27 Surface Processing Operations

The processes discussed in this chapter operate on the surfaces of parts and/or products. The major categories of surface processing operations are (1) cleaning, (2) surface treatments, and (3) coating and thin film deposition. Cleaning refers to industrial cleaning processes that remove soils and contaminants that result from previous processing or the factory environment. They include both chemical and mechanical cleaning methods. Surface treatments are mechanical and physical operations that alter the part surface in some way, such as improving its finish or impregnating it with atoms of a foreign material to change its chemistry and physical properties.

Coating and thin film deposition include various processes that apply a layer of material to a surface. Products made of metal are almost always coated by electroplating (e.g., chrome plating), painting, or other process. Principal reasons for coating a metal are to (1) provide corrosion protection, (2) enhance product appearance (e.g., providing a specified color or texture), (3) increase wear resistance and/or reduce friction of the surface, (4) increase electrical conductivity, (5) increase electrical resistance, (6) prepare a metallic surface for subsequent processing, and (7) rebuild surfaces worn or eroded during service. Nonmetallic materials are also sometimes coated. Examples include (1) plastic parts coated to give them a metallic appearance; (2) antireflection coatings on optical glass lenses; and (3) certain coating and deposition processes used in the fabrication of semiconductor chips (Chapter 33) and printed circuit boards (Chapter 34). In all cases, good adhesion must be achieved between coating and substrate, and for this to occur the substrate surface must be very clean.

27.1   Industrial Cleaning Processes

Most work parts must be cleaned one or more times during their manufacturing sequence. Chemical and/or mechanical processes are used to accomplish this cleaning. Chemical cleaning methods use chemicals to remove unwanted oils and soils from the workpiece surface. Mechanical cleaning involves removal of substances from a surface by mechanical operations of various kinds. These operations often serve other functions such as removing burrs, improving smoothness, adding luster, and enhancing surface properties.

27.1.1   CHEMICAL CLEANING

A typical surface is covered with various films, oils, dirt, and other contaminants (Section 5.3.1). Although some of these substances may operate in a beneficial way (such as the oxide film on aluminum), it is usually desirable to remove contaminants from the surface. This section discusses some general considerations related to cleaning and surveys the principal chemical cleaning processes used in industry.

Some of the important reasons why manufactured parts (and products) must be cleaned are (1) to prepare the surface for subsequent industrial processing, such as a coating application or adhesive bonding; (2) to improve hygiene conditions for workers and customers; (3) to remove contaminants that might chemically react with the surface; and (4) to enhance appearance and performance of the product.

General Considerations in Cleaning   There is no single cleaning method that can be used for all cleaning tasks. Just as various soaps and detergents are required for different household jobs (laundry, dishwashing, pot scrubbing, bathtub cleaning, and so forth), various cleaning methods are also needed to solve different cleaning problems in industry. Important factors in selecting a cleaning method are (1) the contaminant to be removed, (2) degree of cleanliness required, (3) substrate material to be cleaned, (4) purpose of the cleaning, (5) environmental and safety factors, (6) size and geometry of the part, and (7) production and cost requirements.

Various kinds of contaminants build up on part surfaces, either due to previous processing or the factory environment. To select the best cleaning method, one must first identify what must be cleaned. Surface contaminants found in the factory usually divide into one of the following categories: (1) oil and grease, which includes lubricants used in metalworking; (2) solid particles such as metal chips, abrasive grits, shop dirt, dust, and similar materials; (3) buffing and polishing compounds; and (4) oxide films, rust, and scale.

Degree of cleanliness refers to the amount of contaminant remaining after a given cleaning operation. Parts being prepared to accept a coating (e.g., paint, metallic film) or adhesive must be very clean; otherwise, adhesion of the coated material is jeopardized. In other cases, it may be desirable for the cleaning operation to leave a residue on the part surface for corrosion protection during storage, in effect replacing one contaminant on the surface by another that is beneficial. Degree of cleanliness is often difficult to measure in a quantifiable way. A simple test is a *wiping method*, in which the surface is wiped with a clean white cloth, and the amount of soil absorbed by the cloth is observed. It is a nonquantitative but easy test to use.

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The substrate material must be considered in selecting a cleaning method, so that damaging reactions are not caused by the cleaning chemicals. To cite several examples: aluminum is dissolved by most acids and alkalis; magnesium is attacked by many acids; copper is attacked by oxidizing acids (e.g., nitric acid); steels are resistant to alkalis but react with virtually all acids.

Some cleaning methods are appropriate to prepare the surface for painting, while others are better for plating. Environmental protection and worker safety are becoming increasingly important in industrial processes. Cleaning methods and the associated chemicals should be selected to avoid pollution and health hazards.

Chemical Cleaning Processes   Chemical cleaning uses various types of chemicals to effect contaminant removal from the surface. The major chemical cleaning methods are (1) alkaline cleaning, (2) emulsion cleaning, (3) solvent cleaning, (4) acid cleaning, and (5) ultrasonic cleaning. In some cases, chemical action is augmented by other energy forms; for example, ultrasonic cleaning uses high-frequency mechanical vibrations combined with chemical cleaning.

Alkaline cleaning is the most widely used industrial cleaning method. As its name indicates, it employs an alkali to remove oils, grease, wax, and various types of particles (metal chips, silica, carbon, and light scale) from a metallic surface. Alkaline cleaning solutions consist of low-cost, water-soluble salts such as sodium and potassium hydroxide (NaOH, KOH), sodium carbonate (Na_2CO_3), borax ($Na_2B_4O_7$), phosphates and silicates of sodium and potassium, combined with dispersants and surfactants in water. The cleaning method is commonly accomplished by immersion or spraying, usually at temperatures of 50°C to 95°C (120°F–200°F). Following application of the alkaline solution, a water rinse is used to remove the alkali residue. Metal surfaces cleaned by alkaline solutions are typically electroplated or conversion coated.

Electrolytic cleaning, also called *electrocleaning*, is a related process in which a 3–12-V direct current is applied to an alkaline cleaning solution. The electrolytic action results in the generation of gas bubbles at the part surface, causing a scrubbing action that aids in removal of tenacious dirt films.

Emulsion cleaning uses organic solvents (oils) dispersed in an aqueous solution. The use of suitable emulsifiers (soaps) results in a two-phase cleaning fluid (oil-in-water), which functions by dissolving or emulsifying the soils on the part surface. The process can be used on either metal or nonmetallic parts. Emulsion cleaning must be followed by alkaline cleaning to eliminate all residues of the organic solvent prior to plating.

In *solvent cleaning*, organic soils such as oil and grease are removed from a metallic surface by means of chemicals that dissolve the soils. Common application techniques include hand-wiping, immersion, spraying, and vapor degreasing. *Vapor degreasing* uses hot vapors of solvents to dissolve and remove oil and grease on part surfaces. The common solvents include trichlorethylene (C_2HCl_3), methylene chloride (CH_2Cl_2), and perchlorethylene (C_2Cl_4), all of which have relatively low boiling points.[1] The vapor degreasing process consists of heating the liquid solvent to its boiling point in a container to produce hot vapors. Parts to be cleaned are then introduced into the vapor, which condenses on the relatively cold part surfaces, dissolving the contaminants and dripping to the bottom of the container. Condensing coils near

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[1]The highest boiling point of the three solvents is 121°C (250°F) for C_2Cl_4.

the top of the container prevent any vapors from escaping the container into the surrounding atmosphere. This is important because these solvents are classified as hazardous air pollutants under the 1992 Clean Air Act [10].

Acid cleaning removes oils and light oxides from metal surfaces by soaking, spraying, or manual brushing or wiping. The process is carried out at ambient or elevated temperatures. Common cleaning fluids are acid solutions combined with water-miscible solvents, wetting and emulsifying agents. Cleaning acids include hydrochloric (HCl), nitric (HNO_3), phosphoric (H_3PO_4), and sulfuric (H_2SO_4), the selection depending on the base metal and purpose of the cleaning. For example, phosphoric acid produces a light phosphate film on the metallic surface, which can be a useful preparation for painting. A closely related cleaning process is *acid pickling*, which involves a more severe treatment to remove thicker oxides, rusts, and scales; it generally results in some etching of the metallic surface, which serves to improve organic paint adhesion.

Ultrasonic cleaning combines chemical cleaning and mechanical agitation of the cleaning fluid to provide a highly effective method for removing surface contaminants. The cleaning fluid is generally an aqueous solution containing alkaline detergents. The mechanical agitation is produced by high-frequency vibrations of sufficient amplitude to cause cavitation—formation of low-pressure vapor bubbles or cavities. As the vibration wave passes a given point in the liquid, the low-pressure region is followed by a high-pressure front that implodes the cavity, thereby producing a shock wave capable of penetrating contaminant particles adhering to the work surface. This rapid cycle of cavitation and implosion occurs throughout the liquid medium, thus making ultrasonic cleaning effective even on complex and intricate internal shapes. The cleaning process is performed at frequencies between 20 and 45 kHz, and the cleaning solution is usually at an elevated temperature, typically 65°C to 85°C (150°F–190°F).

27.1.2 MECHANICAL CLEANING AND SURFACE TREATMENTS

Mechanical cleaning involves the physical removal of soils, scales, or films from the work surface of the work part by means of abrasives or similar mechanical action. The processes used for mechanical cleaning often serve other functions in addition to cleaning, such as deburring and improving surface finish.

Blast Finishing and Shot Peening   Blast finishing uses the high-velocity impact of particulate media to clean and finish a surface. The most well known of these methods is *sand blasting*, which uses grits of sand (SiO_2) as the blasting media. Various other media are also used in blast finishing, including hard abrasives such as aluminum oxide (Al_2O_3) and silicon carbide (SiC), and soft media such as nylon beads and crushed nut shells. The media is propelled at the target surface by pressurized air or centrifugal force. In some applications, the process is performed wet, in which fine particles in a water slurry are directed under hydraulic pressure at the surface.

In *shot peening*, a high-velocity stream of small cast steel pellets (called *shot*) is directed at a metallic surface with the effect of cold working and inducing compressive stresses into the surface layers. Shot peening is used primarily to improve fatigue strength of metal parts. Its purpose is therefore different from blast finishing, although surface cleaning is accomplished as a by-product of the operation.

FIGURE 27.1 Diagram of tumbling (barrel finishing) operation showing "landslide" action of parts and abrasive media to finish the parts.
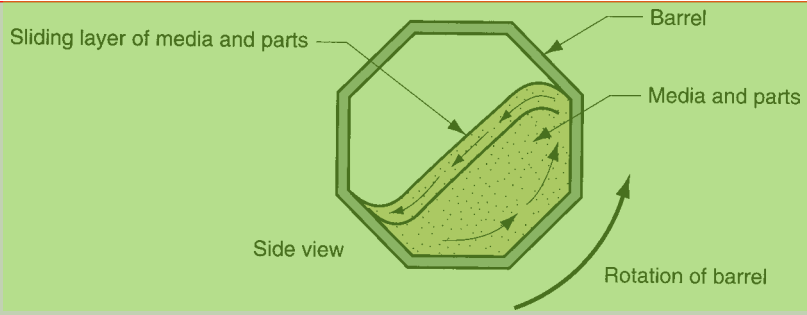
Tumbling and Other Mass Finishing   Tumbling, vibratory finishing, and similar operations comprise a group of finishing processes known as mass finishing methods. *Mass finishing* involves the finishing of parts in bulk by a mixing action inside a container, usually in the presence of an abrasive media. The mixing causes the parts to rub against the media and each other to achieve the desired finishing action. Mass finishing methods are used for deburring, descaling, deflashing, polishing, radiusing, burnishing, and cleaning. The parts include stampings, castings, forgings, extrusions, and machined parts. Even plastic and ceramic parts are sometimes subjected to these mass finishing operations to achieve desired finishing results. The parts processed by these methods are usually small and are therefore uneconomical to finish individually.

Mass finishing methods include tumbling, vibratory finishing, and several techniques that utilize centrifugal force. *Tumbling* (also called *barrel finishing* and *tumbling barrel finishing*) involves the use of a horizontally oriented barrel of hexagonal or octagonal cross-section in which parts are mixed by rotating the barrel at speeds of 10–50 rev/min. Finishing is performed by a "landslide" action of the media and parts as the barrel revolves. As pictured in Figure 27.1, the contents rise in the barrel due to rotation, followed by a tumbling down of the top layer due to gravity. This cycle of rising and tumbling occurs continuously and, over time, subjects all of the parts to the same desired finishing action. However, because only the top layer of parts is being finished at any moment, barrel finishing is a relatively slow process compared to other mass finishing methods. It often takes several hours of tumbling to complete the processing. Other drawbacks of barrel finishing include high noise levels and large floor space requirements.

Vibratory finishing was introduced in the late 1950s as an alternative to tumbling. The vibrating vessel subjects all parts to agitation with the abrasive media, as opposed to only the top layer as in barrel finishing. Consequently, processing times for vibratory finishing are significantly reduced. The open tubs used in this method permit inspection of the parts during processing, and noise is reduced.

Most of the *media* in these operations are abrasive; however, some media perform nonabrasive finishing operations such as burnishing and surface hardening. The media may be natural or synthetic materials. Natural media include corundum, granite, limestone, and even hardwood. The problem with these materials is that they are generally softer (and therefore wear more rapidly) and nonuniform in size (and sometimes clog in the work parts). Synthetic media can be made with greater consistency, both in size and hardness. These materials include Al_2O_3 and SiC, compacted into a desired shape and size using a bonding material such as a polyester resin. The shapes for these media include spheres, cones, angle-cut cylinders, and other regular
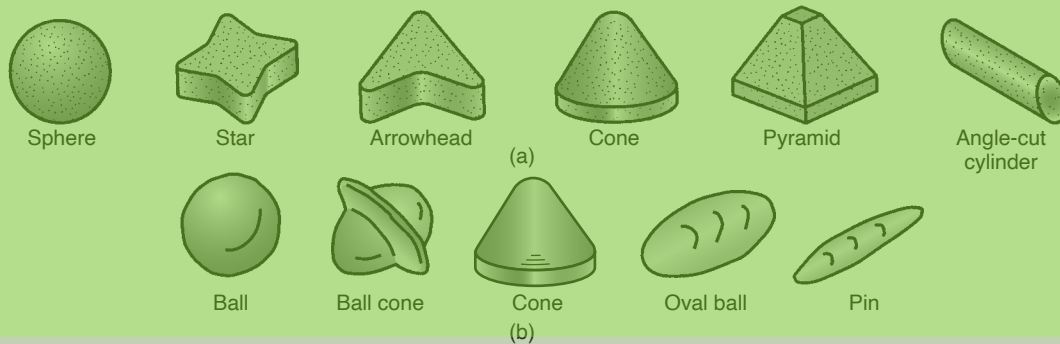
FIGURE 27.2 Typical preformed media shapes used in mass finishing operations: (a) abrasive media for finishing, and (b) steel media for burnishing.

geometric forms, as in Figure 27.2(a). Steel is also used as a mass finishing medium in shapes such as those shown in Figure 27.2(b) for burnishing, surface hardening, and light deburring operations. The shapes shown in Figure 27.2 come in various sizes. Selection of media is based on part size and shape, as well as finishing requirements.

In most mass finishing processes, a compound is used with the media. The mass finishing *compound* is a combination of chemicals for specific functions such as cleaning, cooling, rust inhibiting (of steel parts and steel media), and enhancing brightness and color of the parts (especially in burnishing).

27.2 Diffusion and Ion Implantation

This section discusses two processes in which the surface of a substrate is impregnated with foreign atoms that alter its chemistry and properties.

27.2.1 DIFFUSION

Diffusion involves the alteration of surface layers of a material by diffusing atoms of a different material (usually an element) into the surface (Section 4.3). The diffusion process impregnates the surface layers of the substrate with the foreign element, but the surface still contains a high proportion of substrate material. A typical profile of composition as a function of depth below the surface for a diffusion coated metal part is illustrated in Figure 27.3. The characteristic of a diffusion impregnated surface is that the diffused element has a maximum percentage at the surface and rapidly declines with distance below the surface. The diffusion process has important applications in metallurgy and semiconductor manufacture.

In metallurgical applications, diffusion is used to alter the surface chemistry of metals in a number of processes and treatments. One important example is surface hardening, typified by *carburizing*, *nitriding*, *carbonitriding*, *chromizing*, and *boronizing* (Section 27.4). In these treatments, one or more elements (C and/or Ni, Cr, or Bo) are diffused into the surface of iron or steel.

There are other diffusion processes in which corrosion resistance and/or high-temperature oxidation resistance are main objectives. Aluminizing, and siliconizing are important examples. *Aluminizing*, also known as *calorizing*, involves diffusion
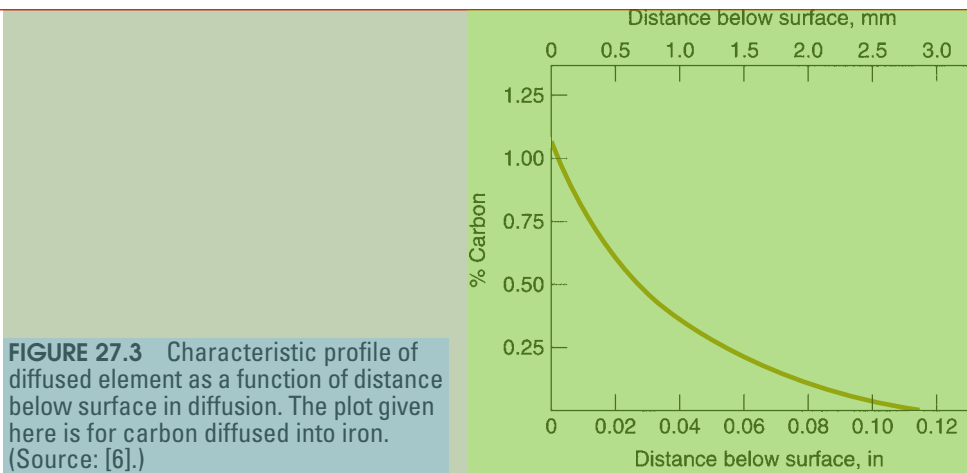
FIGURE 27.3 Characteristic profile of diffused element as a function of distance below surface in diffusion. The plot given here is for carbon diffused into iron. (Source: [6].)

of aluminum into carbon steel, alloy steels, and alloys of nickel and cobalt. The treatment is accomplished by either (1) *pack diffusion*, in which work parts are packed with Al powders and baked at high temperature to create the diffusion layer; or (2) a *slurry method*, in which the work parts are dipped or sprayed with a mixture of Al powders and binders, then dried and baked.
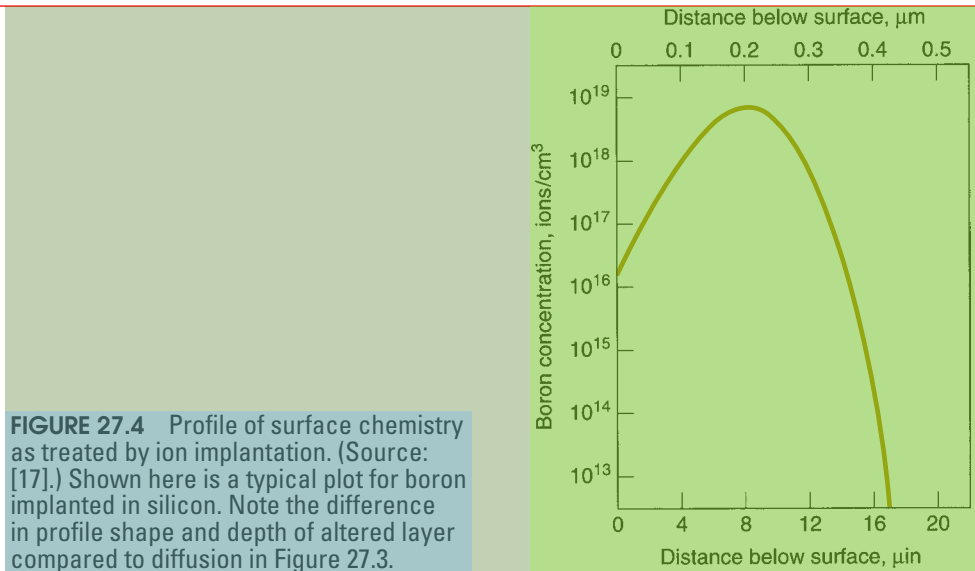
Siliconizing is a treatment of steel in which silicon is diffused into the part surface to create a layer with good corrosion and wear resistance and moderate heat resistance. The treatment is carried out by heating the work in powders of silicon carbide (SiC) in an atmosphere containing vapors of silicon tetrachloride ($SiCl_4$). Siliconizing is less common than aluminizing.

Semiconductor Applications   In semiconductor processing, diffusion of an impurity element into the surface of a silicon chip is used to change the electrical properties at the surface to create devices such as transistors and diodes. How diffusion is used to accomplish this *doping*, as it is called, and other semiconductor processes is examined in Chapter 33.

27.2.2   ION IMPLANTATION

Ion implantation is an alternative to diffusion when the latter method is not feasible because of the high temperatures required. The ion implantation process involves embedding atoms of one (or more) foreign element(s) into a substrate surface using a high-energy beam of ionized particles. The result is an alteration of the chemical and physical properties of the layers near the substrate surface. Penetration of atoms produces a much thinner altered layer than diffusion, as indicated by a comparison of Figures 27.3 and 27.4. Also, the concentration profile of the impregnated element is quite different from the characteristic diffusion profile.

Advantages of ion implantation include (1) low-temperature processing, (2) good control and reproducibility of penetration depth of impurities, and (3) solubility limits can be exceeded without precipitation of excess atoms. Ion implantation finds some of its applications as a substitute for certain coating processes, where its advantages include (4) no problems with waste disposal as in electroplating and

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FIGURE 27.4 Profile of surface chemistry as treated by ion implantation. (Source: [17].) Shown here is a typical plot for boron implanted in silicon. Note the difference in profile shape and depth of altered layer compared to diffusion in Figure 27.3.

many coating processes, and (5) no discontinuity between coating and substrate. Principal applications of ion implantation are in modifying metal surfaces to improve properties and fabrication of semiconductor devices.

27.3 Plating and Related Processes

Plating involves the coating of a thin metallic layer onto the surface of a substrate material. The substrate is usually metallic, although methods are available to plate plastic and ceramic parts. The most familiar and widely used plating technology is electroplating.

27.3.1 ELECTROPLATING

Electroplating, also known as *electrochemical plating*, is an electrolytic process (Section 4.5) in which metal ions in an electrolyte solution are deposited onto a cathode work part. The setup is shown in Figure 27.5. The anode is generally made of the metal being plated and thus serves as the source of the plate metal. Direct current from an external power supply is passed between the anode and the cathode. The

FIGURE 27.5
Setup for electroplating.
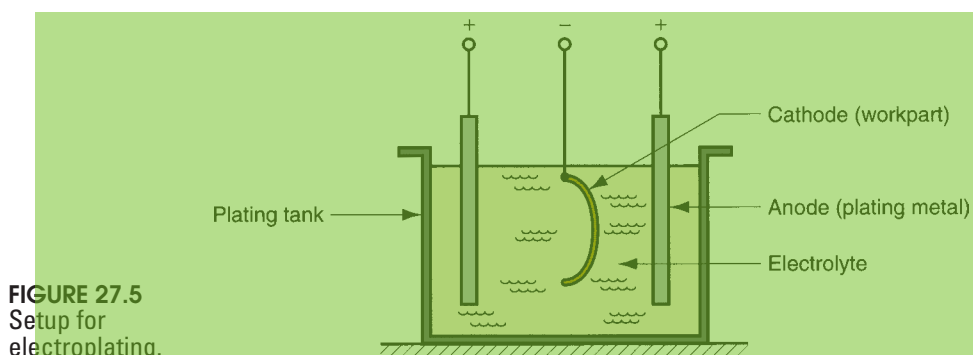
electrolyte is an aqueous solution of acids, bases, or salts; it conducts electric current by the movement of plate metal ions in solution. For optimum results, parts must be chemically cleaned just prior to electroplating.

Principles of Electroplating   Electrochemical plating is based on Faraday's two physical laws. Briefly, the laws state: (1) the mass of a substance liberated in electrolysis is proportional to the quantity of electricity passed through the cell; and (2) the mass of the material liberated is proportional to its electrochemical equivalent (ratio of atomic weight to valence). The effects can be summarized in the equation

$$V = CIt \qquad\qquad (27.1)$$

where V = volume of metal plated, mm^3 (in^3); C = plating constant, which depends on electrochemical equivalent and density, mm^3/amp-s (in^3/amp-min); I = current, amps; and t = time during which current is applied, s (min). The product It (current × time) is the electrical charge passed in the cell, and the value of C indicates the amount of plating material deposited onto the cathodic work part per electrical charge.

For most plating metals, not all of the electrical energy in the process is used for deposition; some energy may be consumed in other reactions, such as the liberation of hydrogen at the cathode. This reduces the amount of metal plated. The actual amount of metal deposited on the cathode (work part) divided by the theoretical amount given by Equation (27.1) is called the ***cathode efficiency***. Taking the cathode efficiency into account, a more realistic equation for determining the volume of metal plated is

$$V = ECIt \qquad\qquad (27.2)$$

where E = cathode efficiency, and the other terms are defined as before. Typical values of cathode efficiency E and plating constant C for different metals are presented in Table 27.1. The average plating thickness can be determined from the following:

$$d = \frac{V}{A} \qquad\qquad (27.3)$$

where d = plating depth or thickness, mm (in); V = volume of plate metal from Equation (27.2); and A = surface area of plated part, mm^2 (in^2).

Example 27.1
Electroplating

A steel part with surface area A = 125 cm^2 is to be nickel plated. What average plating thickness will result if 12 amps are applied for 15 min in an acid sulfate electrolyte bath?

Solution: From Table 27.1, the cathode efficiency for nickel is E = 0.95 and the plating constant C = 3.42(10^{-2}) mm^3/amp-s. Using Equation (27.2), the total amount of plating metal deposited onto the part surface in 15 min is given by

$$V = 0.95\,(3.42 \times 10^{-2})\,(12)\,(15)\,(60) = 350.9\ \text{mm}^3$$

This is spread across an area A = 125 cm^2 = 12,500 mm^2, so the average plate thickness is

$$d = \frac{350.9}{12500} = \textbf{0.028 mm}$$

TABLE • 27.1   Typical cathode efficiencies in electroplating and values of plating constant C.

Plate Metal[a]	Electrolyte	Cathode Efficiency %	Plating Constant C^a	
			mm³/amp-s	in³/amp-min
Cadmium (2)	Cyanide	90	6.73×10^{-2}	2.47×10^{-4}
Chromium (3)	Chromium-acid-sulfate	15	2.50×10^{-2}	0.92×10^{-4}
Copper (1)	Cyanide	98	7.35×10^{-2}	2.69×10^{-4}
Gold (1)	Cyanide	80	10.6×10^{-2}	3.87×10^{-4}
Nickel (2)	Acid sulfate	95	3.42×10^{-2}	1.25×10^{-4}
Silver (1)	Cyanide	100	10.7×10^{-2}	3.90×10^{-4}
Tin (4)	Acid sulfate	90	4.21×10^{-2}	1.54×10^{-4}
Zinc (2)	Chloride	95	4.75×10^{-2}	1.74×10^{-4}

Compiled from [17].
[a]Most common valence given in parenthesis ( ); this is the value assumed in determining the plating constant C. For a different valence, compute the new C by multiplying C value in the table by the most common valence and then dividing by the new valence.

Methods and Applications   A variety of equipment is available for electroplating, the choice depending on part size and geometry, throughput requirements, and plating metal. The principal methods are (1) barrel plating, (2) rack plating, and (3) strip plating. *Barrel plating* is performed in rotating barrels that are oriented either horizontally or at an oblique angle (35°). The method is suited to the plating of many small parts in a batch. Electrical contact is maintained through the tumbling action of the parts themselves and by means of an externally connected conductor that projects into the barrel. There are limitations to barrel plating; the tumbling action inherent in the process may damage soft metal parts, threaded components, parts requiring good finishes, and heavy parts with sharp edges.

Rack plating is used for parts that are too large, heavy, or complex for barrel plating. The racks are made of heavy-gauge copper wire, formed into suitable shapes for holding the parts and conducting current to them. The racks are fabricated so that work parts can be hung on hooks, or held by clips, or loaded into baskets. To avoid plating of the copper itself, the racks are covered with insulation except in locations where part contact occurs. The racks containing the parts are moved through a sequence of tanks that perform the electroplating operation. *Strip plating* is a high-production method in which the work consists of a continuous strip that is pulled through the plating solution by means of a take-up reel. Plated wire is an example of a suitable application. Small sheet-metal parts held in a long strip can also be plated by this method. The process can be set up so that only specific regions of the parts are plated, for example, contact points plated with gold on electrical connectors.

Common coating metals in electroplating include zinc, nickel, tin, copper, and chromium. Steel is the most common substrate metal. Precious metals (gold, silver, platinum) are plated on jewelry. Gold is also used for electrical contacts.

Zinc-plated steel products include fasteners, wire goods, electric switch boxes, and various sheet-metal parts. The zinc coating serves as a sacrificial barrier to the corrosion of the steel beneath. An alternative process for coating zinc onto steel is galvanizing (Section 27.3.4). *Nickel plating* is used for corrosion resistance and decorative purposes over steel, brass, zinc die castings, and other metals. Applications

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include automotive trim and other consumer goods. Nickel is also used as a base coat under a much thinner chrome plate. ***Tin plate*** is still widely used for corrosion protection in "tin cans" and other food containers. Tin plate is also used to improve solderability of electrical components.

Copper has several important applications as a plating metal. It is widely used as a decorative coating on steel and zinc, either alone or alloyed with zinc as brass plate. It also has important plating applications in printed circuit boards (Section 34.2). Finally, copper is often plated on steel as a base beneath nickel and/or chrome plate. ***Chromium plate*** (popularly known as ***chrome plate***) is valued for its decorative appearance and is widely used in automotive products, office furniture, and kitchen appliances. It also produces one of the hardest of all electroplated coatings, and so it is widely used for parts requiring wear resistance (e.g., hydraulic pistons and cylinders, piston rings, aircraft engine components, and thread guides in textile machinery).

27.3.2   ELECTROFORMING

This process is virtually the same as electroplating but its purpose is quite different. Electroforming involves electrolytic deposition of metal onto a pattern until the required thickness is achieved; the pattern is then removed to leave the formed part. Whereas typical plating thickness is only about 0.05 mm (0.002 in) or less, electroformed parts are often substantially thicker, so the production cycle is proportionally longer.

Patterns used in electroforming are either solid or expendable. Solid patterns have a taper or other geometry that permits removal of the electroplated part. Expendable patterns are destroyed during part removal; they are used when part shape precludes a solid pattern. Expendable patterns are either fusible or soluble. The fusible type is made of low-melting alloys, plastic, wax, or other material that can be removed by melting. When nonconductive materials are used, the pattern must be metallized to accept the electrodeposited coating. Soluble patterns are made of a material that can be readily dissolved by chemicals; for example, aluminum can be dissolved in sodium hydroxide (NaOH).

Electroformed parts are commonly fabricated of copper, nickel, and nickel cobalt alloys. Applications include fine molds for lenses, compact discs (CDs), and videodiscs (DVDs); copper foil used to produce blank printed circuit boards; and plates for embossing and printing. Molds for compact discs and videodiscs represent a demanding application because the surface details that must be imprinted on the disc are measured in μm (1 μm = 10^{-6} m). These details are readily obtained in the mold by electroforming.

27.3.3   ELECTROLESS PLATING

Electroless plating is a plating process driven entirely by chemical reactions—no external source of electric current is required. Deposition of metal onto a part surface occurs in an aqueous solution containing ions of the desired plating metal. The process uses a reducing agent, and the work part surface acts as a catalyst for the reaction.

The metals that can be electroless plated are limited; and for those that can be processed by this technique, the cost is generally greater than electrochemical plating. The most common electroless plating metal is nickel and certain of its alloys

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(Ni–Co, Ni–P, and Ni–B). Copper and, to a lesser degree, gold are also used as plating metals. Nickel plating by this process is used for applications requiring high resistance to corrosion and wear. Electroless copper plating is used to plate through holes of printed circuit boards (Section 34.2.3). Cu can also be plated onto plastic parts for decorative purposes. Advantages sometimes cited for electroless plating include (1) uniform plate thickness on complex part geometries (a problem with electroplating); (2) the process can be used on both metallic and nonmetallic substrates; and (3) no need for a DC power supply to drive the process.

27.3.4 HOT DIPPING

Hot dipping is a process in which a metal substrate is immersed in a molten bath of a second metal; upon removal, the second metal is coated onto the first. Of course, the first metal must possess a higher melting temperature than the second. The most common substrate metals are steel and iron. Zinc, aluminum, tin, and lead are the common coating metals. Hot dipping works by forming transition layers of varying alloy compositions. Next to the substrate are normally intermetallic compounds of the two metals; at the exterior are solid solution alloys consisting predominantly of the coating metal. The transition layers provide excellent adhesion of the coating.

The primary purpose of hot dipping is corrosion protection. Two mechanisms normally operate to provide this protection: (1) barrier protection—the coating simply serves as a shield for the metal beneath; and (2) sacrificial protection—the coating corrodes by a slow electrochemical process to preserve the substrate.

Hot dipping goes by different names, depending on coating metal: *galvanizing* is when zinc (Zn) is coated onto steel or iron; *aluminizing* refers to coating of aluminum (Al) onto a substrate; *tinning* is coating of tin (Sn); and *terneplate* describes the plating of lead–tin (Pb-Sn) alloy onto steel. Galvanizing is by far the most important hot dipping process, dating back about 200 years. It is applied to finished steel and iron parts in a batch process; and to sheet, strip, piping, tubing, and wire in an automated continuous process. Coating thickness is typically 0.04 to 0.09 mm (0.0016–0.0035 in). Thickness is controlled largely by immersion time. Bath temperature is maintained at around 450°C (850°F).

Commercial use of aluminizing is on the rise, gradually increasing in market share relative to galvanizing. Hot-dipped aluminum coatings provide excellent corrosion protection, in some cases five times more effective than galvanizing [17]. Tin plating by hot dipping provides a nontoxic corrosion protection for steel in applications for food containers, dairy equipment, and soldering applications. Hot dipping has gradually been overtaken by electroplating as the preferred commercial method for plating of tin onto steel. Terneplating involves hot dipping of a lead–tin alloy onto steel. The alloy is predominantly lead (only 2%–15% Sn); however, tin is required to obtain satisfactory adhesion of the coating. Terneplate is the lowest cost of the coating methods for steel, but its corrosion protection is limited.

27.4 Conversion Coating

Conversion coating refers to a family of processes in which a thin film of oxide, phosphate, or chromate is formed on a metallic surface by chemical or electrochemical reaction. Immersion and spraying are the two common methods of exposing the metal surface to the reacting chemicals. The common metals treated by conversion

coating are steel (including galvanized steel), zinc, and aluminum. However, nearly any metal product can benefit from the treatment. The important reasons for using a conversion coating process are (1) to provide corrosion protection, (2) to prepare the surface for painting, (3) to increase wear resistance, (4) to permit the surface to better hold lubricants for metal forming processes, (5) to increase electrical resistance of surface, (6) to provide a decorative finish, and (7) for part identification [17].

Conversion coating processes divide into two categories: (1) chemical treatments, which involve a chemical reaction only, and (2) anodizing, which consists of an electrochemical reaction to produce an oxide coating (anodize is a contraction of *anodic oxidize*).

27.4.1 CHEMICAL CONVERSION COATINGS

These processes expose the base metal to certain chemicals that form thin, nonmetallic surface films. Similar reactions occur in nature; the oxidation of iron and aluminum are examples. Whereas rusting is progressively destructive of iron, formation of a thin Al_2O_3 coating on aluminum protects the base metal. It is the purpose of these chemical conversion treatments to accomplish the latter effect. The two main processes are phosphate and chromate coating.

Phosphate coating transforms the base metal surface into a protective phosphate film by exposure to solutions of certain phosphate salts (e.g., Zn, Mg, and Ca) together with dilute phosphoric acid (H_3PO_4). The coatings range in thickness from 0.0025 to 0.05 mm (0.0001–0.002 in). The most common base metals are zinc and steel, including galvanized steel. The phosphate coating serves as a useful preparation for painting in the automotive and heavy appliance industries.

Chromate coating converts the base metal into various forms of chromate films using aqueous solutions of chromic acid, chromate salts, and other chemicals. Metals treated by this method include aluminum, cadmium, copper, magnesium, and zinc (and their alloys). Immersion of the base part is the common method of application. Chromate conversion coatings are somewhat thinner than phosphate, typically less than 0.0025 mm (0.0001 in). Usual reasons for chromate coating are (1) corrosion protection, (2) base for painting, and (3) decorative purposes. Chromate coatings can be clear or colorful; available colors include olive drab, bronze, yellow, or bright blue.

27.4.2 ANODIZING

Although the previous processes are normally performed without electrolysis, anodizing is an electrolytic treatment that produces a stable oxide layer on a metallic surface. Its most common applications are with aluminum and magnesium, but it is also applied to zinc, titanium, and other less common metals. Anodized coatings are used primarily for decorative purposes; they also provide corrosion protection.

It is instructive to compare anodizing to electroplating, because they are both electrolytic processes. Two differences stand out. (1) In electrochemical plating, the work part to be coated is the cathode in the reaction. By contrast, in anodizing, the work is the anode, whereas the processing tank is cathodic. (2) In electroplating, the coating is grown by adhesion of ions of a second metal to the base metal surface. In anodizing, the surface coating is formed through chemical reaction of the substrate metal into an oxide layer.

Anodized coatings usually range in thickness between 0.0025 and 0.075 mm (0.0001 and 0.003 in). Dyes can be incorporated into the anodizing process to create a wide variety of colors; this is especially common in aluminum anodizing. Very thick coatings up to 0.25 mm (0.010 in) can also be formed on aluminum by a special process called *hard anodizing*; these coatings are noted for high resistance to wear and corrosion.

27.5 Vapor Deposition Processes

The vapor deposition processes form a thin coating on a substrate by either condensation or chemical reaction of a gas onto the surface of the substrate. The two categories of processes that fall under this heading are physical vapor deposition and chemical vapor deposition.

27.5.1 PHYSICAL VAPOR DEPOSITION

Physical vapor deposition (PVD) is a group of thin film processes in which a material is converted into its vapor phase in a vacuum chamber and condensed onto a substrate surface as a very thin layer. PVD can be used to apply a wide variety of coating materials: metals, alloys, ceramics and other inorganic compounds, and even certain polymers. Possible substrates include metals, glass, and plastics. Thus, PVD represents a versatile coating technology, applicable to an almost unlimited combination of coating substances and substrate materials.

Applications of PVD include thin decorative coatings on plastic and metal parts such as trophies, toys, pens and pencils, watchcases, and interior trim in automobiles. The coatings are thin films of aluminum (around 150 nm) coated with clear lacquer to give a high gloss silver or chrome appearance. Another use of PVD is to apply antireflection coatings of magnesium fluoride (MgF_2) onto optical lenses. PVD is applied in the fabrication of electronic devices, principally for depositing metal to form electrical connections in integrated circuits. Finally, PVD is widely used to coat titanium nitride (TiN) onto cutting tools and plastic injection molds for wear resistance.

All physical vapor deposition processes consist of the following steps: (1) synthesis of the coating vapor, (2) vapor transport to the substrate, and (3) condensation of vapors onto the substrate surface. These steps are generally carried out inside a vacuum chamber, so evacuation of the chamber must precede the actual PVD process.

Synthesis of the coating vapor can be accomplished by any of several methods, such as electric resistance heating or ion bombardment to vaporize an existing solid (or liquid). These and other variations result in several PVD processes. They are grouped into three principal types: (1) vacuum evaporation, (2) sputtering, and (3) ion plating. Table 27.2 presents a summary of these processes.

Vacuum Evaporation   Certain materials (mostly pure metals) can be deposited onto a substrate by first transforming them from solid to vapor state in a vacuum and then letting them condense on the substrate surface. The setup for the vacuum evaporation process is shown in Figure 27.6. The material to be deposited, called the source, is heated to a sufficiently high temperature that it evaporates (or sublimes). Because heating is accomplished in a vacuum, the temperature required for vaporization is significantly below the corresponding temperature required at atmospheric

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**TABLE • 27.2** Summary of physical vapor deposition (PVD) processes.

PVD Process	Features and comparisons	Coating materials
Vacuum evaporation	Equipment is relatively low-cost and simple; deposition of compounds is difficult; coating adhesion not as good as other PVD processes	Ag, Al, Au, Cr, Cu, Mo, W.
Sputtering	Better throwing power and coating adhesion than vacuum evaporation, can coat compounds, slower deposition rates and more difficult process control than vacuum evaporation	Al_2O_3, Au, Cr, Mo, SiO_2, Si_3N_4, TiC, TiN.
Ion plating	Best coverage and coating adhesion of PVD processes, most complex process control, higher deposition rates than sputtering	Ag, Au, Cr, Mo, Si_3N_4, TiC, TiN.

Compiled from [2].

pressure. Also, the absence of air in the chamber prevents oxidation of the source material at the heating temperatures.

Various methods can be used to heat and vaporize the material. A container must be provided to hold the source material before vaporization. Among the important vaporization methods are resistance heating and electron beam bombardment. ***Resistance heating*** is the simplest technology. A refractory metal (e.g., W, Mo) is formed into a suitable container to hold the source material. Current is applied to heat the container, which then heats the material in contact with it. One problem with this heating method is possible alloying between the holder and its contents, so that the deposited film becomes contaminated with the metal of the resistance heating container. In ***electron beam evaporation***, a stream of electrons at high velocity is directed to bombard the surface of the source material to cause vaporization. By contrast with resistance heating, very little energy acts to heat the container, thus minimizing contamination of the container material with the coating.

Whatever the vaporization technique, evaporated atoms leave the source and follow straight-line paths until they collide with other gas molecules or strike a solid surface. The vacuum inside the chamber virtually eliminates other gas molecules, thus reducing the probability of collisions with source vapor atoms. The substrate surface to be coated is usually positioned relative to the source so that it
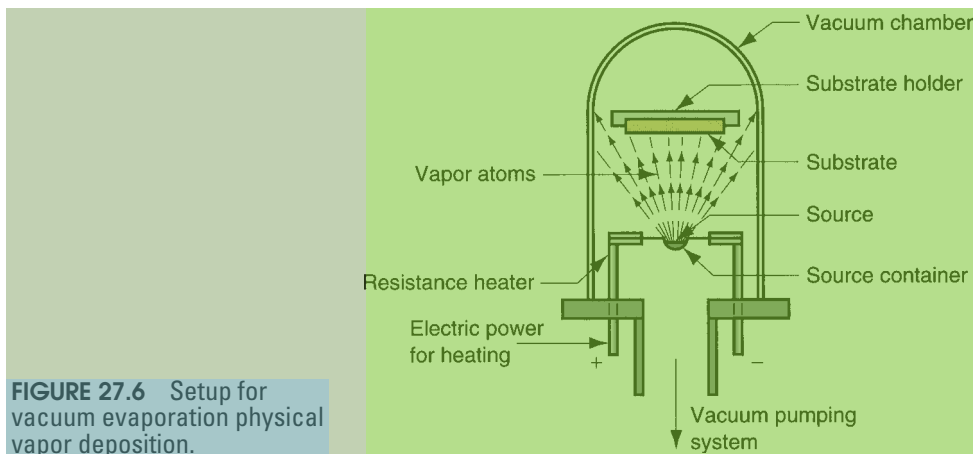
FIGURE 27.6 Setup for vacuum evaporation physical vapor deposition.

is the likely solid surface on which the vapor atoms will be deposited. A mechanical manipulator is sometimes used to rotate the substrate so that all surfaces are coated. Upon contact with the relative cool substrate surface, the energy level of the impinging atoms is suddenly reduced to the point where they cannot remain in a vapor state; they condense and become attached to the solid surface, forming a deposited thin film.

Sputtering   If the surface of a solid (or liquid) is bombarded by atomic particles of sufficiently high energy, individual atoms of the surface may acquire enough energy due to the collision that they are ejected from the surface by transfer of momentum. This is the process known as sputtering. The most convenient form of high energy particle is an ionized gas, such as argon, energized by means of an electric field to form a plasma. As a PVD process, *sputtering* involves bombardment of the cathodic coating material with argon ions (Ar^+), causing surface atoms to escape and then be deposited onto a substrate, forming a thin film on the substrate surface. The substrate must be placed close to the cathode and is usually heated to improve bonding of the coating atoms. A typical arrangement is shown in Figure 27.7.

Whereas vacuum evaporation is generally limited to metals, sputtering can be applied to nearly any material—metallic and nonmetallic elements; alloys, ceramics, and polymers. Films of alloys and compounds can be sputtered without changing their chemical compositions. Films of chemical compounds can also be deposited by employing reactive gases that form oxides, carbides, or nitrides with the sputtered metal.

Drawbacks of sputtering PVD include (1) slow deposition rates and (2) because the ions bombarding the surface are a gas, traces of the gas can usually be found in the coated films, and the entrapped gases sometimes affect mechanical properties adversely.

Ion Plating   Ion plating uses a combination of sputtering and vacuum evaporation to deposit a thin film onto a substrate. The process works as follows. The substrate is set up to be the cathode in the upper part of the chamber, and the source material is placed below it. A vacuum is then established in the chamber. Argon gas is admitted and an electric field is applied to ionize the gas (Ar^+) and establish a plasma. This results in ion bombardment (sputtering) of the substrate so that its surface is scrubbed to a condition of atomic cleanliness (interpret this as "very clean").
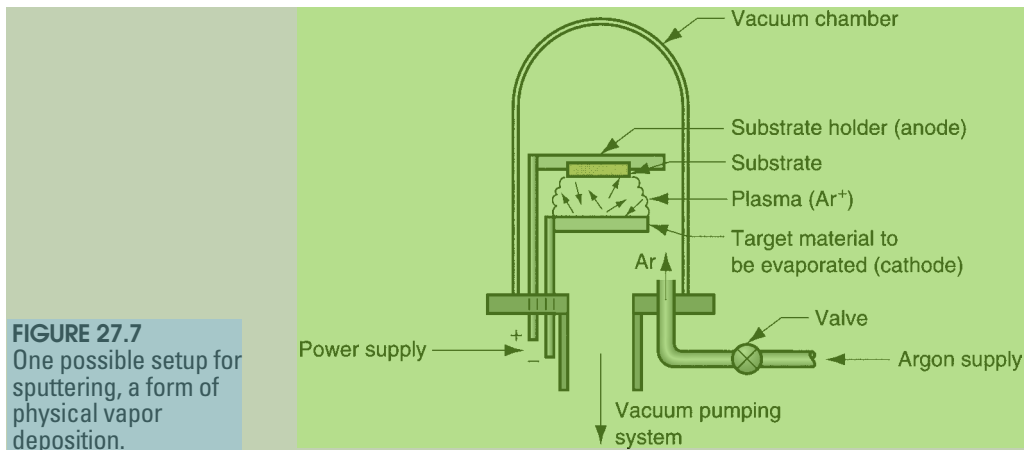

FIGURE 27.7
One possible setup for sputtering, a form of physical vapor deposition.

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Next, the source material is heated sufficiently to generate coating vapors. The heating methods used here are similar to those used in vacuum evaporation: resistance heating, electron beam bombardment, and so on. The vapor molecules pass through the plasma and coat the substrate. Sputtering is continued during deposition, so that the ion bombardment consists not only of the original argon ions but also source material ions that have been energized while being subjected to the same energy field as the argon. The effect of these processing conditions is to produce films of uniform thickness and excellent adherence to the substrate.

Ion plating is applicable to parts having irregular geometries, due to the scattering effects that exist in the plasma field. An example of interest here is TiN coating of high-speed steel cutting tools (e.g., drill bits). In addition to coating uniformity and good adherence, other advantages of the process include high deposition rates, high film densities, and the capability to coat the inside walls of holes and other hollow shapes.

27.5.2   CHEMICAL VAPOR DEPOSITION

Physical vapor deposition involves deposition of a coating by condensation onto a substrate from the vapor phase; it is strictly a physical process. By comparison, *chemical vapor deposition* (CVD) involves the interaction between a mixture of gases and the surface of a heated substrate, causing chemical decomposition of some of the gas constituents and formation of a solid film on the substrate. The reactions take place in an enclosed reaction chamber. The reaction product (either a metal or a compound) nucleates and grows on the substrate surface to form the coating. Most CVD reactions require heat. However, depending on the chemicals involved, the reactions can be driven by other possible energy sources, such as ultraviolet light or plasma. CVD includes a wide range of pressures and temperatures; and it can be applied to a great variety of coating and substrate materials.

Industrial metallurgical processes based on chemical vapor deposition date back to the 1800s (e.g., the Mond process in Table 27.3). Modern interest in CVD is focused on its coating applications such as coated cemented carbide tools, solar cells, depositing refractory metals on jet engine turbine blades, and other applications where resistance to wear, corrosion, erosion, and thermal shock are important. In addition, CVD is an important technology in integrated circuit fabrication.

Advantages typically cited for CVD include (1) capability to deposit refractory materials at temperatures below their melting or sintering temperatures; (2) control of grain size is possible; (3) the process is carried out at atmospheric pressure—it does not require vacuum equipment; and (4) good bonding of coating to substrate surface [1]. Disadvantages include (1) corrosive and/or toxic nature of chemicals generally necessitates a closed chamber as well as special pumping and disposal equipment; (2) certain reaction ingredients are relatively expensive; and (3) material utilization is low.

CVD Materials and Reactions   In general, metals that are readily electroplated are not good candidates for CVD, owing to the hazardous chemicals that must be used and the costs of safeguarding against them. Metals suitable for coating by CVD include tungsten, molybdenum, titanium, vanadium, and tantalum. Chemical vapor deposition is especially suited to the deposition of compounds, such as aluminum oxide (Al_2O_3), silicon dioxide (SiO_2), silicon nitride (Si_3N_4), titanium carbide

**TABLE • 27.3** Some examples of reactions in chemical vapor deposition (CVD).

1. The *Mond process* includes a CVD process for decomposition of nickel from nickel carbonyl ($Ni(CO)_4$), which is an intermediate compound formed in reducing nickel ore:

$$Ni(CO)_4 \xrightarrow{200°C\,(400°F)} Ni + 4CO \qquad (27.4)$$

2. Coating of titanium carbide (TiC) onto a substrate of cemented tungsten carbide (WC–Co) to produce a high-performance cutting tool:

$$TiCl_4 + CH_4 \xrightarrow[\text{excess } H_2]{1000°C\,(1800°F)} TiC + 4HCl \qquad (27.5)$$

3. Coating of titanium nitride (TiN) onto a substrate of cemented tungsten carbide (WC–Co) to produce a high-performance cutting tool:

$$TiCl_4 + 0.5N_2 + 2H_2 \xrightarrow{900°C\,(1650°F)} TiN + 4HCl \qquad (27.6)$$
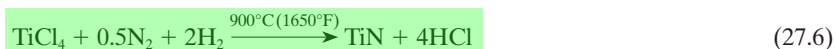
4. Coating of aluminum oxide (Al_2O_3) onto a substrate of cemented tungsten carbide (WC–Co) to produce a high-performance cutting tool:

$$2AlCl_3 + 3CO_2 + 3H_2 \xrightarrow{500°C\,(900°F)} Al_2O_3 + 3CO + 6HCl \qquad (27.7)$$
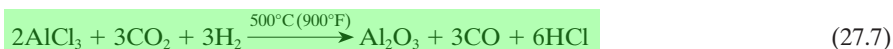
5. Coating of silicon nitride (Si_3N_4) onto silicon (Si), a process in semiconductor manufacturing:

$$3SiF_4 + 4NH_3 \xrightarrow{1000°C\,(1800°F)} Si_3N_4 + 12HF \qquad (27.8)$$

6. Coating of silicon dioxide (SiO_2) onto silicon (Si), a process in semiconductor manufacturing:

$$2SiCl_3 + 3H_2O + 0.5O_2 \xrightarrow{900°C\,(1600°F)} 2SiO_2 + 6HCl \qquad (27.9)$$
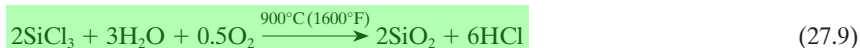
7. Coating of the refractory metal tungsten (W) onto a substrate, such as a jet engine turbine blade:

$$WF_6 + 3H_2 \xrightarrow{600°C\,(1100°F)} W + 6HF \qquad (27.10)$$

Compiled from [6], [13], and [17].

(TiC), and titanium nitride (TiN). Figure 27.8 illustrates the application of both CVD and PVD to provide multiple wear-resistant coatings on a cemented carbide cutting tool.

The commonly used reacting gases or vapors are metallic hydrides (MH_x), chlorides (MCl_x), fluorides (MF_x), and carbonyls ($M(CO)_x$), where M = the metal to be deposited and x is used to balance the valences in the compound. Other gases, such as hydrogen (H_2), nitrogen (N_2), methane (CH_4), carbon dioxide (CO_2), and ammonia (NH_3) are used in some of the reactions. Table 27.3 presents some examples of CVD reactions that result in deposition of a metal or ceramic coating onto a suitable substrate. Typical temperatures at which these reactions are carried out are also given.

Processing Equipment   Chemical vapor deposition processes are carried out in a reactor, which consists of (1) reactant supply system, (2) deposition chamber, and (3) recycle/disposal system. Although reactor configurations differ depending on the

FIGURE 27.8 Photomicrograph of the cross section of a coated carbide cutting tool (Kennametal Grade KC792M); chemical vapor deposition was used to coat TiN and TiCN onto the surface of a WC–Co substrate, followed by a TiN coating applied by physical vapor deposition. (Photo courtesy of Kennametal Inc.)
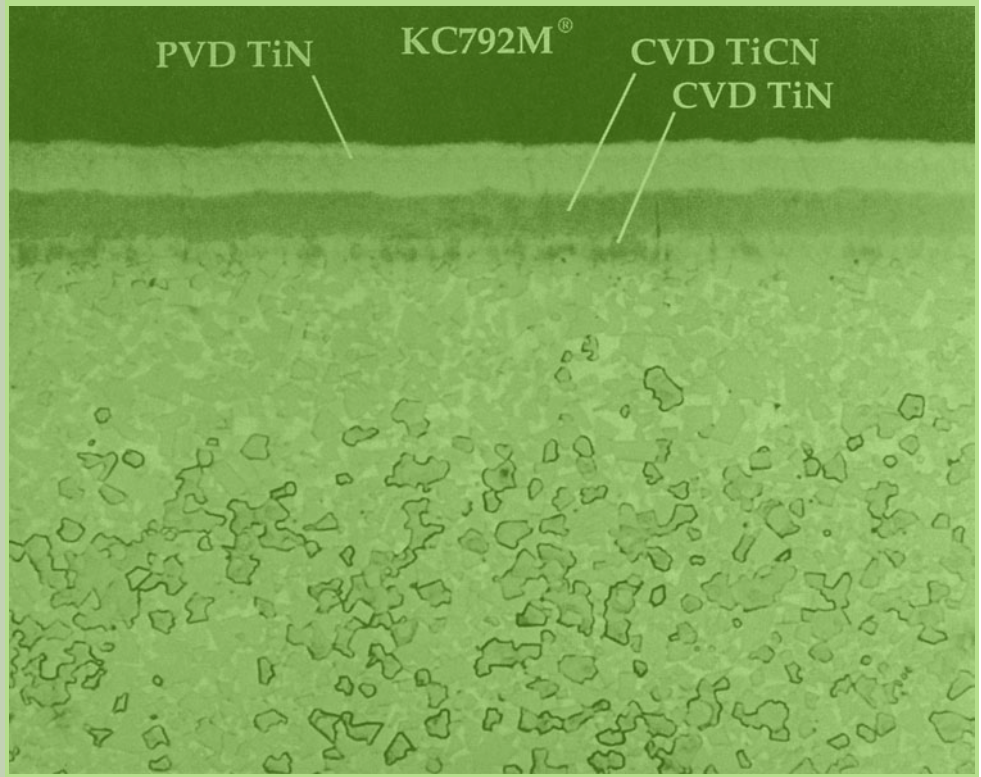
application, one possible CVD reactor is illustrated in Figure 27.9. The purpose of the reactant supply system is to deliver reactants to the deposition chamber in the proper proportions. Different types of supply system are required, depending on whether the reactants are delivered as gas, liquid, or solid (e.g., pellets, powders).

The deposition chamber contains the substrates and chemical reactions that lead to deposition of reaction products onto the substrate surfaces. Deposition occurs at elevated temperatures, and the substrate must be heated by induction heating, radiant heat, or other means. Deposition temperatures for different CVD reactions

FIGURE 27.9 A typical reactor used in chemical vapor deposition.
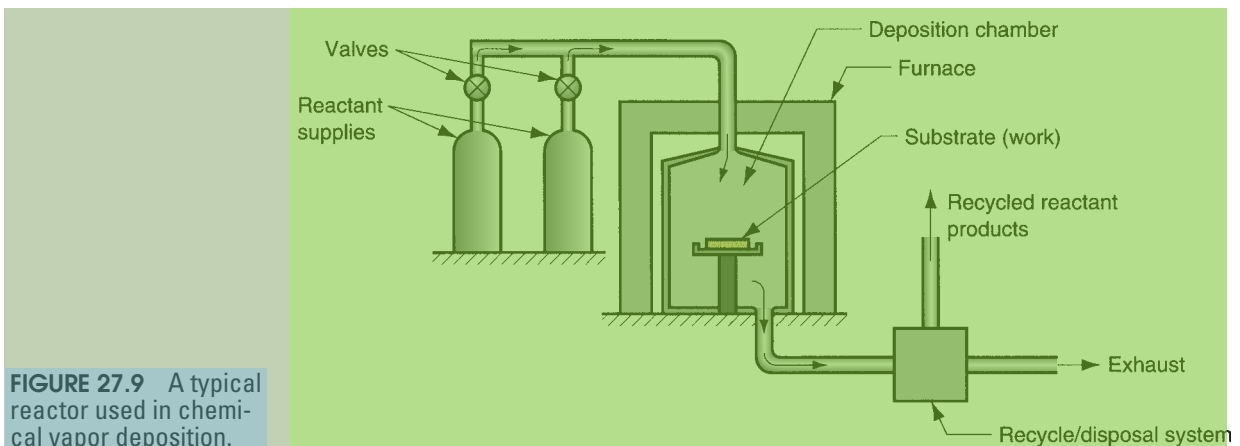
range from 250 to 1950°C (500–3500°F), so the chamber must be designed to meet these temperature demands.

The third component of the reactor is the recycle/disposal system, whose function is to render harmless the byproducts of the CVD reaction. This includes collection of materials that are toxic, corrosive, and/or flammable, followed by proper processing and disposition.

Alternative Forms of CVD   What has been described is *atmospheric pressure chemical vapor deposition*, in which the reactions are carried out at or near atmospheric pressure. For many reactions, there are advantages in performing the process at pressures well below atmospheric. This is called *low-pressure chemi-cal vapor deposition* (LPCVD), in which the reactions occur in a partial vacuum. Advantages of LPCVD include (1) uniform thickness, (2) good control over com-position and structure, (3) low-temperature processing, (4) fast deposition rates, and (5) high throughput and lower processing costs [13]. The technical problem in LPCVD is designing the vacuum pumps to create the partial vacuum when the reaction products are not only hot but may also be corrosive. These pumps must often include systems to cool and trap the corrosive gases before they reach the actual pumping unit.

Another variation of CVD is *plasma assisted chemical vapor deposition* (PACVD), in which deposition onto a substrate is accomplished by reacting the ingredients in a gas that has been ionized by means of an electric discharge (i.e., a plasma). In effect, the energy contained in the plasma rather than thermal energy is used to activate the chemical reactions. Advantages of PACVD include (1) lower substrate temperatures, (2) better covering power, (3) better adhesion, and (4) faster deposition rates [6]. Applications include deposition of silicon nitride (Si_3N_4) in semiconductor processing, TiN and TiC coatings for tools, and polymer coatings. The process is also known as plasma-enhanced chemical vapor deposition, plasma chemical vapor deposition, or just simply plasma deposition.

27.6   Organic Coatings

Organic coatings are polymers and resins, produced either naturally or synthetically, usually formulated to be applied as liquids that dry or harden as thin surface films on substrate materials. These coatings are valued for the variety of colors and textures possible, their capacity to protect the substrate surface, low cost, and ease with which they can be applied. This section considers the compositions of organic coatings and the methods to apply them. Although most organic coatings are applied in liquid form, some are applied as powders, and this alternative is covered in Section 27.6.2.

Organic coatings are formulated to contain the following: (1) binders, which give the coating its properties; (2) dyes or pigments, which lend color to the coating; (3) solvents, to dissolve the polymers and resins and add proper fluidity to the liquid; and (4) additives.

Binders in organic coatings are polymers and resins that determine the solid-state properties of the coating, such as strength, physical properties, and adhesion to the substrate surface. The binder holds the pigments and other ingredients in the coat-ing during and after application to the surface. The most common binders in organic coatings are natural oils (used to produce oil-based paints), and resins of polyesters, polyurethanes, epoxies, acrylics, and cellulosics.

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Dyes and pigments provide color to the coating. *Dyes* are soluble chemicals that color the coating liquid but do not conceal the surface beneath. Thus, dye-colored coatings are generally transparent or translucent. *Pigments* are solid particles of uniform, microscopic size that are dispersed in the coating liquid but insoluble in it. They not only color the coating; they also hide the surface below. Because pigments are particulate matter, they also tend to strengthen the coating.

Solvents are used to dissolve the binder and certain other ingredients in the liquid coating composition. Common solvents used in organic coatings are aliphatic and aromatic hydrocarbons, alcohols, esters, ketones, and chlorinated solvents. Different solvents are required for different binders. *Additives* in organic coatings include surfactants (to facilitate spreading on the surface), biocides and fungicides, thickeners, freeze/thaw stabilizers, heat and light stabilizers, coalescing agents, plasticizers, defoamers, and catalysts to promote cross-linking. These ingredients are formulated to obtain a wide variety of coatings, such as paints, lacquers, and varnishes.

27.6.1   APPLICATION METHODS

The method of applying an organic coating to a surface depends on factors such as composition of the coating liquid, required thickness of the coating, production rate and cost considerations, part size, and environmental requirements. For any of the application methods, it is of utmost importance that the surface be properly prepared. This includes cleaning and possible treatment of the surface such as phosphate coating. In some cases, metallic surfaces are plated prior to organic coating for maximum corrosion protection.

With any coating method, transfer efficiency is a critical measure. *Transfer efficiency* is the proportion of paint supplied to the process that is actually deposited onto the work surface. Some methods yield as low as a 30% transfer efficiency (meaning that 70% of the paint is wasted and cannot be recovered).

Available methods of applying liquid organic coatings include brushing and rolling, spray coating, immersion, and flow coating. In some cases, several successive coatings are applied to the substrate surface to achieve the desired result. An automobile car body is an important example; the following is a typical sequence applied to the sheet-metal car body in a mass-production automobile: (1) phosphate coat applied by dipping, (2) primer coat applied by dipping, (3) color paint coat applied by spray coating, and (4) clear coat (for high gloss and added protection) applied by spraying.

Brushing and *rolling* are the two most familiar application methods to most people. They have a high transfer efficiency—approaching 100%. Manual brushing and rolling methods are suited to low production but not mass production. While brushing is quite versatile, rolling is limited to flat surfaces.

Spray coating is a widely used production method for applying organic coatings. The process forces the coating liquid to atomize into a fine mist immediately prior to deposition onto the part surface. When the droplets hit the surface, they spread and flow together to form a uniform coating within the localized region of the spray. If done properly, spray coating provides a uniform coating over the entire work surface.

Spray coating can be performed manually in spray painting booths, or it can be set up as an automated process. Transfer efficiency is relatively low (as low as 30%) with these methods. Efficiency can be improved by *electrostatic spraying*, in which

the work part is grounded electrically and the atomized droplets are electrostatically charged. This causes the droplets to be drawn to the part surfaces, increasing transfer efficiencies to values up to 90% [17]. Spraying is utilized extensively in the automotive industry for applying external paint coats to car bodies. It is also used for coating appliances and other consumer products.

Immersion applies large amounts of liquid coating to the work part and allows the excess to drain off and be recycled. The simplest method is *dip coating*, in which a part is immersed in an open tank of liquid coating material; when the part is withdrawn, the excess liquid drains back into the tank. A variation of dip coating is *electrocoating*, in which the part is electrically charged and then dipped into a paint bath that has been given an opposite charge. This improves adhesion and permits use of water-based paints (which reduce fire and pollution hazards).

In *flow coating*, work parts are moved through an enclosed paint booth, where a series of nozzles shower the coating liquid onto the part surfaces. Excess liquid drains back into a sump, which allows it to be reused.

Once applied, the organic coating must convert from liquid to solid. The term *drying* is often used to describe this conversion process. Many organic coatings dry by evaporation of their solvents. However, in order to form a durable film on the substrate surface, a further conversion is necessary, called curing. *Curing* involves a chemical change in the organic resin in which polymerization or cross-linking occurs to harden the coating.

The type of resin determines the type of chemical reaction that takes place in curing. The principal methods by which curing is effected in organic coatings are [17] (1) *ambient temperature curing*, which involves evaporation of the solvent and oxidation of the resin (most lacquers cure by this method); (2) *elevated temperature curing*, in which elevated temperatures are used to accelerate solvent evaporation, as well as polymerization and cross-linking of the resin; (3) *catalytic curing*, in which the starting resins require reactive agents mixed immediately prior to application to bring about polymerization and cross-linking (epoxy and polyurethane paints are examples); and (4) *radiation curing*, in which various forms of radiation, such as microwaves, ultraviolet light, and electron beams, are required to cure the resin.

27.6.2 POWDER COATING

The organic coatings discussed above are liquid systems consisting of resins that are soluble (or at least miscible) in a suitable solvent. Powder coatings are different. They are applied as dry, finely pulverized, solid particles that are melted on the surface to form a uniform liquid film, after which they resolidify into a dry coating. Powder coating systems have grown significantly in commercial importance among organic coatings since the mid-1970s.

Powder coatings are classified as thermoplastic or thermosetting. Common thermoplastic powders include polyvinylchloride, nylon, polyester, polyethylene, and polypropylene. They are generally applied as relatively thick coatings, 0.08–0.30 mm (0.003–0.012 in). Common thermosetting coating powders are epoxy, polyester, and acrylic. They are applied as uncured resins that polymerize and cross-link on heating or reaction with other ingredients. Coating thicknesses are typically 0.025 to 0.075 mm (0.001–0.003 in).

There are two principal application methods for powder coatings: spraying and fluidized bed. In the *spraying* method, an electrostatic charge is given to each particle

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in order to attract it to an electrically grounded part surface. Several spray gun designs are available to impart the charge to the powders. The spray guns can be operated manually or by industrial robots. Compressed air is used to propel the powders to the nozzle. The powders are dry when sprayed, and any excess particles that do not attach to the surface can be recycled (unless multiple paint colors are mixed in the same spray booth). Powders can be sprayed onto a part at room temperature, followed by heating of the part to melt the powders; or they can be sprayed onto a part that has been heated to above the melting point of the powder, which usually provides a thicker coating.

The *fluidized bed* is a less commonly used alternative to electrostatic spraying. In this method, the work part to be coated is preheated and passed through a fluidized bed, in which powders are suspended (fluidized) by an airstream. The powders attach themselves to the part surface to form the coating. In some implementations of this coating method, the powders are electrostatically charged to increase attraction to the grounded part surface.

27.7 Porcelain Enameling and Other Ceramic Coatings

Porcelain is a ceramic made from kaolin, feldspar, and quartz (Section 7.2.1). It can be applied to substrate metals such as steel, cast iron, and aluminum as a vitreous porcelain enamel. Porcelain coatings are valued for their beauty, color, smoothness, ease of cleaning, chemical inertness, and general durability. *Porcelain enameling* is the name given to the technology of these ceramic coating materials and the processes by which they are applied.

Porcelain enameling is used in a wide variety of products, including bathroom fixtures (e.g., sinks, bathtubs, lavatories), household appliances (e.g., ranges, water heaters, washing machines, dishwashers), kitchen ware, hospital utensils, jet engine components, automotive mufflers, and electronic circuit boards. Compositions of the porcelains vary, depending on product requirements. Some porcelains are formulated for color and beauty, while others are designed for functions such as resistance to chemicals and weather, ability to withstand high service temperatures, hardness and abrasion resistance, and electrical resistance.

As a process, porcelain enameling consists of (1) preparing the coating material, (2) applying to the surface, (3) drying, if needed, and (4) firing. Preparation involves converting the glassy porcelain into fine particles, called *frit*, that are milled to proper and consistent size. The methods for applying the frit are similar to methods used for applying organic coatings, even though the starting material is entirely different. Some application methods involve mixing frit with water as a carrier (the mixture is called a *slip*), while other methods apply the porcelain as dry powder. The techniques include spraying, electrostatic spraying, flow coating, dipping, and electrodeposition. Firing is accomplished at temperatures around 800°C (1500°F). Firing is a *sintering* process (Section 16.1.4) in which the frit is transformed into nonporous vitreous porcelain. Typical coating thickness ranges from 0.075 to 2 mm (0.003–0.08 in). The processing sequence may be repeated several times to obtain the desired thickness.

In addition to porcelain, other ceramics are used as coatings for special purposes. These coatings usually contain a high content of alumina, which makes them more suited to refractory applications. Techniques for applying the coatings are similar to the preceding, except firing temperatures are higher.

27.8   Thermal and Mechanical Coating Processes

These processes apply discrete coatings that are generally thicker than coatings deposited by other processes considered in this chapter. They are based on either thermal or mechanical energy.

27.8.1   THERMAL SURFACING PROCESSES

These methods use thermal energy in various forms to apply a coating whose function is to provide resistance to corrosion, erosion, wear, and high temperature oxidation. The processes include (1) thermal spraying, (2) hard facing, and (3) the flexible overlay process.

In *thermal spraying*, molten and semimolten coating materials are sprayed onto a substrate, where they solidify and adhere to the surface. A wide variety of coating materials can be applied; the categories are pure metals and metal alloys; ceramics (oxides, carbides, and certain glasses); other metallic compounds (sulfides, silicides); cermet composites; and certain plastics (epoxy, nylon, Teflon, and others). The substrates include metals, ceramics, glass, some plastics, wood, and paper. Not all coatings can be applied to all substrates. When the process is used to apply a metallic coating, the terms *metallizing* or *metal spraying* are used.

Technologies used to heat the coating material are oxyfuel flame, electric arc, and plasma arc. The starting coating material is in the form of wire or rod, or powders. When wire (or rod) is used, the heating source melts the leading end of the wire, thereby separating it from the solid stock. The molten material is then atomized by a high-velocity gas stream (compressed air or other source), and the droplets are spattered against the work surface. When powder stock is used, a powder feeder dispenses the fine particles into a gas stream, which transports them into the flame, where they are melted. The expanding gases in the flame propel the molten (or semimolten) powders against the workpiece. Coating thickness in thermal spraying is generally greater than in other deposition processes; the typical range is 0.05 to 2.5 mm (0.002–0.100 in).

The first applications of thermal spray coating were to rebuild worn areas on used machinery components and to salvage work parts that had been machined undersize. Success of the technique has led to its use in manufacturing as a coating process for corrosion resistance, high temperature protection, wear resistance, electrical conductivity, electrical resistance, electromagnetic interference shielding, and other functions.

Hard facing is a surfacing technique in which alloys are applied as welded deposits to substrate metals. What distinguishes hard facing is that fusion occurs between the coating and the substrate, as in fusion welding (Section 28.1.1), whereas the bond in thermal spraying is typically mechanical interlocking that does not stand up as well to abrasive wear. Thus, hard facing is especially suited to components requiring good wear resistance. Applications include coating new parts and repairing used part surfaces that are heavily worn, eroded, or corroded. An advantage of hard facing that should be mentioned is that it is readily accomplished outside of the relatively controlled factory environment by many of the common welding processes, such as oxyacetylene gas welding and arc welding. Some of the common surfacing materials include steel and iron alloys, cobalt-based alloys, and nickel-based alloys. Coating thickness is usually 0.75 to 2.5 mm (0.030–0.125 in), although thicknesses as great as 9 mm (3/8 in) are possible.

The ***flexible overlay process*** is capable of depositing a very hard coating material, such as tungsten carbide (WC), onto a substrate surface. This is an important advantage of the process compared to other methods, permitting coating hardness up to about 70 Rockwell C. The process can also be used to apply coatings only to selected regions of a work part. In the flexible overlay process*,* a cloth impregnated with hard ceramic or metal powders and another cloth impregnated with brazing alloy are laid onto a substrate and heated to fuse the powders to the surface. Thickness of overlay coatings is usually 0.25 to 2.5 mm (0.010–0.100 in). In addition to coatings of WC and WC–Co, cobalt-based and nickel-based alloys are also applied. Applications include chain saw teeth, rock drill bits, oil drill collars, extrusion dies, and similar parts requiring good wear resistance.

27.8.2 MECHANICAL PLATING

In this coating process, mechanical energy is used to build a metallic coating onto the surface. In mechanical plating*,* the parts to be coated, together with plating metal powders, glass beads, and special chemicals to promote the plating action, are tumbled in a barrel. The metallic powders are microscopic in size—5 μm (0.0002 in) in diameter; while the glass beads are much larger—2.5 mm (0.10 in) in diameter. As the mixture is tumbled, the mechanical energy from the rotating barrel is transmitted through the glass beads to pound the metal powders against the part surface, causing a mechanical or metallurgical bond to result. The deposited metals must be malleable in order to achieve a satisfactory bond with the substrate. Plating metals include zinc, cadmium, tin, and lead. The term ***mechanical galvanizing*** is used for parts that are zinc coated. Ferrous metals are most commonly coated; other metals include brass and bronze. Typical applications include fasteners such as screws, bolts, nuts, and nails. Plating thickness in mechanical plating is usually 0.005 to 0.025 mm (0.0002–0.001 in). Zinc is mechanically plated to a thickness of around 0.075 mm (0.003 in).

References

[1] ***ASM Handbook***, Vol. 5, ***Surface Engineering***, ASM International, Materials Park, Ohio, 1993.
[2] Budinski, K. G. ***Surface Engineering for Wear Resistance***. Prentice Hall, Inc., Englewood Cliffs, New Jersey, 1988.
[3] Durney, L. J. (ed.). ***The Graham's Electroplating Engineering Handbook***, 4th ed. Chapman & Hall, London 1996.
[4] Freeman, N. B. "A New Look at Mass Finishing," Special Report 757, ***American Machinist***, August 1983, pp. 93–104.
[5] George, J. ***Preparation of Thin Films***. Marcel Dekker, Inc., New York, 1992.
[6] Hocking, M. G., Vasantasree, V., and Sidky, P. S. ***Metallic and Ceramic Coatings***. Addison-Wesley Longman, Reading, Massachusetts, 1989.
[7] ***Metal Finishing***, Guidebook and Directory Issue. Metals and Plastics Publications, Inc., Hackensack, New Jersey, 2000.
[8] Morosanu, C. E. ***Thin Films by Chemical Vapour Deposition***. Elsevier, Amsterdam, The Netherlands, 1990.
[9] Murphy, J. A. (ed.). ***Surface Preparation and Finishes for Metals***. McGraw-Hill, New York, 1971.
[10] Sabatka, W. "Vapor Degreasing," Available at www.pfonline.com.
[11] Satas, D. (ed.). ***Coatings Technology Handbook***, 2nd ed. Marcel Dekker, New York, 2000.