain**
  - An individual crystal in a polycrystalline material; it may or may not contain twinned regions and subgrains.
- **grain boundary**
  - A narrow zone in a metal or ceramic corresponding to the transition from one crystallographic orientation to another, thus separating one grain from another; the atoms in each grain are arranged in an orderly pattern.
- **grain-boundary etching**
  - In metallography, the development of intersections of grain faces with the polished surface. Because of severe, localized crystal deformation, grain boundaries have higher dissolution potential than grains themselves. Accumulation of impurities in grain boundaries increases this effect.
- **grain coarsening**
  - A heat treatment that produces excessively large austenitic grains in metals.
- **grain-contrast etching**
  - In metallography, the development of grain surfaces lying in the polished surface of the microsection. These become visible through differences in reflectivity caused by reaction products on the surface or by differences in roughness.
- **grain flow**
  - Fiber-like lines on polished and etched sections of forgings caused by orientation of the constituents of the metal in the direction of working during forging. Grain flow produced by proper die design can improve required mechanical properties of forgings. See also flow lines and forged structure .
- **grain growth**
  - (1) An increase in the average size of the grains in polycrystalline material, usually as a result of heating at elevated temperature. (2) In polycrystalline materials, a phenomenon occurring fairly close below the melting point in which the larger grains grow still larger while the smallest ones gradually diminish and disappear. See also recrystallization .
- **graining**
  - The process of vigorously stirring or agitating a partially solidified material to develop large grains having a thin oxide coating.
- **grain refinement**
  - The manipulation of the solidification process to cause more (and therefore smaller) grains to be formed and/or to cause the grains to form in specific shapes. The term refinement is usually used to denote a chemical addition to the metal but can refer to control of the cooling rate.

- **grain size**
    - (1) For metals, a measure of the areas or volumes of grains in a polycrystalline material, usually expressed as an average when the individual sizes are fairly uniform. In metals containing two or more phases, grain size refers to that of the matrix unless otherwise specified. Grain size is reported in terms of number of grains per unit area or volume, in terms of average diameter, or as a grain-size number derived from area measurements. (2) For grinding wheels, see preferred term grit size .
- **graphitic corrosion**
    - Corrosion of gray iron in which the iron matrix is selectively leached away, leaving a porous mass of graphite behind; it occurs in relatively mild aqueous solutions and on buried pipe and fittings.
- **graphitization**
    - The formation of graphite in iron or steel. Where graphite is formed during solidification, the phenomenon is termed primary graphitization; where formed later by heat treatment, secondary graphitization.
- **greaseless compounds**
    - A variety of buffing compounds in which the abrasive is blended with water and gelatin glue rather that tallow, wax, or oil.
- **green rot**
    - A form of high-temperature attack on stainless steels, nickel-chromium alloys and nickel-chromium-iron alloys subjected to simultaneous oxidation and carburization. Basically, attack occurs first by precipitation of chromium as chromium carbide, then by oxidation of the carbide particles.
- **grindability**
    - A value that represents the efficiency of the grinding process. Grindability = (G-ratio)/(specific energy), where G-ratio = (volume of material removed)/(volume of the grinding wheel used) and specific energy = (grinding power)/(material removal rate).
- **grinding**
    - Removing material from a workpiece with a grinding wheel or abrasive belt. See also various grinding techniques: surface , creep-feed , cylindrical , internal , centerless , gear (form) , and thread .
- **grinding stress**
    - Residual stress , generated by grinding, in the surface layer of work. It may be tensile or compressive, or both.
- **grit blasting**
    - Abrasive blasting with small irregular pieces of steel, malleable cast iron, or hard nonmetallic materials.
- **grit size**
    - Nominal size of abrasive particles in a grinding wheel, corresponding to the number of openings per linear inch in a screen through which the particles can pass.
- **groove**
    - In thermal spraying, a method of surface roughening in which grooves are made and the original surface roughened and spread. Also called rotary roughening.
- **ground coat**
    - (1) A porcelain enamel applied directly to the base metal to function as an intermediate layer between the metal and the cover coat. (2) On sheet steel, a porcelain enamel coating containing adherence-promoting agents that may be used either as an intermediate layer between the metal and the cover coat or as a single coat over the base metal.
- **H**
- **hairline craze**
    - Multiple fine surface separation cracks in composites that exceed 6 mm ( in.) in length and do not penetrate in depth the equivalent of a full ply of reinforcement. See also crazing .
- **half cell**
    - An electrode immersed in a suitable electrolyte . It may be designed to yield a known constant potential, in which case unknown potentials may be measured against it; for example, the calomel half cell .
- **hanging burr**

    - Loose or flexible portions of a burr that are not firmly attached to the workpiece (i.e., hanging from the workpiece). Sometimes called a flag.
- **hard chromium**
    - Chromium electrodeposited for engineering purposes (such as to increase the wear resistance of sliding metal surfaces) rather than as a decorative coating. It is usually applied directly to base metal and is customarily thicker (>1.2 μm, or 0.05 mils) than a decorative deposit, but not necessarily harder.
- **hard coating**
    - In anodizing aluminum, an anodic oxide coating on aluminum with a higher apparent density and thickness and a greater resistance to wear than conventional coatings.
- **hardenability**
    - The relative ability of a ferrous alloy to form martensite when quenched from a temperature above the upper critical temperature. Hardenability is commonly measured as the distance below a quenched surface at which the metal exhibits a specific hardness (50 HRC, for example) or a specific percentage of martensite in the microstructure.
- **hardening**
    - Increasing hardness of metals by suitable treatment, usually involving heating and cooling. When applicable, the following more specific terms should be used: age hardening , case hardening , flame hardening , induction hardening , precipitation hardening and quench hardening .
- **hardfacing**
    - The application of a hard, wear-resistant material to the surface of a component by welding, spraying, or allied welding processes to reduce wear or loss of material by abrasion, impact, erosion, galling , and cavitation . See also surfacing .
- **hardfacing alloys**
    - Wear-resistant materials available as bare welding rod, flux-coated rod, long-length solid wires, long-length tubular wires, or powders that are deposited by hardfacing . Hardfacing materials include a wide variety of alloys, ceramics, and combinations of these materials. Conventional hardfacing alloys are normally classified as steels or low-alloy ferrous materials, chromium white irons, high-alloy ferrous materials, carbides, nickel-base alloys, or cobalt-base alloys.
- **hardness**
    - A measure of the resistance of a material to surface indentation or abrasion; may be thought of as a function of the stress required to produce some specified type of surface deformation. There is no absolute scale for hardness; therefore, to express hardness quantitatively, each type of test has its own scale of arbitrarily defined hardness. Indentation hardness can be measured by Brinell, Rockwell, Vickers , Knoop, and Scleroscope hardness tests.
- **hardness profile**
    - Hardness as a function of distance from a fixed reference point (usually from the surface).
- **Haring cell**
    - A rectangular box of nonconducting material, with principal and auxiliary electrodes so arranged as to permit estimation of throwing power or electrode polarizations and potentials between them.
- **heat-affected zone**
    - That portion of the base metal that was not melted during brazing, cutting, or welding, but whose microstructure and mechanical properties were altered by the heat.
- **heat checking**
    - A process in which fine cracks are formed on the surface of a body in sliding contact due to the buildup of excessive frictional heat.
- **healed-over scratch**
    - A scratch in a metallic object that occurred in an earlier mill operation and was partially masked in subsequent rolling. It may open up during forming.
- **heat mark**
    - Extremely shallow depression or groove in the surface of a plastic visible because of a sharply defined rim or a roughened surface.
- **hiding power**
    - The ability of a paint to mask the color or pattern of a surface. Usually expressed as $ft^2$/gal or $m^2$/L.
- **highlighting**

  - Buffing or polishing selected areas of a complex shape to increase the luster or change the color of those areas.
- **highly deformed layer**
  - In tribology, a layer of severely plastically deformed material that results from the shear stresses imposed on that region during sliding contact. See also Beilby layer and white etching layer .
- **high-solids paint**
  - Paint containing 35 to 80% solids. These products have become popular because of the reduction in solvent emissions associated with their use.
- **high-stress abrasion**
  - A form of abrasion in which relatively large cutting forces are imposed on the particles or protuberances causing the abrasion, and that produces significant cutting and deformation of the wearing surface. In metals, high-stress abrasion can result in significant surface strain hardening. This form of abrasion is common in mining and agricultural equipment, and in highly loaded bearings where hard particles are trapped between mating surfaces. See also low-stress abrasion .
- **high-temperature hydrogen attack**
  - A loss of strength and ductility of steel by high-temperature reaction of absorbed hydrogen with carbides in the steel resulting in decarburization and internal fissuring.
- **hinge area**
  - The juncture of a hanging burr with the more rigidly adhered portion of a burr .
- **Hohman A-6 wear machine**
  - A widely used type of wear and friction testing machine in which a rotating ring specimen is squeezed between two diametrically opposed rub blocks. This design is said to eliminate shaft flexure such as that found in other machines whose load application from the rub block to the ring is from one side only. Block geometry can be changed from flat to conforming or V-block. This type of machine is designed for use with either lubricated or unlubricated specimens.
- **holidays**
  - Discontinuities in a coating (such as porosity, cracks, gaps, and similar flaws) that allow areas of base metal to be exposed to any corrosive environment that contacts the coated surface.
- **homogeneous carburizing**
  - Use of a carburizing process to convert a low-carbon ferrous alloy to one of uniform and higher carbon content throughout the section.
- **honing**
  - A low-speed finishing process used chiefly to produce uniform high dimensional accuracy and fine finish, most often on inside cylindrical surfaces. In honing, very thin layers of stock are removed by simultaneously rotating and reciprocating a bonded abrasive stone or stick that is pressed against the surface being honed with lighter force than is typical of grinding .
- **hot corrosion**
  - An accelerated corrosion of metal surfaces that results from the combined effect of oxidation and reactions with sulfur compounds and other contaminants, such as chlorides, to form a molten salt on a metal surface that fluxes, destroys, or disrupts the normal protective oxide. See also gaseous corrosion .
- **hot dip**
  - Covering a surface by dipping the surface to be coated into a molten bath of the coating material. See also hot dip coating .
- **hot dip coating**
  - A metallic coating obtained by dipping the base metal into a molten metal.
- **hot etching**
  - In metallography, development and stabilization of the microstructure at elevated temperature in etchants or gases.
- **hot shortness**
  - A tendency for some alloys to separate along grain boundaries when stressed or deformed at temperatures near the melting point. Hot shortness is caused by a low-melting constituent, often present only in minute amounts, that is segregated at grain boundaries.
- **Hull cell**
  - A trapezoidal box of nonconducting material with electrodes arranged to permit observation of cathodic or anodic effects over a wide range of current densities.
- **hydrogen damage**

  - A general term for the embrittlement , cracking, blistering , and hydride formation that can occur when hydrogen is present in some metals.
- **hydrogen embrittlement**
  - A process resulting in a decrease of the toughness or ductility of a metal due to the presence of atomic hydrogen. Hydrogen embrittlement has been recognized classically as being of two types. The first, known as internal hydrogen embrittlement, occurs when the hydrogen enters molten metal which becomes supersaturated with hydrogen immediately after solidification. The second type, environmental hydrogen embrittlement, results from hydrogen being absorbed by solid metals. This can occur during elevated-temperature thermal treatments and in service during electroplating, contact with maintenance chemicals, corrosion reactions, cathodic protection , and operating in high-pressure hydrogen. In the absence of residual stress or external loading, environmental hydrogen embrittlement is manifested in various forms, such as blistering , internal cracking, hydride formation, and reduced ductility. With a tensile stress or stress-intensity factor exceeding a specific threshold, the atomic hydrogen interacts with the metal to induce subcritical crack growth leading to fracture. In the absence of a corrosion reaction (polarized cathodically), the usual term used is hydrogen-assisted cracking (HAC) or hydrogen stress cracking (HSC). In the presence of active corrosion, usually as pits or crevices (polarized anodically), the cracking is generally called stress-corrosion cracking (SCC), but should more properly be called hydrogen-assisted stress-corrosion cracking (HSCC). Thus, HSC and electrochemically anodic SCC can operate separately or in combination. In some metals, such as high-strength steels, the mechanism is believed to be all, or nearly all, HSC. The participating mechanism of HSC is not always recognized and may be evaluated under the generic heading of SCC.
- **hydrophilic**
  - (1) Tending to absorb water. (2) Tending to concentrate in the aqueous phase.
- **hydrophobic**
  - (1) Tending to repel water. (2) Lacking an affinity for water.
- **I**
- **identification etching**
  - Etching to expose particular microconstituents; all others remain unaffected.
- **immersion cleaning**
  - Cleaning in which the work is immersed in a liquid solution.
- **immersion coating**
  - A coating produced in a solution by chemical or electrochemical action without the use of external current.
- **immersion etching**
  - Method in which a microsection is dipped face up into etching solution and is moved around during etching. This is the most common etching method.
- **immersion plate**
  - A metallic deposit produced by a displacement reaction in which one metal displaces another from solution, for example: $Fe + Cu^{2+} \rightarrow Cu + Fe^{2+}$.
- **immersion plating**
  - Depositing a metallic coating on a metal immersed in a liquid solution, without the aid of an external electric current. Also called dip plating.
- **impact wear**
  - Wear of a solid surface resulting from repeated collisions between that surface and another solid body. The term erosion (erosive) wear is preferred in the case of multiple impacts and when the impacting body or bodies are very small relative to the surface being impacted.
- **impingement**
  - A process resulting in a continuing succession of impacts between liquid or solid particles and a solid surface. In preferred usage, impingement also connotes that the impacting particles are smaller than the solid surface, and that the impacts are distributed over the surface or a portion of the surface. If all impacts are superimposed on the same point or zone, then the term repeated impact is preferred.
- **impingement attack**
  - Corrosion associated with turbulent flow of liquid. May be accelerated by entrained gas bubbles. See also erosion-corrosion .
- **impregnation**

    - (1) Treatment of porous castings with a sealing medium to stop pressure leaks. (2) The process of filling the pores of a sintered compact, usually with a liquid such as a lubricant. (3) The process of mixing particles of a nonmetallic substance in a cemented carbide matrix, as in diamond-impregnated tools.
- **impression replica**
    - A surface replica made by impression. See also replica .
- **inclusions**
    - (1) A physical and mechanical discontinuity occurring within a material or part, usually consisting of solid, encapsulated foreign material. Inclusions are often capable of transmitting some structural stresses and energy fields, but to a noticeably different degree than from the parent material. (2) Particles of foreign material in a metallic matrix. The particles are usually compounds, such as oxides, sulfides, or silicates, but may be of any substance that is foreign to (and essentially insoluble in) the matrix. See also stringer .
- **induction hardening**
    - A surface-hardening process in which only the surface layer of a suitable ferrous workpiece is heated by electromagnetic induction to above the upper critical temperature and immediately quenched.
- **inhibitor**
    - A substance used to reduce the rate of a chemical or electrochemical reaction, commonly corrosion or pickling .
- **inorganic**
    - Being or composed of matter other than hydrocarbons and their derivatives, or matter that is not of plant or animal origin.
- **interdendritic corrosion**
    - Corrosive attack that progresses preferentially along interdendritic paths. This type of attack results from local differences in composition, such as coring commonly encountered in alloy castings.
- **interface**
    - The boundary between any two phases. Among the three phases (gas, liquid, and solid), there are five types of interfaces: gas-liquid, gas-solid, liquid-liquid, liquid-solid, and solid-solid.
- **intergranular corrosion**
    - Corrosion occurring preferentially at grain boundaries , usually with slight or negligible attack on the adjacent grains. See also interdendritic corrosion .
- **intergranular cracking**
    - Cracking or fracturing that occurs between the grains or crystals in a polycrystalline aggregate. Also called intercrystalline cracking. Contrast with transgranular cracking .
- **intergranular fracture**
    - Brittle fracture of a polycrystalline material in which the fracture is between the grains, or crystals, that form the material. Also called intercrystalline fracture. Contrast with transgranular fracture .
- **intergranular stress-corrosion cracking (IGSCC)**
    - Stress-corrosion cracking in which the cracking occurs along grain boundaries .
- **internal grinding**
    - Grinding an inside of a rotating workpiece by use of a wheel spindle that rotates and reciprocates through the length or depth of the hole being ground.
- **internal oxidation**
    - The formation of isolated particles of corrosion products beneath the metal surface. This occurs as the result of preferential oxidation of certain alloy constituents by inward diffusion of oxygen, nitrogen, sulfur, and so forth. Also called subscale formation.
- **internal shrinkage**
    - A void or network of voids within a casting caused by inadequate feeding of that section during solidification.
- **interrupted-current plating**
    - Plating in which the flow of current is discontinued for periodic short intervals to decrease anode polarization and elevate the critical current density . It is most commonly used in cyanide copper plating.
- **intumescence**

    - The swelling or bubbling of a coating usually because of heating (term currently used in space and fire protection applications).
- **ion**
    - An electrified portion of matter of atomic or molecular dimensions.
- **ion beam assisted deposition**
    - An ion implantation technique in which ion beams are combined with physical vapor deposition .
- **ion beam mixing**
    - An ion implantation technique in which deposited layers (electroplating, sputtering) tens or hundreds of nanometers thick are mixed and bonded to the substrate by an argon or xenon ion beam.
- **ion beam sputtering**
    - An ion implantation technique in which an ion beam of argon or xenon directed at a target sputters material from the target to a substrate ; the sputtered material arrives at the substrate with enough energy to promote good adhesion of the coating to substrate.
- **ion carburizing**
    - A method of surface hardening in which carbon ions are diffused into a workpiece in a vacuum through the use of high-voltage electrical energy. Synonymous with plasma carburizing or glow-discharge carburizing.
- **ion etching**
    - Surface removal by bombarding with accelerated ions in vacuum (1 to 10 kV).
- **ion implantation**
    - The process of modifying the physical or chemical properties of the near surface of a solid (target) by embedding appropriate atoms into it from a beam of ionized particles. The properties to be modified may be electrical, optical, or mechanical, and they may relate to the semiconducting behavior of the material or its corrosion behavior. The solid may be crystalline, polycrystalline, or amorphous and need not be homogeneous. Related techniques are also used in conjunction with ion implantation to increase the ratio of material introduced into the substrate per unit area, to provide appropriate mixtures of materials, or to overcome other difficulties involved in surface modification by ion implantation alone. See also specific techniques: ion beam sputtering , ion beam mixing , plasma ion deposition , and ion beam assisted deposition .
- **ion nitriding**
    - A method of surface hardening in which nitrogen ions are diffused into a workpiece in a vacuum through the use of high-voltage electrical energy. Synonymous with plasma nitriding or glow-discharge nitriding.
- **ion plating**
    - A generic term applied to atomistic film deposition processes in which the substrate surface and/or the depositing film is subjected to a flux of high-energy particles (usually gas ions) sufficient to cause changes in the interfacial region or film properties. Such changes may be in film adhesion to the substrate, film morphology, film density, film stress, or surface coverage by the depositing film material.
- **ion-scattering spectrometry**
    - A technique to elucidate composition and structure of the outermost atomic layers of a solid material, in which principally mono-energetic, singly charged, low-energy (less than 10 keV) probe ions are scattered from the surface and are subsequently detected and recorded as a function of the energy.
- **isocorrosion diagram**
    - A graph or chart that shows constant corrosion behavior with changing solution (environment) composition and temperature.
- **Izod test**
    - A type of impact test in which a V-notched specimen, mounted vertically, is subjected to a sudden blow delivered by the weight at the end of a pendulum arm. The energy required to break off the free end is a measure of the impact strength or toughness of the material. Contrast with Charpy test .
- **J**
- **jet vapor deposition**
    - A vacuum deposition method in which evaporated atoms or molecules are "seeded" into a supersonic jet flow of inert gas into a rapidly pumped vacuum chamber. The jet flow transports the atoms and molecules to the substrate surface, where they are deposited.

- **Jominy test**
  - A laboratory procedure for determining the hardenability of a steel or other ferrous alloy. Hardenability is determined by heating a standard specimen above the upper critical temperature, placing the hot specimen in a fixture so that a stream of cold water impinges on one end, and, after cooling to room temperature is completed, measuring the hardness near the surface of the specimen at regularly spaced intervals along its length. The data are normally plotted as hardness versus distance from the quenched end. Also called the end-quench hardenability test.
- **K**
- **karat**
  - A 24th part by weight; thus 18-karat gold is 18/24 pure.
- **knife coating**
  - A method of coating a substrate (usually paper or fabric) in which the substrate, in the form of a continuous moving web, is coated with a material, the thickness of which is controlled by an adjustable knife or bar set at a suitable angle to the substrate.
- **knife-line attack**
  - Intergranular corrosion of an alloy, usually stabilized stainless steel, along a line adjoining or in contact with a weld after heating into the sensitization temperature range.
- **knurling**
  - Impressing a design into a metallic surface, usually by means of small, hard rollers that carry the corresponding design on their surfaces.
- **L**
- **lacquer**
  - (1) A coating formulation based on thermoplastic film-forming material dissolved in organic solvent. The coating dries primarily by evaporation of the solvent. Typical lacquers include those based on lac, nitrocellulose, other cellulose derivatives, vinyl resins, acrylic resins, and so forth. (2) In lubrication, a deposit resulting from the oxidation and/or polymerization of fuels and lubricants when exposed to high temperatures. Softer deposits are described as varnishes or gums.
- **lamination**
  - In porcelain enamel , a defect resulting from bloating of a sheet steel piece during firing due to a separation in the steel structure.
- **lap**
  - A surface imperfection, with the appearance of a seam , caused by hot metal, fins, or sharp corners being folded over and then being rolled or forged into the surface but without being welded.
- **lapping**
  - Rubbing two surfaces together, with or without abrasives, for the purpose of obtaining extreme dimensional accuracy or superior surface finish .
- **laser surface processing**
  - The use of lasers with continuous outputs of 0.5 to 10 kW to modify the metallurgical structure of a surface and to tailor the surface properties without adversely affecting the bulk properties. The surface modification can take the following three forms. The first is transformation hardening in which a surface is heated so that thermal diffusion and solid-state transformations can take place. The second is surface melting, which results in a refinement of the structure due to the rapid quenching from the melt. The third is surface (laser) alloying, in which alloying elements are added to the melt pool to change the composition of the surface. The novel structures produced by laser surface melting and alloying can exhibit improved electrochemical and tribological behavior.
- **latent solvent**
  - A liquid that cannot itself dissolve a binder but increases the tolerance of the paint for a diluent.
- **lath martensite**
  - Martensite formed partly in steels containing less than approximately 1.0% C and solely in steels containing less than approximately 0.5% C as parallel arrays of packets of lath-shape units 0.1 to 0.3 μm (4 to 12 μin.) thick.
- **lay**
  - Direction of predominant surface pattern remaining after cutting, grinding , lapping , or other processing.
- **ledeburite**

    - The eutectic of the iron-carbon system, the constituents of which are austenite and cementite . The austenite decomposes into ferrite and cementite on cooling below $Ar_1$, the temperature at which transformation of austenite to ferrite or ferrite plus cementite is completed during cooling.
- **leveler lines**
    - Lines on sheet or strip running transverse to the direction of roller leveling. These lines may be seen upon stoning or light sanding after leveling (but before drawing) and can usually be removed by moderate stretching.
- **leveling action**
    - Ability of a plating solution to produce a plated surface smoother than that of the substrate .
- **linishing**
    - A method of finishing by grinding on a continuous abrasive belt.
- **liquid carburizing**
    - Surface hardening of steel by immersion into a molten bath consisting of cyanides and other salts.
- **liquid honing**
    - Producing a finely polished finish by directing an air-ejected chemical emulsion containing fine abrasives against the surface to be finished.
- **liquid nitriding**
    - A method of surface hardening in which ferrous metal parts are exposed to molten nitrogen-bearing fused-salt baths containing cyanates, cyanides, or both at subcritical temperatures. A typical commercial bath is a mixture of sodium and potassium salts. The anions are 30 to 40% cyanate, 1 to 5% cyanide, and the balance carbonate. The operating temperature for these salt baths is 510 to 595 °C (950 to 1100 °F).
- **liquid nitrocarburizing**
    - A nitrocarburizing process utilizing molten liquid salt baths below the lower critical temperature. Liquid nitrocarburizing processes are used to improve wear resistance and fatigue properties of steels and cast irons. See liquid nitriding .
- **liquid penetrant inspection**
    - A type of nondestructive inspection that locates discontinuities that are open to the surface of a metal by first allowing a penetrating dye or fluorescent liquid to infiltrate the discontinuity, removing the excess penetrant, and then applying a developing agent that causes the penetrant to seep back out of the discontinuity and register as an indication. Liquid penetrant inspection is suitable for both ferrous and nonferrous materials, but is limited to the detection of open surface discontinuities in nonporous solids.
- **localized corrosion**
    - Corrosion at discrete sites, for example, crevice corrosion , pitting , and stress-corrosion cracking .
- **long-term etching**
    - Etching times of a few minutes to hours.
- **lower critical temperature**
    - The temperature below which ferrite is the stable phase. Also called the $A_1$ temperature.
- **low-stress abrasion**
    - A form of abrasion in which relatively low contact pressures on the abrading particles or protuberances cause only fine scratches and microscopic cutting chips to be produced. See also high-stress abrasion .
- **lubricant**
    - Any substance interposed between two surfaces in relative motion for the purpose of reducing the friction or wear between them. This definition implies intentional addition of a substance to an interface; however, species such as oxides and tarnishes on certain metals can also act as lubricants even though they were not added to the system intentionally.
- **lubricious (lubricous)**
    - Relating to a substance or surface condition that tends to produce relatively low friction.
- **Lüders lines**
    - Elongated surface markings or depressions in sheet metal, often visible with the unaided eye, caused by discontinuous (inhomogeneous) yielding. Also known as Lüders bands, Hartmann lines, Piobert lines, or stretcher strains .
- **lumps**
    - See beads .
- **luster finish**

    - A bright as-rolled finish, produced on ground metal rolls; it is suitable for decorative painting or plating, but usually must undergo additional surface preparation after forming.
- **M**
- **macroetching**
    - Etching a metal surface to accentuate gross structural details, such as grain flow , segregation, porosity, or cracks, for observation by the unaided eye or at magnifications to 25×.
- **machining**
    - Removing material from a part, usually using a cutting tool, and usually using a power-driven machine.
- **mandrel**
    - A form used as a cathode in electroforming ; a mold or matrix.
- **man-made (synthetic) diamond**
    - A manufactured diamond, darker, blockier, and considered to be more friable than most natural diamonds.
- **mask**
    - A device for protecting a surface from the effects of blasting and/or coating. Masks are generally either reusable or disposable.
- **mass finishing**
    - A group of finishing methods that involve loading of components to be finished into a container together with some abrasive media, water, and compound, and then applying some action to the container in order to cause the media and parts to rub against one another, thereby improving the surface of the components. Mass finishing processes include barrel finishing , tumbling , and vibratory finishing .
- **material removal rate**
    - In grinding , the volume of material removed in a unit of time. Material removal rate = work speed × depth of cut × width of cut.
- **matte finish**
    - (1) A metal finish produced by using a sand blast or acid dip, creating a frosted and nonreflective surface that is free of parallel lines. (2) In porcelain enamel , a slightly roughened surface lacking in luster.
- **mechanical activation**
    - The acceleration or initiation of a chemical reaction by mechanical exposure of a nascent solid surface. Metal cutting (machining) is an effective method of exposing large areas of fresh surface.
- **mechanical bond**
    - The adherence of a thermal sprayed deposit to a roughened surface by the mechanism of particle interlocking.
- **mechanical cleaning**
    - Process for removing dirt, scale, or other deposits from surfaces through the use of mechanical means such as abrasive blasting .
- **mechanical plating**
    - A process whereby hard, small spherical objects (such as glass shot) are tumbled against a metallic surface in the presence of finely divided metal powder (such as zinc dust) and appropriate chemicals for the purpose of covering such surfaces with metal.
- **mechanical polishing**
    - A process that yields a specularly reflecting surface entirely by the action of machining tools, which are usually the points of abrasive particles suspended in a liquid among the fibers of a polishing cloth.
- **mechanical wear**
    - Removal of material due to mechanical processes under conditions of sliding, rolling, or repeated impact. The term mechanical wear includes adhesive wear , abrasive wear , and fatigue wear . Compare with corrosive wear and thermal wear .
- **metallic bond**
    - The principal bond between metal atoms, which arises from the increased spatial extension of valence-electron wave functions when an aggregate of metal atoms is brought close together. An example is the bond formed between base metals and filler metals in all welding processes.
- **metallic wear**

    - Typically, wear due to rubbing or sliding contact between metallic materials that exhibits the characteristics of severe wear, for example, significant plastic deformation , material transfer, and indications that cold welding of asperities possibly has taken place as part of the wear process. See also adhesive wear and severe wear .
- **metallizing**
    - (1) Application of an electrically conductive metallic layer to the surface of nonconductors. (2) The application of metallic coatings by nonelectrolytic procedures such as spraying of molten metal and deposition from the vapor phase.
- **metallurgical bond**
    - Adherence of a coating to the base material characterized by diffusion, alloying, or intermolecular or intergranular attraction at the interface between the coating and the base material.
- **metallurgical burn**
    - Modification of the microstructure near the contact surface due to frictional temperature rise.
- **metal penetration**
    - A surface condition in castings in which metal or metal oxides have filled voids between sand grains without displacing them.
- **metal shadowing**
    - The enhancement of contrast in a microscope by vacuum deposition of a dense metal onto the specimen at an angle generally not perpendicular to the surface of the specimen. See also shadowing .
- **metal spraying**
    - Coating metal objects by spraying molten metal against their surfaces. See also thermal spraying and flame spraying .
- **microfinishing grinding**
    - See microgrinding .
- **microgrinding**
    - A precision grinding process that uses extremely fine abrasive (50 μm and finer). Also known as fine grinding and microfinishing grinding.
- **microstructure**
    - The structure of an object, organism, or material as revealed by a microscope at magnifications greater than 25×.
- **microthrowing power**
    - The ability of a plating solution or a specified set of plating conditions to deposit metal in pores or scratches.
- **mil**
    - One thousandth of an inch 0.001 = 25.4 μm.
- **mild wear**
    - A form of wear characterized by the removal of material in very small fragments. Mild wear is an imprecise term, frequently used in research, and contrasted with severe wear . In fact, the phenomena studied usually involve the transition from mild to severe wear and the factors that influence this transition. Mild wear may be appreciably greater than can be tolerated in practice. With metallic sliders, mild wear debris usually consists of oxide particles. See also normal wear and severe wear .
- **mill addition**
    - Any material added to the ball milling charge of a frit .
- **mill finish**
    - A nonstandard (and typically nonuniform) surface finish on mill products that are delivered without being subjected to a special surface treatment (other than a corrosion-preventive treatment) after the final working or heat-treating step.
- **milling**
    - Using a rotary tool with one or more teeth that engage the workpiece and remove material as the workpiece moves past the rotating cutter.
- **mill scale**
    - The heavy oxide layer that forms during the hot fabrication or heat treatment of metals.
- **minimized spangle**
    - A hot dip galvanized coating of very small grain size, which makes the spangle less visible when the part is subsequently painted.
- **mirror-finish grinding**

  - A class of grinding processes in which extremely fine abrasive particles are used to achieve reflective surfaces of precise geometry. These methods are used in finishing such items as molds and dies used for making contact lenses and optical components.
- **mold coating**
  - (1) Coating to prevent surface defects on permanent mold castings and die castings. (2) Coating on sand molds to prevent metal penetration and to improve metal finish. Also called mold facing or mold dressing.
- **molecular beam epitaxy**
  - A vacuum deposition process used to form epitaxial films on semiconductor materials.
- **molten metal flame spraying**
  - A thermal spraying process variation in which the metallic material to be sprayed is in the molten condition. See also flame spraying .
- **molten salt bath**
  - Same as salt bath .
- **morphology**
  - The characteristic shape, form, or surface texture or contours of the crystals, grains , or particles of (or in) a material, generally on a microscopic scale.
- **motor-generator (MG set)**
  - A machine that consists of one or more motors mechanically coupled to one or more generators. In plating , such a machine in which the generator delivers dc of appropriate amperage and voltage.
- **multilayer coating**
  - Same as composite coating .
- **multiple etching**
  - Sequential etching of a microsection, with specific reagents attacking distinct microconstituents.
- **N**
- **negative replica**
  - A method of reproducing a surface obtained by the direct contact of the replicating material with the specimen. Using this technique, the contour of the replica surface is reversed with respect to that of the original. See also replica .
- **neutralization**
  - The balancing of acidity and alkalinity by interaction. In the context of cleaning, the removal of acid soils by alkalines and alkaline soils by acids.
- **nitriding**
  - Introducing nitrogen into the surface layer of a solid ferrous alloy by holding at a suitable temperature (below $Ac_1$ for ferritic steels) in contact with a nitrogenous material, usually ammonia or molten salt of appropriate composition. Quenching is not required to produce a hard case. See also aerated bath nitriding , bright nitriding , liquid nitriding , and nitrocarburizing .
- **nitrocarburizing**
  - Any of several processes in which both nitrogen and carbon are absorbed into the surface layers of a ferrous material from a molten salt or gaseous atmosphere at temperatures below the lower critical temperature and, by diffusion, create a concentration gradient. Nitrocarburizing is performed primarily to provide an antiscuffing surface layer and to improve fatigue resistance. Compare with carbonitriding .
- **noble metal**
  - A metal that does not readily tend to furnish ions, and therefore does not dissolve readily, nor easily enter into such reactions as oxidation, etc. Contrast with base metal .
- **nodular pearlite**
  - Pearlite that has grown as a colony with an approximately spherical morphology.
- **nonionic detergent**
  - A detergent that produces aggregates of electrically neutral molecules with colloidal properties.
- **normal wear**
  - Loss of material within the design limits expected for the specific intended application. The concept of normal wear depends on economic factors, such as the expendability of a worn part.
- **notch sensitivity**
  - The extent to which the sensitivity of a material to fracture is increased by the presence of a stress concentration, such as a notch, a sudden change in cross section, a crack, or a scratch. Low notch

sensitivity is usually associated with ductile materials, and high notch sensitivity is usually associated with brittle materials.

- **nucleation**
  - In plating of plastics, the preplating step in which a catalytic material, often a palladium or gold compound, is absorbed on a surface of the plastic substrate to act as sites for initial stages of deposition.
- **O**
- **oblique evaporation shadowing**
  - The condensation of evaporated material onto a substrate that is inclined to the direct line of the vapor stream to produce shadows. See also shadowing .
- **oil-based paints**
  - Paints with films that form solids by the air-induced cross-linking of certain unsaturated plant oils known as drying oils. Oxygen is consumed in the process.
- **one-coat ware**
  - (1) Workpieces finished in a single coat of porcelain enamel . Also known as one-coat work. (2) Sometimes a contraction of one-cover-coat ware in which the finish consists of a single cover coat applied over the ground coat.
- **opacifier**
  - A material that imparts or increases the diffuse reflectance of porcelain enamel .
- **opacity**
  - In porcelain enamel , the property of reflecting light diffusely and nonselectively.
- **orange peel**
  - (1) In painting, a pebbled film surface caused by too rapid drying after spraying, by failure of the coating material to exhibit the desired leveling effects, or by uneven flow (application) in roller coating techniques. (2) In porcelain enamel , a surface condition characterized by an irregular waviness that resembles an orange skin in texture; sometimes considered a defect. (3) A surface roughening in the form of a pebble-grained pattern that occurs when a metal of unusually coarse grain size is stressed beyond its elastic limit. Also called pebbles and alligator skin.
- **organic solvent**
  - See chlorinated solvent .
- **organic zinc-rich paint**
  - Coating containing zinc powder pigment and an organic resin.
- **overfiring**
  - In porcelain enamel , a condition sometimes occurring during firing when the temperature of the furnace is too high or the ware is left in the furnace for a greater length of time than necessary.
- **overpickling**
  - Using pickling solutions of greater strength or at higher temperature than recommended, or allowing the workpiece to remain in the pickling tanks for a greater length of time than necessary. Overpickling can lead to blistering of subsequently applied porcelain enamel finishes.
- **oxidation**
  - A reaction in which electrons are removed from a reactant. Sometimes, more specifically the combination of a reactant with oxygen. Contrast with reduction .
- **oxidation reduction**
  - To change the valence state of oxide scale and rust to soluble forms for removal from metal surfaces. Rust is chemically changed in this way to a more soluble form, easily dissolved by acids.
- **oxidative wear**
  - (1) A corrosive wear process in which chemical reaction with oxygen or oxidizing environment predominates. (2) A type of wear resulting from the sliding action between two metallic components that generates oxide films on the metal surfaces. These oxide films prevent the formation of a metallic bond between the sliding surfaces, resulting in fine wear debris and low wear rates.
- **oxide film replica**
  - A thin film of an oxide of the specimen to be examined. The replica is prepared by air, oxygen, chemical, or electrochemical oxidation of the parent metal and is subsequently freed mechanically or chemically for examination. See also replica .
- **oxidized steel surface**

  - Surface having a thin, tightly adhering oxidized skin (from straw to blue in color), which forms when steel is heated in an oxidizing atmosphere.
- **oxidizing agent**
  - A compound that causes oxidation, thereby itself being reduced.
- **oxygen deficiency**
  - A form of crevice corrosion in which galvanic corrosion proceeds because oxygen is prevented from diffusing into the crevice.
- **P**
- **pack carburizing**
  - A method of surface hardening of steel in which parts are packed in a steel box with a carburizing compound and heated to elevated temperatures. Common carburizing compounds contain 10 to 20% alkali or alkaline earth metal carbonates (for example, barium carbonate, $BaCO_3$) bound to hardwood charcoal or to coke by oil, tar, or molasses. This process has been largely supplanted by gas and liquid carburizing processes.
- **pack cementation**
  - A coating process akin to pack carburizing that involves packing the parts to be coated into a retort with a carefully blended mixture of powders and then exposing the pack under hermetically sealed conditions or an inert atmosphere to elevated temperatures. Pack cementation is principally used for the application of aluminum diffusion coatings and ceramic coatings.
- **paint**
  - A material that when applied as a liquid to a surface forms a solid film for the purpose of decoration and/or protection. Generally, a paint contains a binder(s), solvent(s), and a pigment(s). Often other materials are present to give special properties to the paint film. Examples of such additives are rust inhibitors, light stabilizers, and softening agents (plasticizers ).
- **passivation**
  - (1) A reduction of the anodic reaction rate of an electrode involved in corrosion . (2) The process in metal corrosion by which metals become passive. (3) The changing of a chemically active surface of a metal to a much less reactive state. Contrast with activation . (4) The formation of an insulating layer directly over a semiconductor surface to protect the surface from contaminants, moisture, and so forth.
- **passivator**
  - A type of corrosion inhibitor that appreciably changes the potential of a metal to a more noble (positive) value.
- **passive**
  - (1) A metal corroding under the control of a surface reaction product. (2) The state of the metal surface characterized by low corrosion rates in a potential region that is strongly oxidizing for the metal.
- **passive-active cell**
  - A corrosion cell in which the anode is a metal in the active state and the cathode is the same metal in the passive state.
- **passivity**
  - A condition in which a piece of metal, because of an impervious covering of oxide or other compound, has a corrosion rate much less than that of the metal in the active state.
- **patina**
  - The coating, usually green, that forms on the surface of metals such as copper and copper alloys exposed to the atmosphere. Also used to describe the appearance of a weathered surface of any metal.
- **pearlite**
  - A metastable lamellar aggregate of ferrite and cementite resulting from the transformation of austenite at temperatures above the bainite range.
- **peeling**
  - The detaching of one layer of a coating from another, or from the base metal , because of poor adherence.
- **periodic reverse plating**
  - A method of plating in which the current is reversed periodically. The cycles are usually no longer than a few minutes and may be much less.
- **pH**

    - The negative logarithm of the hydrogen-ion activity or hydrogen-ion concentration in gram equivalents per liter that is used in expressing both acidity and alkalinity on a scale of values running from 0 to 14; 0 to 7 represents acidity; 7 neutrality, and 7 to 14 alkalinity.
- **phosphate coating**
    - Same as phosphating .
- **phosphating**
    - Forming an adherent phosphate coating on a metal by immersion in a suitable aqueous phosphate solution. Also called phosphatizing. See also conversion coating .
- **photoresist**
    - (1) A radiation-sensitive material which, when properly applied to a variety of substrates and then properly exposed and developed, masks portions of the substrate with a high degree of integrity. (2) A photosensitive coating that is applied to a laminate and subsequently exposed through a photo tool (film) and developed to create a pattern that can be either plated or etched.
- **physical vapor deposition (PVD)**
    - A coating process whereby the deposition species are transferred and deposited in the form of individual atoms or molecules. The most common PVD methods are sputtering and evaporation. Sputtering, which is the principal PVD process, involves the transport of a material from a source (target) to a substrate by means of the bombardment of the target by gas ions that have been accelerated by a high voltage. Atoms from the target are ejected by momentum transfer between the incident ions and the target. These ejected particles move across the vacuum chamber to be deposited on the substrate. Evaporation, which was the first PVD process used, involves the transfer of material to form a coating by physical means alone, essentially vaporization. The streaming vapor is generated by melting and evaporating a coating material source bar, by an electron beam in a vacuum chamber. Because both of these methods are line-of-sight processes, it is necessary to use specially shaped targets or multiple evaporation sources and to rotate or move the substrate uniformly to expose all areas. PVD coatings are used to improve the wear, friction, and hardness properties of cutting tools and as corrosion-resistant coatings.
- **pickle**
    - See pickling .
- **pickle stain**
    - Discoloration of metal due to chemical cleaning without adequate washing and drying.
- **pickling**
    - The chemical removal of surface oxides (scale ) from iron and steel by immersion in an aqueous acid solution. The most common pickling solutions for carbon steels are sulfuric and hydrochloric acids.
- **pickup**
    - (1) Transfer of metal from tools to part or from part to tools during a forming operation. (2) Small particles of oxidized metal adhering to the surface of a mill product. (3) The amount of slip retained per unit area on dipped porcelain enamel ware.
- **pigment**
    - Small particles added to the paint to influence properties such as color, corrosion resistance , and mechanical strength.
- **pinhole porosity**
    - Porosity consisting of numerous small gas holes distributed throughout a metal; found in weld metal, castings, and electrodeposited metal.
- **pinhole**
    - A porcelain enamel surface defect caused by gas evolution and characterized by a small hole resembling a pin prick that may extend to the base metal .
- **pit**
    - A porcelain enamel surface defect similar to a dimple but slightly smaller.
- **pitting**
    - (1) Forming small sharp cavities in a surface by corrosion , wear, or other mechanically assisted degradation. (2) Localized corrosion of a metal surface, confined to a point or small area, that takes the form of cavities.
- **planishing**
    - Producing a smooth finish on metal by a rapid succession of blows delivered by highly polished dies or by a hammer designed for the purpose, or by rolling in a planishing mill.
- **plasma**

  - A gas of sufficient energy so that a large fraction of the species present is ionized and thus conducts electricity. Plasmas may be generated by the passage of a current between electrodes, by induction, or by a combination of these methods.
- **plasma-assisted chemical vapor deposition**
  - A chemical vapor deposition process that uses low-pressure glow-discharge plasmas to promote the chemical deposition reactions. Also called plasma-enhanced chemical vapor deposition.
- **plasma ion deposition**
  - An ion implantation technique in which ion beams are used to create coatings having special phases, especially ion beam formed carbon coatings in the diamond phase or ion beam formed boron nitride coatings.
- **plasma spraying**
  - A thermal spraying process in which the coating material is melted with heat from a plasma torch that generates a nontransferred arc; molten powder coating material is propelled against the base metal by the hot, ionized gas issuing from the torch.
- **plastic deformation**
  - The permanent (inelastic) distortion of materials under applied stresses that strain the material beyond its elastic limit.
- **plasticizer**
  - A lower molecular weight material added to polymeric materials such as paints, plastics, or adhesives to improve the flexibility.
- **plastic replica**
  - In fractography and metallography, a reproduction in plastic of the surface to be studied. It is prepared by evaporation of the solvent from a solution of plastic, polymerization of a monomer, or solidification of a plastic on the surface.
- **plastisol**
  - A suspension of a finely divided resin in a plasticizer that can be converted to a continuous film by the application of heat. Distinct from baking enamels etc. in that substantially all the original mixture becomes a part of the film; there is no significant evaporation of solvent. The films are usually much thicker than obtainable from coatings that depend on the evaporation of a volatile solvent.
- **plate martensite**
  - Martensite formed partly in steel containing more than approximately 0.5% C and solely in steel containing more than approximately 1.0% C that appears as lenticular-shape plates (crystals).
- **plating**
  - Forming an adherent layer of metal on an object; often used as a shop term for electroplating . See also electrodeposition and electroless plating .
- **plating rack**
  - A fixture used to hold work and conduct current to it during electroplating .
- **plowing**
  - In tribology, the formation of grooves by plastic deformation of softer of two surfaces in relative motion.
- **plunge grinding**
  - Grinding wherein the only relative motion of the wheel is radially toward the work.
- **plymetal**
  - Sheet consisting of bonded layers of dissimilar metals.
- **Poisson burr**
  - A burr formed predominantly by the phenomenon that is responsible for Poisson's ratio. Sometimes called a flow-type burr.
- **polarization**
  - The change in the potential of a electrode during electrolysis , such that the potential of an anode always becomes more noble and that of a cathode less noble than their respective static potentials. Equal to the difference between the static electrode potential and the dynamic electrode potential .
- **polished surface**
  - A surface prepared for metallographic inspection that reflects a large proportion of the incident light in a specular manner.
- **polishing**

- The smoothing of a metal surface by means of the action of abrasive particles attached by adhesive to the surface of wheels or endless belts usually driven at a high speed.

- **polishing wear**
  - An extremely mild form of wear for which the mechanism has not been clearly identified, but that may involve extremely fine-scale abrasion, plastic smearing of micro-asperities, and/or tribochemical material removal.
- **polymers**
  - A high molecular weight organic compound, natural or synthetic, with a structure that can be represented by a repeated small unit, the mer. Synthetic polymers are formed by addition or condensation polymerization of monomers. When two or more dissimilar monomers are involved, the product is called a copolymer. The lengths of polymer chains, usually measured by molecular weight, have very significant effects on the performance properties of plastics and profound effects on processability.
- **pop-off**
  - Loss of small portions of a porcelain enamel coating. The usual cause is outgassing of hydrogen or other gases from the base metal during firing , but pop-off may also occur because of oxide particles or other debris on the surface of the base metal. Usually, the pits are minute and cone shaped, but when pop-off is the result of severe fishscale the pits may be much larger and irregular.
- **porcelain**
  - A glazed or unglazed vitreous ceramic whiteware used for technical purposes. This term designates such products as electrical, chemical, mechanical, structural, and thermal wares when they are vitreous. This term is frequently used as a synonym for china.
- **porcelain enamel**
  - A substantially vitreous or glassy, inorganic coating (borosilicate glass) bonded to metal by fusion at a temperature above 425 °C (800 °F). Porcelain enamels are applied primarily to components made of sheet iron or steel, cast iron, aluminum, or aluminum-coated steels.
- **pore**
  - (1) A small opening, void, interstice, or channel within a consolidated solid mass or agglomerate, usually larger than atomic or molecular dimensions. (2) A minute cavity in a powder metallurgy compact, sometimes added intentionally. (3) A minute perforation in an electroplated coating.
- **porosity**
  - (1) Fine holes or pores within a solid; the amount of these pores is expressed as a percentage of the total volume of the solid. (2) Cavity-type discontinuities in weldments formed by gas entrapment during solidification. (3) A characteristic of being porous, with voids or pores resulting from trapped air or shrinkage in a casting. See also gas porosity and pinhole porosity .
- **positive replica**
  - A replica whose contours correspond directly to the surface being replicated. Contrast with negative replica .
- **post-nucleation**
  - The step where, if necessary, the catalyst is converted to its final form when plating on plastic substrates. This is the final step prior to electroless plating .
- **poultice corrosion**
  - Same as deposit corrosion .
- **powder adhesion**
  - In dry process enameling , the ability of an electrostatic powder to remain attached by static attraction to a grounded substrate.
- **powder flame spraying**
  - A thermal spraying process variation in which the material to be sprayed is in powder form. See also flame spraying .
- **precipitation**
  - The consolidation of soil particles (the opposite of dispersion ) in a cleaning bath, permitting their removal as sludge and prolonging bath life. The hardness of water can be reduced by precipitation with soda ash or trisodium phosphate.
- **precipitation (deposit) etching**
  - Development of microstructure in a metallographic specimen through formation of reaction products at the surface of the microsection. See also staining .
- **precipitation hardening**

- Hardening in metals caused by the precipitation of a constituent from a supersaturated solid solution. See also age hardening and aging .
- **precision grinding**
  - Machine grinding to specified dimensions and low tolerances.
- **precoated metal products**
  - Mill products that have a metallic, organic, or conversion coating applied to their surfaces before they are fabricated into parts.
- **preshadowed replica**
  - A replica for fractographic or metallographic inspection that is formed by the application of shadowing material to the surface to be replicated. It is formed before the thin replica film is cast or otherwise deposited on the surface. See also shadowing .
- **primary boiling**
  - The evolution of gas during the initial firing of porcelain enamel ; sometimes considered a defect.
- **primer**
  - A coating applied to a surface prior to the application of a paint topcoat or adhesive to improve the performance of the bond.
- **primes**
  - Metal products, principally sheet and plate, of the highest quality and free from blemishes or other visible imperfections.
- **proeutectoid carbide**
  - Primary crystals of cementite formed directly in ferrous alloys from the decomposition of austenite exclusive of that cementite resulting from the eutectoid reaction. See also eutectoid .
- **proeutectoid ferrite**
  - Primary crystals of ferrite formed directly in ferrous alloys from the decomposition of austenite exclusive of that ferrite resulting from the eutectoid reaction. See also eutectoid .
- **proeutectoid phase**
  - Particles of a phase in ferrous alloys that precipitate during cooling after austenitizing but before the eutectoid transformation takes place. See also eutectoid .
- **protective atmosphere**
  - (1) A gas envelope surrounding the part to be brazed, welded, or thermal sprayed, with the gas composition controlled with respect to chemical composition, dew point, pressure, flow rate, and so forth. Examples are inert gases, combusted fuel gases, hydrogen, and vacuum. (2) The atmosphere in a heat treating or sintering furnace designed to protect the parts or compacts from oxidation, nitridation, or other contamination from the environment.
- **pull through**
  - See copperhead .
- **Q**
- **quantitative metallography**
  - Determination of specific characteristics of a microstructure by quantitative measurements on micrographs or metallographic images. Quantities so measured include volume concentration of phases, grain size, particle size, mean free path between like particles or secondary phases, and surface area to volume ratio of microconstituents, particles, or grains.
- **quench-age embrittlement**
  - Embrittlement of low-carbon steels resulting from precipitation of solute carbon at existing dislocations and from precipitation hardening of the steel caused by differences in the solid solubility of carbon in ferrite at different temperatures. Quench-age embrittlement usually is caused by rapid cooling of the steel from temperatures slightly below $Ac_1$ (the temperature at which austenite begins to form), and can be minimized by quenching from lower temperatures.
- **quench hardening**
  - (1) Hardening suitable alpha-beta alloys (most often certain copper or titanium alloys) by solution treating and quenching to develop a martensitic-like structure. (2) In ferrous alloys, hardening by austenitizing and then cooling at a rate such that a substantial amount of austenite transforms to martensite.
- **R**
- **rack**
  - Same as plating rack .
- **rain erosion**

  - A form of liquid impingement erosion in which the impinging liquid particles are raindrops. This form of erosion is of particular concern to designers and material selectors for external surfaces of rotary-wing and fixed-wing aircraft. See also erosion .
- **rattail**
  - A surface imperfection on a casting, occurring as one or more irregular lines, caused by expansion of sand in the mold. Compare with buckle (2).
- **reactive evaporation**
  - A vacuum deposition process in which trace amounts of an active gas are added to the vacuum chamber; the gas reacts with an evaporating material in the chamber, promoting deposition of the material on a substrate.
- **real area of contact**
  - Same as actual contact area .
- **reamer**
  - A rotary cutting tool with one or more cutting elements (teeth), used for enlarging a hole to desired size and contour. It is supported principally by the metal around the hole it cuts.
- **reaming**
  - An operation in which a previously formed hole is sized and contoured accurately by using a rotary cutting tool (reamer ) with one or more cutting elements (teeth). The principal support for the reamer during the cutting action is supplied by the workpiece.
- **reboiling**
  - In porcelain enamel , gas evolution occurring and recurring during repeated firing of the ground coat; sometimes considered a defect.
- **recalescence**
  - (1) The increase in temperature that occurs after undercooling, because the rate of liberation of heat during transformation of a material exceeds the rate of dissipation of heat. (2) A phenomenon, associated with the transformation of gamma iron to alpha iron on cooling (supercooling) of iron or steel, that is revealed by the brightening (reglowing) of the metal surface owing to the sudden increase in temperature caused by the fast liberation of the latent heat of transformation. Contrast with decalescence .
- **reclain**
  - Porcelain enamel overspray that is removed from the spray booth and reconditioned for use.
- **recrystallization**
  - (1) The formation of a new, strain-free grain structure from that existing in cold-worked metal, usually accomplished by heating. (2) The change from one crystal structure to another, as occurs on heating or cooling through a critical temperature. (3) A process, usually physical, by which one crystal species is grown at the expense of another or at the expense of others of the same substance but smaller in size.
- **rectification**
  - The conversion of alternating current into direct current.
- **rectifier**
  - A device that converts alternating current into direct current by virtue of a characteristic permitting appreciable flow of current in only one direction.
- **reduction**
  - A reaction in which electrons are added to a reactant. More specifically, the addition of hydrogen or the abstraction of oxygen. Such a reaction takes place, for example, at the cathode in electrolysis . Contrast with oxidation .
- **reflector sheet**
  - A clad product consisting of a facing layer of high-purity aluminum capable of taking a high polish, for reflecting heat or light, and a base of commercially pure aluminum or an aluminum-manganese alloy, for strength and formability.
- **reflowing**
  - Melting of an electrodeposit followed by solidification. The surface has the appearance and physical characteristics of a hot dipped surface (especially tin or tin alloy plates). Also called flow brightening .
- **Rehbinder effect**
  - Modification of the mechanical properties at or near the surface of a solid, attributable to interaction with a surfactant .
- **relieving**

  - The removal of material from selected portions of a colored metal surface by mechanical means to achieve a multicolored effect.
- **replica**
  - A reproduction of a surface in a material. It is usually accomplished by depositing a thin film of suitable material, such as a plastic, onto the specimen surface. This film is subsequently extracted and examined by optical microscopy, scanning electron microscopy , or transmission electron microscopy , the latter being the most common. Replication techniques can be classified as either surface replication or extraction replication. Surface replicas provide an image of the surface topography of a specimen, while extraction replicas lift particles from the specimen. See also atomic replica , cast replica , collodion replica , Formvar replica , gelatin replica , impression replica , negative replica , oxide film replica , plastic replica , positive replica , preshadowed replica , tape replica method (faxfilm) , and vapor-deposited replica .
- **residual stress**
  - (1) The stress existing in a body at rest, in equilibrium, at uniform temperature, and not subjected to external forces. Often caused by the forming or thermal processing curing process. (2) An internal stress not depending on external forces resulting from such factors as cold working, phase changes, or temperature gradients. (3) Stress present in a body that is free of external forces or thermal gradients. (4) Stress remaining in a structure or member as a result of thermal or mechanical treatment or both. Stress arises in fusion welding primarily because the weld metal contracts on cooling from the solidus to room temperature.
- **resinoid wheel**
  - A grinding wheel bonded with a synthetic resin.
- **resist**
  - (1) Coating material used to mask or protect selected areas of a substrate from the action of an etchant , solder, or plating . (2) A material applied to a part of a cathode or plating rack to render the surface nonconductive.
- **reverse cleaning**
  - Same as anodic cleaning .
- **rinsability**
  - The relative ease with which a substance can be removed from a metal surface with a liquid such as water.
- **ripple (dc)**
  - Regular modulations in the dc output wave of a rectifier unit, or a motor-generator set, originating from the harmonics of the ac input system in the case of a rectifier, or from the harmonics of the induced voltage of a motor-generator set.
- **ripple formation**
  - Formation of periodic ridges and valleys transverse to the direction of motion on a solid surface. Also referred to as rippling.
- **robber**
  - An extra cathode or cathode extension that reduces the current density on what would otherwise be a high-current-density area on work being electroplated.
- **Rochelle copper**
  - (1) A copper electrodeposit obtained from copper cyanide plating solution to which Rochelle salt (sodium potassium tartrate) has been added for grain refinement , better anode corrosion, and cathode efficiency. (2) The solution from which a Rochelle copper electrodeposit is obtained.
- **rolling-contact wear**
  - Wear to a solid surface that results from rolling contact between that surface and another solid surface or surfaces.
- **rollover burr**
  - Burr formed by a cutter when it exits over a surface and allows the chip to be rolled away from the cutter, rather than sheared.
- **root mean square (rms)**
  - A term describing the surface roughness of a machined surface, $R_q$, calculated as the square root of the average of the squared distance of the surface from the mean line. See also surface roughness .
- **rosette graphite**
  - Arrangement of graphite flakes in which the flakes extend radially from the center of crystallized areas in gray cast iron.

- **rotary roughening**
    - A method of surface roughening prior to thermal spraying wherein a revolving roughening tool is pressed against the surface being prepared, while either the work, or the tool, or both, move.
- **rouge finish**
    - A highly reflective finish produced with rouge (finely divided, hydrated iron oxide) or other very fine abrasive, similar in appearance to the bright polish or mirror finish on sterling silver utensils.
- **rough grinding**
    - Grinding where surface generation occurs at a rapid rate, and tolerances or surface features are less critical compared to the production rate. Usually followed by a subsequent operation.
- **roughness**
    - (1) Relatively finely spaced surface irregularities, the heights, widths, and directions of which establish the predominant surface pattern. (2) The microscopic peak-to-valley distances of surface protuberances and depressions. See also surface roughness .
- **rough-polishing process**
    - A polishing process having the primary objective of removing the layer of significant damage produced during earlier machining and abrasion stages of a metallographic preparation sequence. A secondary objective is to produce a finish of such quality that a final polish can be produced easily. See also final polishing .
- **running-in**
    - The process by which machine parts improve in conformity, surface topography, and frictional compatibility during the initial stage of use. Chemical processes, including formation of an oxide skin, and metallurgical processes, such as strain hardening, may contribute.
- **rust**
    - A visible corrosion product consisting of hydrated oxides of iron. Applicable only to ferrous alloys. See also white rust .
- **S**
- **sacrificial protection**
    - The form of corrosion protection wherein one metal corrodes in preference to another, thereby protecting the latter from corrosion.
- **sagging**
    - (1) A defect characterized by a wavy line or lines appearing on those surfaces of porcelain enamel that have been fired in a vertical position. (2) A defect characterized by irreversible downward bending in a porcelain enamel article insufficiently supported during the firing cycle.
- **salt bath**
    - A molten, usually anhydrous inorganic solution used for heat treating or surface diffusion treatments wherein nitrogen, carbon, or other elements are diffused into the work. Specialized compositions are used for removal of scale , refractory materials, and organic materials from work surfaces.
- **sandblasting**
    - Abrasive blasting with sand. See also blasting or blast cleaning and compare with shotblasting .
- **sanitary ware**
    - Porcelain enamel ware such as sinks, lavatories, and bathtubs.
- **saponification**
    - The conversion of insoluble fats and fatty acids to water-soluble soaps by alkalies. The cleaning of buffing compounds from metallic surfaces can be achieved by saponification.
- **satin finish**
    - A diffusely reflecting surface finish on metals, lustrous but not mirrorlike. One type is a butler finish .
- **scab**
    - A defect on the surface of a casting that appears as a rough, slightly raised surface blemish, crusted over by a thin porous layer of metal, under which is a honeycomb or cavity that usually contains a layer of sand; defect common to thin-wall portions of the casting or around hot areas of the mold.
- **scale**
    - Surface oxidation, consisting of partially adherent layers of corrosion products, left on metals by heating or casting in air or in other oxidizing atmospheres.
- **scaling**

  - (1) Forming a thick layer of oxidation products on metals at high temperature. Scaling should be distinguished from rusting, which involves the formation of hydrated oxides. See also rust . (2) Depositing water-insoluble constituents on a metal surface, as in cooling tubes and water boilers.
- **scanning Auger microscopy (SAM)**
  - An analytical technique that measures the lateral distribution of elements on the surface of a material by recording the intensity of their Auger electrons versus the position of the electron beam.
- **scanning electron microscopy (SEM)**
  - An analytical technique in which an image is formed on a cathode-ray tube whose raster is synchronized with the raster of a point beam of electrons scanned over an area of the sample surface. The brightness of the image at any point is proportional to the scattering by or secondary emissions from the point on the sample being struck by the electron beam.
- **scanning laser acoustic microscopy (SLAM)**
  - A high-resolution, high-frequency (10 to 500 MHz) ultrasonic inspection technique that produces images of features in a sample throughout its entire thickness. In operation, ultrasound is introduced to the bottom surface of the sample by a piezoelectric transducer, and the transmitted wave is detected on the top side by a rapidly scanning laser beam.
- **scanning transmission electron microscopy (STEM)**
  - An analytical technique in which an image is formed on a cathode-ray tube whose raster is synchronized with the raster of a point beam of electrons scanned over an area of the sample. The brightness of the image at any point is proportional to the number of electrons that are transmitted through the sample at the point where it is struck by the beam.
- **scoring**
  - (1) The formation of severe scratches in the direction of sliding. Scoring may be due to local solid-phase welding or to abrasion. In the United States, the term scuffing is sometimes used as a synonym for scoring. Minor damage should be called scratching rather than scoring. (2) In tribology, a severe form of wear characterized by the formation of extensive grooves and scratches in the direction of sliding. (3) The act of producing a scratch or narrow groove in a surface by causing a sharp instrument to move along that surface. (4) The marring or scratching of any formed metal part by metal pickup on the punch or die. (5) The reduction in thickness of a material along a line to weaken it intentionally along that line.
- **scouring**
  - (1) A wet or dry cleaning process involving mechanical scrubbing. (2) A wet or dry mechanical finishing operation, using fine abrasive and low pressure, carried out by hand or with a cloth or wire wheel to produce satin or butler -type finishes.
- **scratch**
  - A groove produced in a solid surface by the cutting and/or plowing action of a sharp particle or protuberance moving along that surface.
- **scratch brush finish**
  - A finish on nonferrous metals produced by buffing that shows a combination of coarse lines with a slight underlying luster.
- **scratch-resistant coatings**
  - Coating applied to glass surfaces to reduce the effects of frictive damage. Examples are $SnO_2$ or $TiO_2$ coatings applied to glass containers.
- **screen test**
  - A standard test for fineness of porcelain enamel slip or powder.
- **scuffing**
  - Same as scoring .
- **scumming**
  - A defect characterized by areas of poor gloss on the surface of a porcelain enamel that can be caused by uneven heat distribution in the furnace, overfiring, or underfiring.
- **sealed (anodic) coating**
  - In anodizing aluminum, an anodic oxide coating on aluminum that has been treated in aqueous or steam medium resulting in reduced porosity of the coating.
- **sealing of anodic coating**
  - A process which, by absorption, chemical reaction, or other mechanism, increases the resistance of an anodic coating to staining and corrosion , improves the durability of colors produced in the coating, or imparts other desirable properties.

- **seam**
  - (1) On a metal surface, an unwelded fold or lap that appears as a crack, usually resulting from a discontinuity. (2) A surface defect on a casting related to but of lesser degree than a cold shut . (3) A ridge on the surface of a casting caused by a crack in the mold face.
- **secondary gas**
  - In thermal spraying, the gas constituting the minor constituent of the arc gas fed to the gun to produce the plasma. The primary arc gas, usually argon or nitrogen, is supplemented with secondary gases such as nitrogen, helium, and/or hydrogen, in order to increase the temperature of the plasma.
- **secondary ion mass spectroscopy (SIMS)**
  - An analytical technique that measures the masses of ions emitted from the surface of a material when exposed to a beam of incident ions. The incident ions are usually monoenergetic and are all of the same species, for example, 5-keV $Ne^+$ ions.
- **sectioning**
  - The removal of a conveniently sized, representative specimen from a larger sample for metallographic inspection. Sectioning methods include shearing, sawing (using hacksaws, band saws, and diamond wire saws), abrasive cutting, and electrical discharge machining.
- **segregation (coring) etching**
  - Development of segregation (coring ) mainly in macrostructures and microstructures of castings.
- **seizing**
  - The stopping of a moving part by a mating surface as a result of excessive friction.
- **selective leaching**
  - Corrosion in which one element is preferentially removed from an alloy, leaving a residue (often porous) of the elements that are more resistant to the particular environment. Also called dealloying or parting. See also decarburization , decobaltification , denickelification , dezincification , and graphitic corrosion .
- **selective plating**
  - Same as brush plating .
- **self-fluxing alloys**
  - In thermal spraying, certain materials that "wet" the substrate and coalesce when heated to their melting point, without the addition of a fluxing agent.
- **self-limiting characteristic**
  - Characteristic of electrostatic powders to build only a limited amount of surface film during application due to the buildup of a layer of charged particles that will repel particles of like charge. See also back emission .
- **sensitization**
  - (1) The absorption of a reducing agent, often a stannous compound, on the surface of a plastic substrate . (2) The effect caused by a sensitizing heat treatment .
- **sensitizing heat treatment**
  - A heat treatment, whether accidental, intentional, or incidental (as during welding), that causes precipitation of constituents at grain boundaries , often causing the alloy to become susceptible to intergranular corrosion or intergranular stress-corrosion cracking .
- **sequestration and chelation**
  - To inactivate calcium, magnesium, and iron salts in water so that they will not interfere with cleaning. Chelated alkaline compounds can remove oxides and rust from steel surfaces, eliminating the need for acids that may react with the metal to cause hydrogen embrittlement.
- **serial sectioning**
  - A metallographic technique in which an identified area on a section surface is observed repeatedly after successive layers of known thickness have been removed from the surface. It is used to construct a three-dimensional morphology of structural features. See also sectioning .
- **set**
  - A flow property of porcelain enamel slip affecting the rate of draining, residual thickness, and uniformity of coating.
- **setting-up agent**
  - An electrolyte used to increase the measured pickup of a slip . Also known as set-up agent.
- **severe wear**
  - A form of wear characterized by removal of material in relatively large fragments. Severe wear is an imprecise term, frequently used in research, and contrasted with mild wear. In fact, the

phenomena studied usually involve the transition from mild to severe wear and the factors that influence that transition. With metals, the fragments are usually predominantly metallic rather than oxidic. Severe wear is frequently associated with heavy loads and/or adhesive contact. See also mild wear and normal wear .

- **shadow angle**
  - In shadowing of replicas, the angle between the line of motion of the evaporated atoms and the surface being shadowed. See also replica and shadowing .
- **shadow cast replica**
  - A replica that has been shadowed. See also replica and shadowing .
- **shadowing**
  - Directional deposition of carbon or a metallic film on a plastic replica so as to highlight features to be analyzed by transmission electron microscopy . Most often used to provide maximum detail and resolution of the features of fracture surfaces. See also metal shadowing , oblique evaporation shadowing , and shadow angle .
- **shadow mask**
  - A thermal spraying process variation in which an area is partially shielded during the thermal spraying operation, thus permitting some overspray to produce a feathering at the coating edge.
- **shales**
  - Abrasive particles of platelike shape. The term is applied particularly to diamond abrasives.
- **shaving**
  - (1) As a finishing operation, the accurate removal of a thin layer of a work surface by straightline motion between a cutter and the surface. (2) Trimming parts such as stampings, forgings, and tubes to remove uneven sheared edges or to improve accuracy.
- **sheet**
  - A flat-rolled metal product of some maximum thickness and minimum width arbitrarily dependent on the type of metal. It has a width-to-thickness ratio greater than about 50. Generally, such flat products under 6.5 mm ( in.) thick are called sheets, and those 6.5 mm ( in.) thick and over are called plates. Occasionally, the limiting thickness for steel to be designated as sheet steel is No. 10 Manufacturer's Standard Gage for sheet steel, which is 3.42 mm (0.1345 in.) thick.
- **shelf roughness**
  - Roughness on upward-facing surfaces where undissolved solids have settled on parts during a plating operation.
- **shelling**
  - (1) A term used in railway engineering to describe an advanced phase of spalling . (2) A mechanism of deterioration of coated abrasive products in which entire abrasive grains are removed from the cement coating that held the abrasive to the backing layer of the product.
- **shielding**
  - (1) A material barrier that prevents radiation or a flowing fluid from impinging on an object or a portion of an object. (2) In an electron-optical instrument, the protection of the electron beam from distortion due to extraneous electric and magnetic fields. Because the metallic column of the microscope is at ground potential, it provides electrostatic shielding. (3) Placing an object in an electrolytic bath so as to alter the current distribution on the cathode . A nonconductor is called a shield; a conductor is called a robber , a thief, or a guard.
- **short-term etching**
  - In metallographic preparation of specimens, etching times of seconds to a few minutes.
- **shot**
  - (1) Small, spherical particles of metal. (2) The injection of molten metal into a die casting die. The metal is injected so quickly that it can be compared to the shooting of a gun.
- **shotblasting**
  - Blasting with metal shot ; usually used to remove deposits or mill scale more rapidly or more effectively than can be done by sandblasting .
- **shot peening**
  - A method of cold working metals in which compressive stresses are induced in the exposed surface layers of parts by the impingement of a stream of shot , directed at the metal surface at high velocity under controlled conditions. It differs from blast cleaning in primary purpose and in the extent to which it is controlled to yield accurate and reproducible results. Although shot

peening cleans the surface being peened, this function is incidental. The major purpose of shot peening is to increase fatigue strength. Shot for peening usually is made of iron, steel, or glass.

- **shrinkage cavity**
  - A void left in cast metal as a result of solidification shrinkage. Shrinkage cavities can appear as either isolated or interconnected irregularly shaped voids.
- **sieve analysis**
  - A method of determining particle size distribution, usually expressed as the weight percentage retained upon each of a series of standard screens of decreasing mesh size.
- **sigma-phase embrittlement**
  - Embrittlement of iron-chromium alloys (most notably austenitic stainless steels) caused by precipitation at grain boundaries of the hard, brittle intermetallic sigma phase during long periods of exposure to temperatures between approximately 560 and 980 °C (1050 and 1800 °F). Sigma-phase embrittlement results in severe loss in toughness and ductility, and can make the embrittled material susceptible to intergranular corrosion .
- **siliconizing**
  - Diffusing silicon into solid metal, usually low-carbon steels, at an elevated temperature in order to improve corrosion or wear resistance.
- **size**
  - In composites manufacturing, a treatment consisting of starch, gelatin, oil, wax, or other suitable ingredients applied to yarn or fibers at the time of formation to protect the surface and aid the process of handling and fabrication or to control the fiber characteristics. The treatment contains ingredients that provide surface lubricity and binding action, but unlike a finish, contains no coupling agent. Before final fabrication into a composite, the size is usually removed by heat cleaning, and a finish is applied.
- **skid-polishing process**
  - A mechanical polishing process in which the surface of the metallographic specimen to be polished is made to skid across a layer of paste, consisting of the abrasive and the polishing fluid, without contacting the fibers of the polishing cloth.
- **skin**
  - A thin outside metal layer, not formed by bonding as in cladding or electroplating, that differs in composition, structure, or other characteristics from the main mass of metal.
- **skin lamination**
  - In flat-rolled metals, a surface rupture resulting from the exposure of a subsurface lamination by rolling.
- **skinning**
  - The formation of a thin, tough film on the surface of a liquid paint film, usually due to reaction with the air or to rapid solvent loss.
- **slab**
  - A flat-shaped semifinished rolled metal ingot with a width not less than 250 mm (10 in.) and a cross-sectional area not less than 105 $cm^2$ (16 $in.^2$).
- **slip**
  - A suspension of finely divided ceramic material in liquid.
- **sliver**
  - An imperfection consisting of a very thin elongated piece of metal attached by only one end to the parent metal into whose surface it has been worked.
- **sludge**
  - An accumulation of insoluble materials and reaction products that collects in cleaning and processing tanks.
- **slump test**
  - A test used to determine the consistency of slip in which measurement is made of the spreading of a specified volume of slip over a flat plate.
- **slurry**
  - A suspension of solids in water.
- **slurry erosion**
  - Erosion produced by the movement of a slurry past a solid surface.
- **smearing**
  - Mechanical removal of material from a surface, usually involving plastic shear deformation, and redeposition of the material as a thin layer on one or both surfaces. See also transfer .

- **smelt**
    - A batch or lot of frit .
- **smut**
    - A reaction product sometimes left on the surface of a metal after pickling , electroplating, or etching .
- **soak cleaning**
    - Immersion cleaning without the use of current, usually in alkaline solution.
- **soil**
    - Undesirable material on a surface that is not an integral part of the surface. Oil, grease, and dirt can be soils; a decarburized skin and excess hard chromium are not soils. Loose scale is soil; hard scale may be an integral part of the surface and, hence, not soil.
- **solid lubricant**
    - Any solid used as a powder or thin film on a surface to provide protection from damage during relative movement and to reduce friction and wear. Examples include molybdenum disulfide, graphite, polytetra-fluoroethylene (PTFE), and mica.
- **soluble oil**
    - A mineral oil containing additives that enable it to form a stable emulsion with water. Soluble oils are used as cutting or grinding fluids.
- **solvency**
    - The property of removal of soils by dissolving in a cleaning solution. For example, oils and fats are soluble in some solvents.
- **solvent**
    - A usually liquid substance capable of dissolving or dispersing other substances. See chlorinated solvent .
- **solvent cleaning**
    - Cleaning by means of organic solvents.
- **sour gas**
    - A gaseous environment containing hydrogen sulfide and carbon dioxide in hydrocarbon reservoirs. Prolonged exposure to sour gas can lead to hydrogen damage , sulfide-stress cracking , and/or stress-corrosion cracking in ferrous alloys.
- **spalling**
    - (1) Separation of particles from a surface in the form of flakes. The term spalling is commonly associated with rolling-element bearings and with gear teeth. Spalling is usually a result of subsurface fatigue and is more extensive than pitting. (2) In tribology, the separation of macroscopic particles from a surface in the form of flakes or chips, usually associated with rolling-element bearings and gear teeth, but also resulting from impact events. (3) The spontaneous chipping, fragmentation, or separation of a surface or surface coating. (4) A chipping or flaking of a surface due to any kind of improper heat treatment or material dissociation.
- **spangle**
    - The characteristic crystalline form in which a hot dipped zinc coating solidifies on steel strip.
- **specking**
    - Discoloration of an enamel surface due to foreign particles, dirt, or scale embedding themselves in the enamel. May also be caused by base coat migration up through the cover coat in two coat/one fire powder systems. Also known as black specking.
- **spotting out**
    - The delayed appearance of spots and blemishes on plated or finished surfaces that is most prevalent on porous base metals or substrates .
- **spray angle**
    - In thermal spraying, the angle of particle approach, measured from the surface of the substrate to the axis of the spray nozzle.
- **spray cleaning**
    - Cleaning by means of spraying.
- **spray deposit**
    - A coating applied by any of the thermal spray methods. See also thermal spraying .
- **sputter deposition**
    - Same as sputtering .
- **sputtering**

  - The bombardment of a solid surface with a flux of energetic particles (ions) that results in the ejection of atomic species. The ejected material may be used as a source for deposition. See also physical vapor deposition .
- **stabilizing gas**
  - In plasma spraying, the arc gas, which is ionized to form the plasma. Introduced into the arc chamber tangentially, the relatively cold gas chills the outer surface of the arc stream, tending to constrict the arc, raise its temperature, and force it out of the front anode nozzle in a steady, relatively unfluctuating stream.
- **stain**
  - On an enameled surface, an iridescent spot caused by the action of fruit juice or chemicals.
- **staining**
  - Precipitation etching that causes contrast by distinctive staining of microconstituents; different interference colors originate from surface layers of varying thickness. Also known as color etching.
- **standard electrode potential**
  - An equilibrium electrode potential for an electrode in contact with an electrolyte in which all of the components of a specified chemical reaction are in their standard states. The standard for state for an ionic constituent is unit ion activity.
- **stardusting**
  - An extremely fine form of roughness on the surface of a metal deposit.
- **star marks**
  - A defect that sometimes occurs in sheet steel or iron porcelain enamel cover coats where the dried ware is set down too hard on the firing fixture points and the enamel coating is fractured.
- **stars**
  - In porcelain enamel , a defect in the fired surface that appears as a series of small hairlines radiating from a common center. Similar to star marks . Typical of porcelain enamel powder systems.
- **starting sheet**
  - A thin sheet of metal used as the cathode in electrolyte refining.
- **static coefficient of friction**
  - The coefficient of friction corresponding to the maximum friction force that must be overcome to initiate macroscopic motion between two bodies.
- **static electrode potential**
  - The electrode potential measured when no net current is flowing between the electrode and the electrolyte .
- **steadite**
  - A hard structural constituent of cast iron that consists of a binary eutectic of ferrite , containing some phosphorus in solution, and iron phosphide ($Fe_3P$). The eutectic consists of 10.2% P and 89.8% Fe. The melting temperature is 1050 °C (1920 °F).
- **stereophotogrammetry**
  - A method of generating topographic maps of fracture surfaces by the use of a stereoscopic microscope interfaced to a microcomputer that calculates the three-dimensional coordinates of the fracture surface and produces the corresponding profile map, contour plot, or carpet plot.
- **stippled finish**
  - A pebbly textured porcelain enamel , often multicolored.
- **stopping off**
  - (1) The application of a resist to any part of an electrode: cathode , anode , or plating rack . (2) Depositing a metal (copper, for example) in localized areas to prevent carburization, decarburization , or nitriding in those areas.
- **strain etching**
  - Metallographic etching that provides information on deformed and undeformed areas if present side by side. In strained areas, more compounds are precipitated.
- **stray current**
  - Current through paths other than the intended circuit, such as through heating coils or the tank.
- **stray-current corrosion**
  - Corrosion resulting from direct current flow through paths other than the intended circuit. For example, by an extraneous current in the earth.
- **stress-corrosion cracking (SCC)**

  - A cracking process that requires the simultaneous action of a corrodent and sustained tensile stress. This excludes corrosion-reduced sections that fail by fast fracture. It also excludes intercrystalline or transcrystalline corrosion, which can disintegrate an alloy without applied or residual stress. Stress-corrosion cracking may occur in combination with hydrogen embrittlement .
- **stress relieving**
  - Heating to a suitable temperature, holding long enough to reduce residual stresses, and then cooling slowly enough to minimize the development of new residual stresses.
- **stretcher strains**
  - Elongated markings that appear on the surface of some sheet materials when deformed just past the yield point. These markings lie approximately parallel to the direction of maximum shear stress and are the result of localized yielding. See also Lüders lines .
- **strike**
  - (1) A thin electrodeposited film of metal to be overlaid with other plated coatings. (2) A plating solution of high covering power and low efficiency designed to electroplate a thin, adherent film of metal.
- **striking**
  - Electrodepositing, under special conditions, a very thin film of metal that will facilitate further plating with another metal or with the same metal under different conditions.
- **stringer**
  - In wrought materials, an elongated configuration of microconstituents or foreign material aligned in the direction of working. The term is commonly associated with elongated oxide or sulfide inclusions in steel.
- **strip**
  - (1) A process or solution used for the removal of a coating from a base metal or an undercoat . (2) To remove a coating from the base metal or undercoat.
- **submicron powder**
  - Any powder whose particles are smaller than 1 μm.
- **substrate**
  - (1) The material, workpiece, or substance on which a coating is deposited. (2) A material upon the surface of which an adhesive-containing substance is spread for any purpose, such as bonding or coating. A broader term than adherend . (3) In electronic devices, a body, board, or layer of material on which some other active or useful material(s) or component(s) may be deposited or laid; for example, electronic circuitry laid on an alumina ceramic board. (4) In catalysts , the formed, porous, high-surface area carrier on which the catalytic agent is widely and thinly distributed for reasons of performance and economy.
- **substrate temperature**
  - In thermal spraying, the temperature attained by the base material as the coating is applied. Proper control of the substrate temperature by intermittent spraying or by the application of external cooling will minimize stresses caused by substrate and coating thermal expansion differences.
- **subsurface corrosion**
  - Formation of isolated particles of corrosion products beneath a metal surface. This results from the preferential reactions of certain alloy constituents to inward diffusion of oxygen, nitrogen, or sulfur.
- **sulfidation**
  - The reaction of a metal or alloy with a sulfur-containing species to produce a sulfur compound that forms on or beneath the surface of the metal or alloy.
- **sulfide stress cracking (SSC)**
  - Brittle fracture by cracking under the combined action of tensile stress and corrosion in the presence of water and hydrogen sulfide. See also environmental cracking .
- **sulfochlorinated lubricant**
  - A lubricant containing chlorine and sulfur compounds, which react with a rubbing surface at elevated temperatures to form a protective film. There may be a synergistic effect, producing a faster reaction than with sulfur or chlorine additives alone.
- **sulfurized lubricant**
  - A lubricant containing sulfur or a sulfur compound that reacts with a rubbing surface at elevated temperatures to form a protective film. The shear strength of the sulfide film formed on ferrous

materials is lower than that of the metal but greater than that of the film formed by reaction with a chlorinated lubricant .

- **superabrasives**
  - Exceptionally hard and abrasion-resistant synthetic materials used for a wide variety of abrasive or cutting applications. Synthetic diamond and cubic boron nitride (CBN) are the two superabrasives used for grinding applications. Diamond is the hardest material known, and CBN is the second hardest.
- **superfines**
  - The portion of a metal powder that is composed of particles smaller than a specified size, usually 10 m.
- **superfinishing**
  - An abrasive process utilizing either a curved bonded honing stick (stone) for a cylindrical workpiece or a cup wheel for flat and spherical work. A large contact area, 30% approximately, exists between workpiece and abrasive. The object of superfinishing is to remove surface fragmentation and to correct inequalities in geometry, such as grinding feed marks and chatter marks. Also known as microhoning. See also honing .
- **surface active agent**
  - A substance that affects markedly the interfacial or surface tension of solutions even when present in very low concentrations.
- **surface alterations**
  - Irregularities or changes on the surface of a material due to machining or grinding operations. The types of surface alterations associated with metal removal practices include mechanical (for example, plastic deformation , hardness variations, cracks, etc.), metallurgical (for example, phase transformations, twinning, recrystallization , and untempered or overtempered martensite), chemical (for example, intergranular attack, embrittlement , and pitting ), thermal (heat-affected zone, recast, or redeposited metal, and resolidified material), and electrical surface alterations (conductivity change or resistive heating).
- **surface damage**
  - In tribology, damage to a solid surface resulting from mechanical contact with another substance, surface, or surfaces moving relatively to it and involving the displacement or removal of material. In certain contexts, wear is a form of surface damage in which material is progressively removed. In another context, surface damage involves a deterioration of function of a solid surface even though there is no material loss from that surface. Surface damage may therefore precede wear.
- **surface finish**
  - (1) The geometric irregularities in the surface of a solid material. Measurement of surface finish shall not include inherent structural irregularities unless these are the characteristics being measured. (2) Condition of a surface as a result of a final treatment. See also roughness .
- **surface grinding**
  - Producing a flat surface with a rotating grinding wheel as the workpiece passes under.
- **surface hardening**
  - A generic term covering several processes applicable to a suitable ferrous alloy that produces a surface layer that is harder or more wear resistant than the core. The processes commonly used are carbonitriding , carburizing , induction hardening , flame hardening , nitriding , and nitrocarburizing . Use of the applicable specific process name is preferred.
- **surface integrity**
  - A technology that involves the specification and manufacture of unimpaired or enhanced surfaces through the control of the many possible alterations produced in a surface layer during manufacture. Surface integrity is achieved by the proper selection and control of manufacturing processes and the ability to estimate their effects on the significant engineering properties of work materials. See also surface alterations .
- **surface modification**
  - The alteration of surface composition or structure by the use of energy or particle beams. Elements may be added to influence the surface characteristics of the substrate by the formation of alloys, metastable alloys or phases, or amorphous layers. Surface-modified layers are distinguished from conversion or coating layers by their greater similarity to metallurgical alloying versus chemically reacted, adhered, or physically bonded layers. However, surface structures are produced that differ significantly from those obtained by conventional

metallurgical processes. This latter characteristic further distinguishes surface modification from other conventional processes, such as amalgamation or thermal diffusion. Two types of surface modification methods commonly employed are ion implantation and laser surface processing .

- **surface roughness**
  - Fine irregularities in the surface texture of a material, usually including those resulting from the inherent action of the production process. Surface roughness is usually reported as the arithmetic roughness average, $R_a$, and is given in micrometers or microinches.
- **surface tension**
  - That property, due to molecular forces, that exists in the surface film of all liquids and tends to prevent the liquid from spreading.
- **surface texture**
  - The roughness, waviness , lay , and flaws associated with a surface.
- **surface void**
  - A void which is located at the surface of a material and is a consequence of processing, that is, a surface reaction layer, as distinguished from a volume distributed flaw such as a pore or inclusion .
- **surfacing**
  - The deposition of filler metal (material) on a base metal (substrate ) to obtain desired properties or dimensions. See also buttering , cladding , coating , and hardfacing .
- **surfactant**
  - (1) A chemical substance characterized by a strong tendency to form adsorbed interfacial films when in solution, emulsion, or suspension, thus producing effects such as low surface tension, penetration, boundary lubrication, wetting , and dispersing. (2) A compound that affects interfacial tensions between two liquids. It usually reduces surface tension. See also Rehbinder effect .
- **synthetic cold rolled sheet**
  - A hot rolled pickled sheet given a sufficient final temper pass to impart a surface approximating that of cold rolled steel.
- **T**
- **tape replica method (faxfilm)**
  - A method of producing a replica by pressing the softened surface of tape or plastic sheet material onto the surface to be replicated.
- **taper section**
  - A section cut obliquely (acute angle) through a surface and prepared metallographically. The angle is often chosen to increase the vertical magnification of surface features by a factor of 5 or 10. Taper sectioning is usually carried out for microstructural examination of coated metal specimens.
- **tarnish**
  - (1) The dulling, staining , or discoloration of metals due to superficial corrosion . (2) The film so formed.
- **tear burr**
  - Burr formed by the sides of a cutter as the cutter tears a chip from the workpiece. Also a ragged form of the Poisson burr caused by a built-up edge on the cutting tool.
- **tearing**
  - A defect in the surface of porcelain enamel characterized by short breaks or cracks that have been healed.
- **temper**
  - (1) In heat treatment, reheating hardened steel or hardened cast iron to some temperature below the eutectoid temperature for the purpose of decreasing hardness and increasing toughness. The process also is sometimes applied to normalized steel. (2) In tool steels, temper is sometimes used, but inadvisedly, to denote the carbon content. (3) In nonferrous alloys and in some ferrous alloys (steels that cannot be hardened by heat treatment), the hardness and strength produced by mechanical or thermal treatment, or both, and characterized by a certain structure, mechanical properties, or reduction in area during cold working.
- **temper color**
  - A thin, tightly adhering oxide skin (only a few molecules thick) that forms when steel is tempered at a low temperature, or for a short time, in air or a mildly oxidizing atmosphere. The color,

which ranges from straw to blue depending on the thickness of the oxide skin, varies with both tempering time and temperature.

- **tempered layer**
  - A surface or subsurface layer in a steel specimen that has been tempered by heating during some stage of the metallographic preparation sequence (usually grinding) . When observed in a section after etching , the layer appears darker than the base material.
- **tempered martensite**
  - The decomposition products that result from heating martensite below the ferrite-austenite transformation temperature. Under the optical microscope, darkening of the martensite needles is observed in the initial stages of tempering. Prolonged tempering at high temperatures produces spheroidized carbides in a matrix of ferrite . At the higher resolution of the electron microscope, the initial stage of tempering is observed to result in a structure containing a precipitate of fine iron carbide particles. At approximately 260 °C (500 °F), a transition occurs to a structure of larger and elongated cementite particles in a ferrite matrix. With further tempering at higher temperatures, the cementite particles become spheroidal, decrease in number, and increase in size.
- **tempered martensite embrittlement**
  - Embrittlement of high-strength alloy steels caused by tempering in the temperature range of 205 to 370 °C (400 to 700 °F); also called 350 °C or 500 °F embrittlement. Tempered martensite embrittlement is thought to result from the combined effects of cementite precipitation on prior-austenite grain boundaries or interlath boundaries and the segregation of impurities at prior-austenite grain boundaries. It differs from temper embrittlement in the strength of the material and the temperature exposure range. In temper embrittlement, the steel is usually tempered at a relatively high temperature, producing lower strength and hardness, and embrittlement occurs upon slow cooling after tempering and during service at temperatures within the embrittlement range. In tempered martensite embrittlement, the steel is tempered within the embrittlement range, and service exposure is usually at room temperature.
- **temper embrittlement**
  - Embrittlement of low-alloy steels caused by holding within or cooling slowly through a temperature range (generally 300 to 600 °C, or 570 to 1110 °F) just below the transformation range. Embrittlement is the result of the segregation at grain boundaries of impurities such as arsenic, antimony, phosphorus, and tin; it is usually manifested as an upward shift in ductile-to-brittle transition temperature. Temper embrittlement can be reversed by retempering above the critical temperature range, then cooling rapidly. Compare with tempered martensite embrittlement .
- **tempering**
  - In heat treatment, reheating hardened steel to some temperature below the eutectoid temperature to decrease hardness and/or increase toughness.
- **temper rolling**
  - Light cold rolling of sheet steel to improve flatness, to minimize the formation of stretcher strains , and to obtain a specified hardness or temper.
- **tensile burr**
  - The burr produced in blanking or piercing operations in which the slug separates from the stock as a result of tensile stresses.
- **tensile-plus-compressive burr**
  - The burr produced in blanking or piercing operations in which the slug separates from the stock in a stress field that is initially tensile, but changes to compressive at actual separation. This burr is usually associated with small die clearances and short die life.
- **terne**
  - An alloy of lead containing 3 to 15% Sn, used as a hot dip coating for steel sheet or plate. The term long terne is used to describe terne-coated sheet, whereas short terne is used for terne-coated plate. Terne coatings, which are smooth and dull in appearance (terne means dull or tarnished in French), give the steel better corrosion resistance and enhance its ability to be formed, soldered, or painted.
- **thermal embrittlement**
  - Intergranular fracture of maraging steels with decreased toughness resulting from improper processing after hot working. Thermal embrittlement occurs upon heating above 1095 °C (2000 °F) and then slow cooling through the temperature range of 980 to 815 °C (1800 to 1500 °F), and

has been attributed to precipitation of titanium carbides and titanium carbonitrides at austenite grain boundaries during cooling through the critical temperature range.

- **thermal etching**
  - Heating a specimen (usually a ceramic) in air, vacuum, or inert gases in order to delineate the grain structure. Used primarily in high-temperature microscopy.
- **thermal fatigue**
  - Fracture resulting from the presence of temperature gradients that vary with time in such a manner as to produce cyclic stresses in a structure. See also craze cracking .
- **thermal spraying**
  - A group of coating or welding processes in which finely divided metallic or nonmetallic materials are deposited in a molten or semimolten condition to form a coating. The coating material may be in the form of powder, ceramic rod, wire, or molten materials. See also electric arc spraying , flame spraying , plasma spraying , and powder flame spraying .
- **thermal spray powder**
  - A metal, carbide, or ceramic powder mixture designed for use with hardfacing and thermal spraying operations.
- **thermal wear**
  - Removal of material due to softening, melting, or evaporation during sliding or rolling. Thermal shock and high-temperature erosion may be included in the general description of thermal wear. Wear by diffusion of separate atoms from one body to the other, at high temperatures, is also sometimes denoted as thermal wear.
- **thermogalvanic corrosion**
  - Corrosion resulting from an electrochemical cell caused by a thermal gradient.
- **thermomechanical working**
  - A general term covering a variety of metal forming processes combining controlled thermal and deformation treatments to obtain synergistic effects, such as improvement in strength without loss of toughness. Same as thermal-mechanical treatment.
- **thermoplastic**
  - A type of polymer that softens and melts when heated and then resolidifies upon cooling. Thermoplastics generally have linear or branched structures.
- **thermoreactive deposition/diffusion process (TRD)**
  - A method of coating steels with a hard, wear-resistant layer of carbides, nitrides, or carbonitrides. In the TRD process, the carbon and nitrogen in the steel substrate diffuse into a deposited layer with a carbide-forming or nitride-forming element such as vanadium, niobium, tantalum, chromium, molybdenum, or tungsten. The diffused carbon or nitrogen reacts with the carbide- and nitride-forming elements in the deposited coating so as to form a dense and metallurgically bonded carbide or nitride coating at the substrate surface.
- **thermosetting**
  - A type of polymer that does not soften appreciably when heated. Thermosets may char when heated in air. They are generally cross-linked polymers.
- **thick-film circuit**
  - A circuit that is fabricated by the deposition of materials having between 5 and 20 μm (0.2 and 0.8 mil) thickness, such as screen-printed cermet pastes on a ceramic substrate, which are fired in a kiln to create permanent conductive patterns. Compare with thin-film circuit .
- **thick-film lubrication**
  - A condition of lubrication in which the film thickness of the lubricant is appreciably greater than that required to cover the surface asperities when subjected to the operating load, so that the effect of the surface asperities is not noticeable. Also known as full-film lubrication. See also thin-film lubrication .
- **thief**
  - A racking device or nonfunctional pattern area used in the electroplating process to provide a more uniform current density on plated parts. Thieves absorb the unevenly distributed current on irregularly shaped parts, thereby ensuring that the parts will receive an electroplated coating of uniform thickness.
- **thin-film circuit**
  - A circuit fabricated by the deposition of material several thousand angstroms thick (such as a circuit fabricated by vapor deposition). Compare with thick-film circuit .
- **thin-film lubrication**

  - A condition of lubrication in which the film thickness of the lubricant is such that the friction and wear between the surfaces is determined by the properties of the surfaces as well as the viscosity of the lubricant. Under thin-film conditions, the coefficient of friction is often 10 to 100 times greater than under thick-film conditions and wear is no longer negligible. Compare with thick-film lubrication .
- **thread grinding**
  - Thread cutting by use of suitably formed grinding wheel.
- **threading and knurling**
  - A method of surface roughening in which spiral threads are prepared, followed by upsetting with a knurling tool.
- **throwing power**
  - The ability of an electrodeposit to coat recessed areas of an irregularly shaped cathode , usually measured by noting the coating distance up a cylindrical tube that is coated in an electrodeposition bath. Compare with covering power .
- **tiger stripes**
  - Continuous bright lines on sheet or strip in the rolling direction.
- **tint etching**
  - Immersing metallographic specimens in specially formulated chemical etchants in order to produce a stable film on the specimen surface. When viewed under an optical microscope, these surface films produce colors that correspond to the various phases in the alloy. Also known as color etching.
- **titania**
  - A white water-insoluble powder of composition $TiO_2$ that is produced commercially from the minerals ilmenite and rutile. Used in paints and cosmetics and as an ingredient in porcelain enamels , ceramic whiteware, and ophthalmic glasses. Pure $TiO_2$ is also used as thin- or thick-film semiconductors.
- **titanium carbide**
  - Very hard, heat-resistant ceramic materials of the composition TiC used in cermets and tungsten carbide cutting tools. Chemical vapor deposited TiC coatings are also used to extend the life of cemented carbide cutting tools.
- **titanium nitride**
  - A hard, high-melting-point ceramic (2950 °C, or 5342 °F) of the composition TiN that is used in cermets and as a coating material for cemented carbide cutting tools. See also carbide tools .
- **tolerance**
  - The specified permissible deviation from a specified nominal dimension, or the permissible variation in size or other quality characteristic of a part.
- **topcoat**
  - Usually the final paint film applied to a surface.
- **topography**
  - The configuration of a surface including its relief and the position of its natural and man-made features.
- **total cyanide**
  - Cyanide content of an electroplating bath (including both simple and complex ions).
- **toughness**
  - Ability of a material to absorb energy and deform plastically before fracturing. Toughness is proportional to the area under the stress-strain curve from the origin to the breaking point. In metals, toughness is usually measured by the energy absorbed in a notch impact test.
- **T-peel strength**
  - The average load per unit width of adhesive bond line required to produce progressive separation of two bonded, flexible adherends, under standard test conditions.
- **transcrystalline cracking**
  - Cracking or fracturing that occurs through or across a crystal. Also termed intracrystalline cracking.
- **transfer**
  - In tribology, the process by which material from one sliding surface becomes attached to another surface, possibly as the result of interfacial adhesion. Transfer is usually associated with adhesion, but the possibility of mechanical interlocking adherence, without adhesive bonding, exists in certain occurrences. Material may also back transfer to the surface from which it came.

- **transfer efficiency**
  - In powder coating, the rate at which a powder is deposited on a target per unit of time divided by the gun output.
- **transferred arc**
  - A plasma arc established between the electrode and the workpiece during plasma arc welding, cutting, and thermal spraying.
- **transgranular cracking**
  - Cracking or fracturing that occurs through or across a crystal or grain. Also called transcrystalline cracking. Contrast with intergranular cracking .
- **transgranular fracture**
  - Fracture through or across the crystals or grains of a material. Also called transcrystalline fracture or intracrystalline fracture. Contrast with intergranular fracture .
- **transition diagram**
  - In tribology, a plot of two or more experimental or operating variables that indicates the boundaries between various regimes of wear or surface damage. The IRG transition diagram is a plot of normal force (ordinate) versus sliding velocity (abscissa), and is used to identify three regions with differing lubrication effectiveness. Various plots have been called transition diagrams, and the context of usage must be established.
- **transmission electron microscopy (TEM)**
  - An analytical technique in which an image is formed by an electron beam directly on a photographic film of phosphor-coated plate. Image contrast is formed by the scattering of electrons out of the beam. TEM is used for very high magnification characterization of metals, ceramics, minerals, polymers, and biological materials.
- **traverse speed**
  - The lineal velocity at which the torch is passed across the substrate during the thermal spraying operation.
- **trees**
  - Branched or irregular projections formed on a cathode during electrodeposition , especially at edges and other areas of high current density .
- **tribology**
  - (1) The science and technology of interacting surfaces in relative motion and of the practices related thereto. (2) The science concerned with the design, friction, lubrication, and wear of contacting surfaces that move relative to each other (as in bearings, cams, or gears, for example).
- **tribosurface**
  - Any solid surface whose intermittent, repeated, or continuous contact with another surface or surfaces, in relative motion, results in friction, wear, and/or surface damage. The surface of a body subjected to a catastrophic collision would not generally be considered a tribosurface because significant damage to the entire body is involved.
- **trimming**
  - The mechanical shearing of flash from molded and forged parts.
- **tripoli compound**
  - A buffing compound containing approximately 75% free or crystalline silica.
- **truing**
  - The removal of the outside layer of abrasive grains on a grinding wheel for the purpose of restoring its face.
- **trunk**
  - The thick base of a burr .
- **tuberculation**
  - The formation of localized corrosion products scattered over the surface in the form of knoblike mounds called tubercles. The formation of tubercles is usually associated with biological corrosion.
- **tumble grinding**
  - Various surfacing operations ranging from deburring and polishing to honing and microfinishing metallic parts before and after plating.
- **tumbling**
  - Rotating workpieces, usually castings or forgings, in a barrel partly filled with metal slugs or abrasives, to remove sand, scale , or fins. It may be done dry, or with an aqueous solution added to the contents of the barrel. See also barrel finishing .

- **turning**
    - Removing material by forcing a single-point cutting tool against the surface of a rotating workpiece. The tool may or may not be moved toward or along the axis of rotation while it cuts away material.
- **U**
- **ultrahard tool materials**
    - Very hard, wear-resistant materials--specifically, polycrystalline diamond and polycrystalline cubic boron nitride--that are fabricated into solid or layered cutting tool blanks for machining applications. See also superabrasives .
- **ultraprecision finishing**
    - Machining processes used to alter surface characteristics such as finish, waviness, roundness, etc., without substantial removal of the work material. Examples include lapping and polishing of optical lenses, computer chips, or magnetic heads, and honing of cylinder liners.
- **ultrasonic cleaning**
    - Immersion cleaning aided by ultrasonic waves that cause microagitation and microcavitation.
- **ultrasonic C-scan inspection**
    - A method for displaying the relative attenuation of ultrasonic waves across the surface (plan view) of a structural component. An ultrasonic transducer is used to scan the surface of a material mechanically in an *x-y* raster scan mode while generating and receiving waves. Either the material is immersed in a water bath or columns of water are provided between the transducer and the material as a medium for ultrasonic energy transmissions. The received wave signals are electronically conditioned and measured to determine relative energy losses of the wave as it progresses through the material at each particular location on the specimen. Ultrasonic C-scan has been used extensively to determine both the initial integrity of a manufactured part and the void content, and to follow the initiation and progression of damage resulting from environmental loading.
- **ultrasonic impact grinding**
    - Material removal by means of an abrasive slurry and the ultrasonic vibration of a nonrotating tool. The abrasive slurry flows through a gap between the workpiece and the vibrating tool. Material removal occurs when the abrasive particles, suspended in the slurry, are struck on the downstroke of the vibrating tool. The velocity imparted to the abrasive particles causes microchipping and erosion as the particles impinge on the workpiece. See also ultrasonic machining .
- **ultrasonic inspection**
    - A nondestructive method in which beams of high-frequency sound waves are introduced into materials for the detection of surface and subsurface flaws in the material. The sound waves travel through the material with some attendant loss of energy (attenuation) and are reflected at interfaces. The reflected beam is displayed and then analyzed to define the presence and location of flaws or discontinuities. Most ultrasonic inspection is done at frequencies between 0.1 and 25 MHz--well above the range of human hearing, which is about 20 Hz to 20 kHz.
- **ultrasonic machining**
    - A process for machining of hard, brittle, nonmetallic materials that involves the ultrasonic vibration of a rotating diamond core drill or milling tool. Rotary ultrasonic machining is similar to the conventional drilling of glass and ceramic with diamond core drills, except that the rotating core drill is vibrated at an ultrasonic frequency of 20 kHz. Rotary ultrasonic machining does not involve the flow of an abrasive slurry through a gap between the workpiece and the tool. Instead, the tool contacts and cuts the workpiece, and a liquid coolant, usually water, is forced through the bore of the tube to cool and flush away the removed material. See also ultrasonic impact grinding .
- **ultraviolet radiation**
    - High-energy short-wavelength radiation used in coatings to cross link primarily acrylic and methacrylic systems by means of free-radical reactions.
- **undercoat**
    - A deposited coat of material that acts as a substrate for a subsequent thermal spray deposit. See also bond coat .
- **underfilm corrosion**
    - Corrosion that occurs under organic films in the form of randomly distributed threadlike filaments or spots. In many cases this is identical to filiform corrosion .

- **underfiring**
  - Firing a porcelain enamel coating at a lower temperature than that recommended, allowing an insufficient length of time in the furnace, or applying too heavy a layer of the enamel. Likely to cause blisters or boiling of the ground coat through the cover coat, or the enamel ground coat may fishscale before the cover coat can be applied and fired.
- **uniform corrosion**
  - (1) A type of corrosion attack (deterioration) uniformly distributed over a metal surface. (2) Corrosion that proceeds at approximately the same rate over a metal surface. Also called general corrosion .
- **unlubricated sliding**
  - Sliding without lubricant but not necessarily under completely dry conditions. Unlubricated sliding is often used to mean "not intentionally lubricated," but surface species such as naturally formed surface oxides and other interfacial contaminants may act in a lubricious manner in nominally lubricated sliding.
- **upper critical temperature**
  - The temperature above which austenite is the stable phase. Also called the $A_3$ temperature.
- **UV stabilizers**
  - Chemicals added to paint to absorb the ultraviolet radiation present in sunlight. Ultraviolet radiation decomposes the polymer molecules in a paint film, and thus UV stabilizers are used to prolong paint life.
- **V**
- **vacuum carburizing**
  - A high-temperature gas carburizing process using furnace pressures between 13 and 67 kPa (0.1 to 0.5 torr) during the carburizing portion of the cycle. Steels undergoing this treatment are austenitized in a rough vacuum, carburized in a partial pressure of hydrocarbon gas, diffused in a rough vacuum, and then quenched in either oil or gas. Both batch and continuous furnaces are used.
- **vacuum deposition**
  - Deposition of a metal film onto a substrate in a vacuum by metal evaporation techniques.
- **vacuum metallizing**
  - A process in which surfaces are thinly coated by exposing them to a metal vapor under vacuum.
- **vacuum nitrocarburizing**
  - A subatmospheric nitrocarburizing process using a basic atmosphere of 50% ammonia/50% methane, containing controlled oxygen additions of up to 2%.
- **vapor degreasing**
  - See degreasing .
- **vapor-deposited replica**
  - A replica formed of a metal or a salt by the condensation of the vapors of the material onto the surface to be replicated.
- **vapor-phase lubrication**
  - A type of lubrication in which one or more gaseous reactants are supplied to the vicinity of the surface to be lubricated and which subsequently react to form a lubricious deposit on that surface.
- **vapor plating**
  - Deposition of a metal or compound on a heated surface by reduction or decomposition of a volatile compound at a temperature below the melting points of the deposit and the base material. The reduction is usually accomplished by a gaseous reducing agent such as hydrogen. The decomposition process may involve thermal dissociation or reaction with the base material. Occasionally used to designate deposition on cold surfaces by vacuum evaporation. See also vacuum deposition .
- **varnish**
  - (1) In lubrication, a deposit resulting from the oxidation and/or polymerization of fuels, lubricating oils, or organic constituents of bearing materials. Harder deposits are described as lacquers , softer deposits are described as gums. (2) A transparent surface coating which is applied as a liquid and then changes to a hard solid; all varnishes are solutions of resinous materials in a solvent.
- **vehicle**
  - The combination of a paint binder and solvents or diluents, which are used to put the binder in a liquid, usable form.

- **veining**
    - A subboundary structure in a metal that can be delineated because of the presence of a greater than average concentration of precipitate or solute atoms.
- **vibratory cavitation**
    - Cavitation caused by the pressure fluctuations within a liquid, induced by the vibration of a solid surface immersed in the liquid.
- **vibratory finishing**
    - A process for deburring and surface finishing in which the product and an abrasive mixture are placed in a container and vibrated.
- **vibratory polishing**
    - A mechanical polishing process in which a metallographic specimen is made to move around the polishing cloth by imparting a suitable vibratory motion to the polishing system. See also polishing .
- **Vickers hardness test**
    - A microindentation hardness test employing a 136° diamond pyramid indenter (Vickers) and variable loads, enabling the use of one hardness scale for all ranges of hardness--from very soft lead to tungsten carbide. Also known as diamond pyramid hardness test.
- **VI improver**
    - An additive, usually a polymer , that reduces the variation of viscosity with temperature, thereby increasing the viscosity index of an oil.
- **viscosity**
    - The property of a liquid that enables it to resist flow, often measured by the time required for a given volume of liquid to flow through a small hole in the bottom of a cup under controlled conditions. A thick liquid-like molasses has a high viscosity.
- **visual examination**
    - The qualitative observation of physical characteristics, observed by using the unaided eye or perhaps aided by the use of a simple hand-held lens (up to 10×).
- **void**
    - (1) A shrinkage cavity produced in castings or weldments during solidification. (2) A term generally applied to paints to describe holidays , holes, and skips in a film.
- **volatile organic compounds (VOC)**
    - Volatile organic materials, such as solvents, that are present in many coating products.
- **volatiles**
    - Materials, such as water and alcohol, in a sizing or resin formulation, that are capable of being driven off as a vapor at room temperature or at slightly elevated temperature. See also size .
- **W**
- **Wallner lines**
    - A distinct pattern of intersecting sets of parallel lines, sometimes producing a set of V-shaped lines, sometimes observed when viewing brittle fracture surfaces at high magnification in an electron microscope. Wallner lines are attributed to interaction between a shock wave and a brittle crack front propagating at high velocity. Sometimes Wallner lines are misinterpreted as fatigue striations .
- **warpage**
    - (1) Deformation other than contraction that develops in a casting between solidification and room temperature. (2) The distortion that occurs during annealing, stress relieving, and high-temperature service.
- **water break test**
    - A test to determine if a surface is chemically clean by the use of a drop of water, preferably distilled water. If the surface is clean, the water will break and spread; a contaminated surface will cause the water to bead.
- **water marks**
    - Defects in a fired porcelain enamel surface due to water (perspiration) dropping on the dried enamel or not being thoroughly removed from crevices in the workpiece during the drying step after pickling or cleaning. Similar defects may also be caused by too much water in an enamel slip or poor suspension of the enamel slip. Also called water lines or water streaks.
- **waviness**
    - A wavelike variation from a perfect surface, generally much larger and wider than the roughness caused by tool or grinding marks. See also roughness .

- **wear**
    - Damage to a solid surface, generally involving progressive loss of material, due to a relative motion between that surface and a contacting surface or substance. Compare with surface damage .
- **wear debris**
    - Particles that become detached in a wear process.
- **wear scar**
    - The portion of a solid surface that exhibits evidence that material has been removed from it due to the influence of one or more wear processes.
- **weathering steels**
    - Copper-bearing high-strength low-alloy steels that exhibit high resistance to atmospheric corrosion in the unpainted condition.
- **wedge effect**
    - The establishment of a pressure wedge in a lubricant. See also wedge formation (2).
- **wedge formation**
    - (1) In sliding metals, the formation of a wedge or wedges of plastically sheared metal in local regions of interaction between sliding surfaces. This type of wedge is also known as a prow. It is similar to a built-up edge . (2) In hydrodynamic lubrication, the establishment of a pressure gradient in a fluid flowing into a converging channel. This is also known as wedge effect .
- **weld decay**
    - Intergranular corrosion , usually of stainless steels or certain nickel-base alloys, that occurs as the result of sensitization in the heat-affected zone during the welding operation.
- **wet blasting**
    - A process for cleaning or finishing by means of a slurry of abrasive in water directed at high velocity against the workpieces. Many different kinds and sizes of abrasives can be used in wet blasting. Sizes range from 20-mesh (very coarse) to 5000-mesh (which is much finer than face powder). Among the types of abrasives used are: organic or agricultural materials such as walnut shells and peach pits; novaculite, which is a soft type (6 to 6.5 Mohs hardness) of silica (99.46% silica); silica, quartz, garnet, and aluminum oxide; other refractory abrasives; and glass beads.
- **wet etching**
    - In metallography, revealing the microstructure in metals through the use of liquids, such as acids, bases, neutral solutions, or mixtures of solutions.
- **wet milling**
    - The grinding of porcelain enamel materials with sufficient liquid to form a slurry .
- **wet process enameling**
    - A method of porcelain enameling in which slip is applied to a metal article at ambient temperature, dried, and fired.
- **wetting**
    - The penetration of soil by the cleaning solution. Soap and/or wetting agents wetting increase the wetting action of water or solvents on a surface or soil by reducing surface tension. This wetting action helps in dislodging and removing soil.
- **wetting agent**
    - A substance that reduces the surface tension of a liquid, thereby causing it to spread more readily on a solid surface.
- **whiskers**
    - Metallic filamentary growths, often microscopic, sometimes formed during electrodeposition and sometimes spontaneously during storage or service, after finishing. Common on electrical contacts plated with zinc or cadmium.
- **white-etching layer**
    - A surface layer in a steel that, as viewed in a section after etching, appears whiter than the base metal . The presence of the layer may be due to a number of causes, including plastic deformation induced by machining, or surface rubbing, heating during a metallographic preparation stage to such an extent that the layer is austenitized and then hardened during cooling, and diffusion of extraneous elements into the surface.
- **white layer**
    - Surface layer on nitrided steels that is made up of intermetallic compounds, which do not etch and appear white in light microscopy.
- **white rust**

    - Zinc oxide; the powder product of corrosion of zinc or zinc-coated surfaces.
- **wiped coat**
    - A hot dipped galvanized coating from which virtually all free zinc is removed by wiping prior to solidification, leaving only a thin zinc-iron alloy layer.
- **wipe solvent cleaning**
    - A method for removing contaminants from a surface by wetting a clean cloth with a solvent , wiping the surface to be cleaned, and then removing the residual solvent from the surface with a clean, dry cloth.
- **wiping**
    - In tribology, the smearing or removal of material from one point, often followed by the redeposition of the material at another point, on the surface of two bodies in sliding contact. The smeared metal is usually softened or melted.
- **wire flame spraying**
    - A thermal spraying process variation in which the material to be sprayed is in wire or rod form. See also flame spraying .
- **X**
- **x-ray tomography**
    - A method of imaging the internal structure of materials in which an x-ray beam is passed through the sample in multiple directions. The density throughout the sample is reconstructed by a computer from the transmitted x-ray signal.
- **x-ray topography**
    - A technique that comprises topography and x-ray diffraction. The term topography refers to a detailed description and mapping of physical (surface) features in a region. In the context of the x-ray diffraction, topographic methods are used to survey the lattice structure and imperfections in crystalline materials.
- **Z**
- **Zincrometal**
    - A steel coil-coated product consisting of a mixed-oxide underlayer containing zinc particles and a zinc-rich organic (epoxy) topcoat. It is weldable, formable, paintable, and compatible with commonly used adhesives. Zincrometal is used to protect outer body panels in automobiles from corrosion.
- **zinc worms**
    - Surface imperfections, characteristic of high-zinc brass castings, that occur when zinc vapor condenses at the mold/metal interface, where it is oxidized and then becomes entrapped in the solidifying metals.

## Abbreviations, Symbols, and Tradenames

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### Abbreviations and Symbols

- ***a***
    - area
- **A**
    - austenite; ampere
- ***A***
    - cross-sectional area; contact area
- Å
    - angstrom
- **ac**
    - alternating current
- **ABS**
    - acrylonitrile butadiene styrene
- **AC**
    - air cool
- **$Ac_1$**
    - temperature at which austenite begins to form during heating

- **$Ac_3$**
    - temperature at which transformation of ferrite to austenite is completed during heating
- **$AC_{cm}$**
    - in hypereutectoid steel, temperature at which cementite completes solution in austenite
- **$A_e$**
    - surface area
- **$Ae_{cm}$, $Ae_1$, $Ae_3$**
    - equilibrium transformation temperatures in steel
- **AEM**
    - analytical electron microscope/microscopy
- **AES**
    - Auger electron spectroscopy; acoustic emission spectroscopy
- **AESF**
    - American Electroplaters and Surface Finishers Society
- **AFM**
    - atomic force microscope
- **AG**
    - aged; alternating grinding
- **AGMA**
    - American Gear Manufacturers Association
- **AISI**
    - American Iron and Steel Institute
- **Ams**
    - Amsler circumferential, rotating disk-on-disk machine
- **AMS**
    - Aerospace Material Specification; acoustic material signature
- **ANSI**
    - American National Standards Institute
- **APCVD**
    - atmospheric-pressure chemical vapor desposition
- **API**
    - American Petroleum Institute
- **$Ar_1$**
    - temperature at which transformation to ferrite or to ferrite plus cementite is completed on cooling
- **$Ar_3$**
    - temperature at which transformation of austenite to ferrite begins on cooling
- **$Ar_{cm}$**
    - temperature at which cementite begins to precipitate from austenite on cooling
- **ARE**
    - activated reactive evaporation
- **ARIP**
    - activated reactive ion plating
- **ARP**
    - Aerospace Recommended Practice
- **ASLE**
    - American Society of Lubrication Engineers (former name of STLE)
- **ASM**
    - American Society for Metals (now ASM International)
- **ASME**
    - American Society of Mechanical Engineers
- **ASTM**
    - American Society for Testing and Materials
- **at.%**
    - atomic percent
- **atm**
    - atmospheres (pressure)
- **AWS**

    - American Welding Society
- **B**
    - bainite
- **$B$**
    - gaseous reaction product
- **bal**
    - balance
- **BARE**
    - biased activated reactive evaporation
- **bcc**
    - body-centered cubic
- **bct**
    - body-centered tetragonal
- **Bé**
    - Baumé (specific-gravity scale)
- **BUE**
    - built-up edge
- **$c$**
    - edge length in crystal structure; speed of light; specific heat; constant; conductivity
- **C**
    - cementite; coulomb; heat capacity
- **$C$**
    - constant; velocity of light; shock wave velocity
- **CAD/CAM**
    - computer-aided design/computer-aided manufacturing
- **CAE**
    - corrosion-affected erosion
- **CANMET**
    - Canada Center for Mineral and Energy Technology
- **CBED**
    - convergent-beam electron diffraction
- **CBN**
    - cubic boron nitride
- **CCT**
    - continuous-cooling transformation
- **cd**
    - candela
- **CE**
    - carbon equivalent
- **CERCLA**
    - Comprehensive Environmental Response, Compensation, and Liability Act
- **$C_\mathrm{f}$**
    - bearing friction factor
- **CFC**
    - chlorofluorocarbon
- **CFG**
    - creep feed grinding
- **CFR**
    - Code of Federal Regulations
- **cgs**
    - centimeter-gram-second (system of units)
- **CI**
    - compression ignition
- **CLA**
    - center-line average
- **cm**
    - centimeter

- **CMA**
    - cylindrical mirror analyzer
- **CMOS**
    - complementary metal-oxide semiconductor
- **CNC**
    - computer numerical control
- **cP**
    - centipoise
- **CSOM**
    - confocal scanning optical microscope
- **cSt**
    - centistokes
- **CTE**
    - coefficient of thermal expansion
- **CVD**
    - chemical vapor deposition
- **CVI**
    - chemical vapor infiltration
- **CVN**
    - Charpy V-notch (impact test or specimen)
- **cw**
    - continuous wave
- **d**
    - day
- ***d***
    - used in mathematical expressions involving a derivative (denotes rate of change); depth; diameter; interatomic distance
- ***D***
    - diameter; penetration depth
- ***da*/*dN***
    - fatigue crack growth rate
- **dB**
    - decibel
- **$D_{\mathrm{B}}$**
    - ball diameter of Brinell hardness tester
- **DBT**
    - ductile-to-brittle transition
- **dc**
    - direct current
- **dhcp**
    - double hexagonal close-packed
- **diam**
    - diameter
- **DIBS**
    - dual-ion-beam sputtering
- **DIN**
    - Deutsche Industrie-Normen (German Industrial Standards)
- **DLC**
    - diamondlike carbon
- ***dL*/*dX***
    - loading rate
- **dpa**
    - displacements per incident atom
- **DPH**
    - diamond pyramid hardness (Vickers hardness)
- ***e***
    - natural log base, 2.71828; charge of an electron

- ***E***
  - erosion rate; Young's modulus; modulus of elasticity; applied voltage; energy; activation energy
- **EAW**
  - electric arc wire (spray)
- **EB**
  - electron beam
- **EBM**
  - electron-beam machining
- **$E_c$**
  - Young's modulus of coating
- **E/C**
  - erosion/corrosion
- **ECCS**
  - electrolytic chromium-coated steel
- **ECD**
  - electrochemical deburring
- **ECM**
  - electrochemical machining
- **ECP**
  - electron channeling pattern
- **ECR**
  - electron cyclotron resonance
- **$E_d$**
  - displacement energy
- **EDM**
  - electrical discharge machining
- **EDS**
  - energy-dispersive spectrometer
- **EDX**
  - energy-dispersive spectroscopy
- **EDXA**
  - energy dispersive x-ray analysis
- **EEC**
  - erosion-enhanced corrosion
- **EELS**
  - electron energy loss spectroscopy
- **EHD**
  - elastohydrodynamic
- **EHL**
  - elastohydrodynamic lubrication
- **ELI**
  - extra-low interstitial
- **emf**
  - electromotive force
- **EP**
  - extreme pressure
- **EPA**
  - Environmental Protection Agency
- **EPMA**
  - electron probe microanalysis
- **Eq**
  - equation
- **ESCA**
  - electron spectroscopy for chemical analysis
- **ESD**
  - electrospark deposition; electron-stimulated desorption
- **ESR**

  - electroslag remelting
- **et al.**
  - and others
- **ETP**
  - electrolytic tin-plated (steel strip)
- **eV**
  - electron volt
- **exp**
  - base of the natural logarithm
- ***f***
  - frequency; friction coefficient; volume fraction
- **F**
  - ferrite
- ***F***
  - load; force
- **FAA**
  - Federal Aviation Administration
- **FBC**
  - fluidized bed combustion
- **fcc**
  - face-centered cubic
- **FCC**
  - fluid catalytic cracking
- **fct**
  - face-centered tetragonal
- **FEA**
  - finite element analysis
- **Fig.**
  - figure
- **ft**
  - foot
- **FTIR**
  - Fourier transform infrared spectroscopy
- **g**
  - gram
- ***g***
  - acceleration due to gravity
- **G**
  - graphite; gauss
- **gal**
  - gallon
- **gf**
  - gram force
- **GPa**
  - gigapascal
- **GTA**
  - gas tungsten arc
- **h**
  - hour; vertical thickness; Planck's constant ($6.626 \times 10^{-27}$ erg · s)
- **H**
  - Henry
- ***H***
  - enthalpy; hardness; magnetic field; height; depth of wear
- **HAIM**
  - high-frequency acoustic imaging
- **HAZ**
  - heat-affected zone

- **HB**
    - Brinell hardness
- **hcp**
    - hexagonal close-packed
- **HCT**
    - high coiling temperature
- **HDPE**
    - high-density polyethylene
- **HERF**
    - high-energy-rate forming
- **HIP**
    - hot isostatic pressing
- **HK**
    - Knoop hardness
- **hp**
    - horsepower
- **HR**
    - Rockwell hardness (requires scale designation, such as HRC for Rockwell C hardness)
- **HREM**
    - high-resolution electron microscopy (microhardness)
- **HRMF**
    - Rockwell microficial (microhardness)
- **HSLA**
    - high-strength low-alloy
- **HSS**
    - high-speed steel(s)
- **HV**
    - Vickers hardness
- **HVOF**
    - high-velocity oxyfuel (thermal-spray coating)
- **Hz**
    - hertz
- ***I***
    - intensity; electrical current; bias current
- **IBAD**
    - ion-beam-assisted deposition
- **IC**
    - integrated circuit
- **ICB**
    - ionized cluster beam (deposition)
- **ID**
    - inside diameter
- **in.**
    - inch
- **IP**
    - conventional ion plating
- **IR**
    - infrared
- **ISCC**
    - intergranular stress-corrosion cracking
- **ISO**
    - International Organization for Standardization
- **ISS**
    - ion scattering spectroscopy
- **J**
    - joule
- ***J***

  - ion current density
- **k**
  - Boltzmann constant
- $k$
  - thermal conductivity; Boltzmann constant; wear factor; wear coefficient
- **K**
  - kelvin
- $K$
  - wear coefficient; specific wear rate
- **kg**
  - kilogram
- **kgf**
  - kilogram force
- $K_{\mathrm{Ic}}$
  - plane-strain fracture toughness
- $K_{\mathrm{ISCC}}$
  - threshold stress intensity to produce stress-corrosion cracking
- **km**
  - kilometer
- **kN**
  - kilonewton
- **kPa**
  - kilopascal
- **ksi**
  - kips (1000 lbf) per square inch
- **kV**
  - kilovolt
- **kW**
  - kilowatt
- $l$
  - length
- $\ell$
  - length
- **L**
  - longitudinal; liter
- **lb**
  - pound
- **lbf**
  - pound force
- **LCVD**
  - laser-induced chemical vapor deposition
- **LCL**
  - lower control limit
- **LCP**
  - liquid crystal polymer
- **LCSM**
  - laser confocal scanning microscope
- **LCT**
  - low coiling temperature
- **LDPE**
  - low-density polyethylene
- **LEED**
  - low-energy electron diffraction
- **ln**
  - natural logarithm (base $e$)
- **log**
  - common logarithm (base 10)

- **LPCVD**
    - low-pressure chemical vapor deposition
- **LSI**
    - large-scale integrated (circuit)
- **LT**
    - long transverse (direction)
- **m**
    - meter
- ***m***
    - constant shear, or frictional factor; Weibull slope, for reliability above 90%; Weibull distribution; dispersion parameter; molecular weight
- **mA**
    - milliampere
- **MAS**
    - Microbeam Analysis Society
- **MBE**
    - molecular-beam epitaxy
- **mc**
    - microcracked (chromium electroplate)
- **MCM**
    - multichip module
- **MEP**
    - mean effective pressure
- **MeV**
    - megaelectronvolt
- **$M_f$**
    - temperature at which martensite formation finishes during cooling
- **MFP**
    - mean free path
- **mg**
    - milligram
- **Mg**
    - megagram (metric tonne, or kg × $10^3$)
- **MID**
    - molded interconnect device
- **MIG**
    - metal inert gas (welding)
- **min**
    - minute; minimum
- **mL**
    - milliliter
- **mm**
    - millimeter
- **MMC**
    - metal-matrix composite
- **MOCVD**
    - metal-organic chemical vapor deposition
- **mp**
    - microporous (chromium electroplate)
- **mPa**
    - millipascal
- **MPa**
    - megapascal
- **mpg**
    - miles per gallon
- **mph**
    - miles per hour

- **MRR**
    - material removal rate
- **ms**
    - millisecond
- **$M_s$**
    - temperature at which martensite starts to form from austenite on cooling
- **MS**
    - megasiemens; magnetron sputtering
- **MSA**
    - methane sulfonic acid
- **MSDS**
    - material safety data sheet
- **mT**
    - millitesla
- **mV**
    - millivolt
- **MV**
    - megavolt
- **MVVA**
    - metal vapor vacuum arc
- **N**
    - newton
- ***N***
    - number of cycles; normal solution; normal force
- **NASA**
    - National Aeronautics and Space Administration
- **NBS**
    - National Bureau of Standards (former name of NIST)
- **NCCA**
    - National Coil Coaters Association
- **NDE**
    - nondestructive evaluation
- **NF**
    - nonfluoborate (tin-lead electroplating solution)
- **NIST**
    - National Institute of Standards and Technology
- **nm**
    - nanometer
- **No.**
    - number
- **ns**
    - nanosecond
- **OCG**
    - optical gas controller
- **Oe**
    - oersted
- **OFD**
    - oxyfuel detonation (spray)
- **OFP**
    - oxyfuel powder (spray)
- **OFW**
    - oxyfuel wire (spray)
- **OMCVD**
    - organo-metallic chemical vapor deposition
- **ORNL**
    - Oak Ridge National Laboratory
- **OSHA**

    - Occupational Safety and Health Administration
- **oz**
    - ounce
- **p**
    - page
- ***p***
    - pressure
- **P**
    - pearlite
- ***P***
    - specific load or unit load; pressure
- **Pa**
    - Pascal
- **PA**
    - plasma arc (spray); prealloyed; polyamide
- **PACVD**
    - plasma-assisted chemical vapor deposition
- **PAN**
    - polyacrylonitrile
- **PAO**
    - polyalphaolefin
- **PAPVD**
    - plasma-assisted physical vapor deposition
- **PBT**
    - polybutylene terephthalate
- **PCD**
    - polycrystalline diamond
- **Pe**
    - Péclet number
- **PECVD**
    - plasma-enhanced chemical vapor deposition
- **PEM**
    - plasma emission monitor
- **PES**
    - polyether sulfone
- **PFPE**
    - polyperfluoroalkylether
- **PGM**
    - platinum-group metal
- **pH**
    - negative logarithm of hydrogen-ion activity
- **PH**
    - precipitation hardenable
- **PLD**
    - pulsed-laser deposition
- **P/M**
    - powder metallurgy
- **PMMA**
    - polymethyl methacrylate
- **POP**
    - plating on plastic
- **ppb**
    - parts per billion
- **ppba**
    - parts per billion atomic
- **ppm**
    - parts per million

- **ppmm**
  - parts per million by mass
- **ppt**
  - parts per trillion
- **psi**
  - pounds per square inch
- **psia**
  - pounds per square inch absolute
- **psig**
  - gage pressure (pressure relative to ambient pressure) in pounds per square inch
- **PSII**
  - plasma-source ion implantation
- **PSZ**
  - partially stabilized zirconia
- **PTFE**
  - polytetrafluoroethylene
- **PTH**
  - plated-through-hole (printed wiring board)
- **PVC**
  - polyvinyl chloride
- **PVD**
  - physical vapor deposition
- **PWB**
  - printed wiring board
- **QWP**
  - quarter-wave plate
- ***r***
  - radius; resistivity
- **R**
  - roentgen; force vector
- ***R***
  - radius; gas constant; resistance
- **$R_a$**
  - surface roughness in terms of arithmetic average
- **RA**
  - reduction in area
- **RCRA**
  - Resource Conservation and Recovery Act
- **RE**
  - rare earth
- **Ref**
  - reference
- **rf**
  - radio frequency
- **RH**
  - relative humidity
- **RHEED**
  - reflection high-energy electron diffraction
- **RIBAD**
  - reactive ion-beam-assisted deposition
- **RIP**
  - reactive ion plating
- **rms**
  - root mean square
- **rpm**
  - revolutions per minute
- **$R_q$**

  - rms (root mean square) roughness
- **RS**
  - reactive sputtering
- **RT**
  - room temperature
- **RTP**
  - rapid thermal processing
- **s**
  - second
- ***s***
  - standard deviation
- **S**
  - sand cast; siemens
- ***S***
  - sputtering yield; Sommerfeld number; rotational speed; rms average surface roughness
- **SAD**
  - selected-area diffraction
- **SAE**
  - Society of Automotive Engineers
- **SAM**
  - scanning acoustic microscope/microscopy
- **SARA**
  - Superfund Amendments and Reauthorization Act
- **SCaM**
  - scanning capacitance microscope
- **SCC**
  - stress-corrosion cracking
- **SCE**
  - saturated calomel electrode
- **SCR**
  - selective catalytic reduction
- **SE**
  - spectroscopic ellipsometry
- **SEM**
  - scanning electron microscope/microscopy
- **sfm**
  - surface feet per minute
- **SHE**
  - standard hydrogen electrode
- **SI**
  - Système International d'Unités
- **SIMS**
  - secondary ion mass spectroscopy
- **SIP**
  - sputter ion plating
- **SLAM**
  - scanning laser acoustic microscope/microscopy
- **SMA**
  - shielded metal arc
- **SMAW**
  - shielded metal arc welding
- **SPC**
  - statistical process control
- **SPE**
  - solid particle erosion
- **sp gr**
  - specific gravity

- **SPL**
    - spent pickle liquor
- **SRM**
    - Standard Reference Materials
- **ST**
    - short transverse (direction)
- **STA**
    - solution-treated and aged
- **std**
    - standard
- **STEM**
    - scanning transmission electron microscope/microscopy
- **STLE**
    - Society of Tribologists and Lubrication Engineers (formerly ASLE)
- **STM**
    - scanning tunneling microscope/microscopy
- **SUS**
    - Saybolt Universal Seconds (viscosity)
- **SWE**
    - single-wavelength ellipsometry
- **Sv**
    - sievert
- **SZM**
    - structure-zone model
- $t$
    - thickness; time
- **T**
    - tesla
- $T$
    - temperature; thickness
- $T_c$
    - contact temperature; critical temperature; Curie temperature
- **TEM**
    - transmission electron microscope/microscopy
- **TFS**
    - tin-free steel
- **TFT**
    - thin film transistor
- **TGA**
    - thermogravimetric analysis
- **TGS**
    - threshold galling stress
- **TIG**
    - tungsten inert gas (welding)
- **TLA**
    - thin layer activation
- **TLV**
    - threshold level value
- $T_m$
    - mean contact temperature; melting temperature
- **TR**
    - temper rolled
- **TRS**
    - transverse rupture strength
- **TSCA**
    - Toxic Substances Control Act
- **tsi**

    - tons per square inch
- **TSM**
    - tandem scanning microscope/microscopy
- **TTT**
    - time-temperature transformation
- **UHDPE**
    - ultrahigh-density polyethylene
- **UHMWPE**
    - ultrahigh-molecular-weight polyethylene
- **UHV**
    - ultrahigh vacuum
- **UNS**
    - Unified Numbering System
- **UTS**
    - ultimate tensile strength
- ***v***
    - velocity; particle velocity
- **V**
    - volt
- ***V***
    - sliding speed; velocity; volume
- **VAR**
    - vacuum arc remelted
- **VHN**
    - Vickers microindenter hardness number
- **VI**
    - viscosity index
- **VIM-VAR**
    - vacuum induction melted-vacuum arc remelted
- **VOC**
    - volatile organic compound
- **vol**
    - volume
- **vol%**
    - volume percent
- **VPE**
    - vapor-phase epitaxy
- ***w***
    - width
- **W**
    - watt
- ***W***
    - load; weight of body; abrasive wear resistance; wear volume
- **WDS**
    - wavelength-dispersive spectrometer
- **WPC**
    - wear particle concentration
- **WRP**
    - work removal parameter
- **wt%**
    - weight percent
- **XPS**
    - x-ray photoelectron spectroscopy
- **XRD**
    - x-ray diffraction
- **XRF**
    - x-ray fluorescence

- **XTEM**
    - cross-sectional transmission electron microscopy
- ***Y***
    - yield stress in tension
- **YAG**
    - yttrium-aluminum-garnet
- **yr**
    - year
- **ZTA**
    - zirconia-toughened alumina
- **°**
    - angular measure; degree
- **°C**
    - degree Celsius (centigrade)
- **°F**
    - degree Fahrenheit
- **!**
    - direction of reaction
- **÷**
    - divided by
- **=**
    - equals
- ≅
    - approximately equals
- ≠
    - not equal to
- ≡
    - identical with
- >
    - greater than
- >>
    - much greater than
- ≥
    - greater than or equal to
- ∞
    - infinity
- ∝
    - is proportional to; varies as
- ∫
    - integral of
- <
    - less than
- <<
    - much less than
- ≤
    - less than or equal to
- ±
    - maximum deviation
- **-**
    - minus; negative ion charge
- ×
    - diameters (magnification); multiplied by
- ·
    - multiplied by
- /
    - per
- **%**

  - percent
- +
  - plus; positive ion charge
- $\sqrt{\ }$
  - square root of
- ~
  - approximately; similar to
- $\partial$
  - partial derivative
- $\alpha$
  - nominal contact angle; thermal diffusivity; taper angle; angle of incidence
- $\beta$
  - coefficient of friction
- $\gamma$
  - shear strain rate
- $\delta$
  - film width
- $\Delta$
  - change in quantity; an increment; a range; critical amplitude
- $\varepsilon$
  - lubricant film thickness; tribocontact parameter; emissivity; strain
- $\dot{e}$
  - strain rate
- $\eta$
  - lubricant viscosity; efficiency of material removal; degree of wear; abrasive fraction
- $\theta$
  - angle
- $\lambda$
  - wavelength; pressure coefficient of viscosity; film thickness-to-roughness ratio; lambda ratio; specific film thickness
- $\Lambda$
  - specific film thickness; compressibility number; film thickness parameter
- $\mu$
  - friction coefficient; magnetic permeability
- **μF**
  - microfarads
- **μin.**
  - microinch
- **μm**
  - micrometer (micron)
- **μs**
  - microsecond
- $u$
  - Poisson's ratio
- $x$
  - Poisson's ratio
- $\pi$
  - pi (3.141592)
- $\rho$
  - density
- $\sigma$
  - stress; standard deviation; root-mean-square roughness; Stefan-Boltzmann constant
- $\sigma_s$
  - shear stress
- $\Sigma$
  - summation of
- $t$

  - applied stress
- *f*
  - standard normal distribution
- Φ
  - energy rate; work function
- **ψ**
  - rolling angle
- **ω**
  - angular velocity; frequency
- **Ω**
  - ohm

- **Greek Alphabet**
- **A, α**
  - alpha
- **B, β**
  - beta
- Γ**, γ**
  - gamma
- Δ**, δ**
  - delta
- **E, ε**
  - epsilon
- **Z,** *z*
  - zeta
- **H, η**
  - eta
- Θ**, θ**
  - theta
- **I,** *i*
  - iota
- **K, κ**
  - kappa
- Λ**, Lambda;**
  - lambda
- **M, μ**
  - mu
- **N,** *u*
  - nu
- Ξ**,** *x*
  - xi
- **O, o**
  - omicron
- Π**, π**
  - pi
- **P, ρ**
  - rho
- Σ**, σ**
  - sigma
- **T,** *t*
  - tau
- ϒ**,** *u*
  - upsilon
- Φ**,** *f*
  - phi
- **X, χ**

    - chi
- **ψ,**
    - psi
- **Ω, ω**
    - omega

- **Tradenames**
- **Amplate**
    - is a tradename of Amorphous Technologies International
- **Argental**
    - is a tradename of Ingold Me β technik GmbH
- **Falex**
    - is a trademark of Falex Corporation
- **Ferrostan**
    - is a trademark of USX Corporation
- **Galvalume**
    - is a trademark of Bethlehem Steel Corporation
- **Galvan**
    - is a trademark of USX Corporation
- **Inconel, Incoloy, and Nimonic**
    - are trademarks of Inco Alloys International, Inc.
- **Haynes and Hastelloy**
    - are trademarks of Haynes International, Inc.
- **Scotch-Brite and Scotch-Weld**
    - are trademarks of 3M Company
- **Super D-Gun**
    - is a tradename of Praxair Surface Technologies, Inc.
- **Taber Abraser**
    - is a trademark of Taber Industries

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