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METALLIC COATINGS, SURVEY

Metallic coatings provide an inexpensive way to modify or control the properties of a base material. Coatings (qv) may be functional or decorative, permanent or temporary, sacrificial, or noble. The metallic coating may be continuous, or it may be patterned into discontinuous functional or decorative areas. The base material may be metallic, nonmetallic inorganic, or organic such as plastic, paper, or fiber. The common criterion for the purposes herein is that the metallic coating is functionally bonded to the base material (1–4). Galvanized zinc items, gold clad jewelry, electroplated materials, and semiconductor chips are among the most common types of materials having metallic coatings (see Electroplating; Electronics, coatings; Integrated circuits; and Semiconductors).

Some types of metallic coating have been used since ancient times, initially for jewelry and decorative applications. One of the earliest techniques, used by the ancient Egyptians, was the use of gold foil. Gold foil, produced by beating gold to thicknesses of $<0.1\ \mu\text{m}$ can be easily bonded to all types of metals, paper (qv), leather (qv), and other materials. Many early artifacts originally thought to have been fabricated by means of a chemical displacement coating of a precious metal, were probably made by selective dissolution of the less noble components of an alloy. Glass mirrors formerly were made by amalgamating a thin tin sheet with mercury, pressing it to a glass sheet, and heating to vaporize the mercury and form a direct metal-to-glass bond (5). Soldering is an ancient metal coating technique used for joining two metals, used as of the 1990s in highest volume in the electronics industry.

Some of the first electroplating applications in the early 1800s involved attempts to coat inexpensive base metals with thin layers of pure gold, or even more cheaply, gold-colored brass. Economic reasons are almost always foremost in the decision of coating selection. Exceptions are where environmental or legislative measures require more expensive, less toxic coatings, as in replacement of cadmium [7440-67-7]. The use of metallic coatings often conserves rare metals, allowing the more abundant materials to serve as substrates. Bulk corrosion-resistant materials such as stainless steel or Monel use large amounts of scarce nickel and chromium. One metal may serve many different functions, depending on the application. Thus gold [7440-57-5] may be the permanent decorative coating on jewelry, a permanent functional coating on electrical connectors (qv) or anodes, or a temporary functional and protective coating for solder joint connections on printed circuit boards in which the thin gold layer protects the underlying nickel from oxidation then dissolves in the molten solder to allow solder bonding to the nickel (see Solders and brazing filler metals).

Metallic coatings are most often selected for protective function. Decorative ability is a common secondary function. Most coatings applied by hot dipping, such as galvanizing or aluminizing, use a film of a more chemically reactive metal over a less reactive material such as iron alloy. These are sacrificial coatings because the zinc or aluminum slowly dissolves instead of the underlying steel. The sacrificial metal protects the underlying iron even if the coating is scratched or broken. In this case the slowly dissolving metal acts as a battery, keeping the iron at a cathodic potential and preventing the iron from rusting. In contrast, a protective coating of a more noble metal such as gold, must be absolutely break-free. If a break occurs in this type of coating, the battery effect makes the underlying metal anodic, thus causing accelerated corrosion of the base metal (4, 6–9).

Decorative coatings must be sufficiently corrosion resistant to maintain an attractive appearance during the anticipated life of the composite product. Composites of multiple metal layers or mixtures of metallic and nonmetallic coatings are becoming increasingly common as material properties are selectively tailored. Aluminum [7429-90-5] coatings on mirrors, laser disks, and compact disks are given a protective sealer coating of transparent plastic to inhibit the sacrificial oxidation of the shiny aluminum to the dulled aluminum oxide. Thin transparent rhodium [7440-16-6] coatings are used to make tarnish-resistant silver jewelry. Chromium [7440-47-3] coatings combine both decoration and corrosion resistance.

Another important function of metallic coatings is to provide wear resistance. Hard chromium, electroless nickel, composites of nickel and diamond, or diffusion or vapor-phase deposits of silicon carbide [409-21-2], SiC;, SiC; tungsten carbide [56780-56-4], WC; and boron carbide [12069-32-8], B_4C, are examples. Chemical resistance at high temperatures is provided by alloys of aluminum and platinum [7440-06-4] or other precious metals (10–14).

The most technologically demanding types of coatings are those grown in precisely defined multiple layers. Experimental work is being done on multiple metal layer films using repetitive layers of two metals such as copper [7440-50-8] and nickel [7440-02-0], deposited in very thin and accurately repeated layers. These alloy-modulated layered electrodeposits may have increased tensile strength and electrical resistivity, higher saturated magnetization, or increased elastic modulus (15) (see Magnetic materials). All semiconductor chips start with a base layer of silicon or other semiconductor, then use a combination of bulk and selective deposition steps to give multiple layers of metals and insulators that form the three-dimensional devices. Printed circuit board processing is similar but on a much larger scale, beginning with laminated copper–epoxy sheets and ending with a complex multilayered structure of epoxy–glass, laminated copper, electroless plated and electroplated copper, plated nickel and gold, and molten applied solder.

Plating and galvanizing are the most common methods of applying metallic coatings, but many other processes, such as hot dipping, cementation, thermal spraying, sputtering, and chemical vapor deposition, have been developed (see also Coating processes). All metallizing techniques are potential sources of pollution, a subject of increasing ecological, economic, legislative, and public health interest. Metallizing has been combined with metal removal and associated functions such as physical or chemical surface modification, by the U.S. EPA as part of the “Metal Finishing” category for pollution control legislative purposes.

There are a plethora of commercially useful methods for applying a metallic coating. Many more techniques have been demonstrated in the laboratory. Each method has different critical parameters, ie, maximum and minimum coating thickness producible, substrate temperature, bulk or imagewise deposition, coating adhesion value, type and cost of coating equipment, labor requirement, scrap rate, rework capability, and safety and waste disposal aspects. For convenience, metallic coating methods may be divided into classes defined by the general way in which the metal is applied, eg, liquid-phase, gas-phase, and vacuum-phase metallizing, as well as metallizing by direct physical or thermal bonding.

The two largest volume processes, in terms of amount of metal used and amount of surface area coated, are the liquid-phase metallizing processes hot dip and coating electroplating (qv). One of the newer developments in hot dip galvanizing is its use on whole fabricated auto bodies giving lower cost resulting from ease of initial fabrication followed by complete zinc coverage, including into hidden and welded areas. This process, especially applicable to complex-shaped parts, had been used only on much smaller assemblies.

Many of the newer coating methods give metallized coatings that are quite distinct from simple single or multiple coatings of metals or alloys. Many of these newer coatings, which cannot be made except by one or a small family of processes, are defined as much by process method as physical and chemical structure. Examples of these coatings include ion-plated surfaces, laser heat-treated surfaces, modifications of existing surfaces to predetermined depths by selective additions of atoms or heat; and Teflon–electroless nickel composite coatings (6, 7, 12–14, 16–19).

1. Liquid-Phase Metallizing Techniques

1.1. Hot Dip Galvanizing

The largest single type of metallic coating process in terms of amount of metal used is hot dip galvanizing. In 1990 zinc [7440-66-6] production was ca 2 million metric tons (see Zinc and zinc alloys). Approximately 40% of all the zinc mined (8×10^5 t) is used for zinc coatings of all sorts. Hot dip galvanizing accounts for over 90% ($>7 \times 10^5$ t) of the coatings usage and the proportion of steel (qv) which is coated with zinc is slowly rising. As of this writing (ca 1995) about 6% or ca 40 million metric tons of world steel production is zinc coated. Half of all galvanized zinc is used on steel coils, one-third is employed for coating of parts after fabrication, and the remainder for wires and tubes. The other uses, in approximate order, are electroplating, zinc-filled paints, zinc spray processes, zinc foils having conductive adhesive, and mechanical zinc plating (1, 4, 8, 9, 11, 12, 18, 20, 21).

In hot dip galvanizing, zinc is applied to iron (qv) and steel parts by immersing the parts into a bath of molten zinc. Whereas in principle almost any metal could be coated with molten zinc, this coating serves no worthwhile purpose on most metals. The combination of zinc and ferrous materials are almost uniquely suited to each other. Aluminum and cadmium are the only other similar combinations. Zinc provides iron parts with better corrosion protection by developing a coating of zinc and zinc compounds on the base metal surface. Protection is achieved for the following reasons. (*1*) Zinc has a much lower corrosion rate in comparison to that of iron in the atmosphere as well as in water (see Corrosion and corrosion control). Zinc develops adherent corrosion products and iron does not. (*2*) Zinc is anodic to iron, thus corroding in place of iron. (*3*) The durability and wear resistance of zinc and the basal iron–zinc intermetallic compounds, Fe_3Zn_{10} [12182-98-8], $FeZn_7$ [12023-07-3], and $FeZn_{13}$ [12140-55-5], develop successively on the iron surface. The intermetallic compound formation is about one-tenth of the coating thickness and is essential for complete adherent bonding of zinc and steel. Any residual oxides or dirt inhibit this reaction. In addition, subsequent painting can easily and inexpensively be accomplished to increase protection further, or for decorative reasons. The best results are obtained using steels that contain $<0.25\%$ carbon, $<0.05\%$ phosphorus, $<1.35\%$ manganese, and $<0.5\%$ silicon. The primary factor in determining the degree of corrosion protection provided by a zinc coating, is thickness, which depends on the duration of immersion, the speed of withdrawal from the bath, and the temperature of the bath.

The effect of galvanizing on the mechanical properties of steels varies with the alloy and treatment. There is no effect on hot rolled steels, but increased strength resulting from cold working or heat treating is reduced by galvanizing. Impact toughness and fatigue strength are slightly reduced, as well as formability. Cracks can develop in the zinc coat upon bending. Residual stresses are reduced by 50 to 60% in welded structures. Hydrogen embrittlement does not result from hot dip galvanizing, unlike zinc electroplating where embrittlement can be a problem.

The pretreatment of the parts to be hot dip galvanized includes degreasing in a heated alkaline cleaner followed by acid pickling in dilute sulfuric or hydrochloric acid. The steel surface must be clean and completely wettable by the molten zinc. Usually the cleaned steel is immersed in an acid flux bath just prior to immersion in the molten zinc, to ensure instant wetting. Much zinc coated steel is marketed as being coated with raw zinc. The rest of the galvanized steel is given a post-treatment which depends on the application and the environmental conditions. A very thin chromate layer is used for relatively short-term protection, and where weldability is important. A chromate, or preferably a phosphate and a chromate coating, is used when the parts must be painted (see Metal surface treatments).

The zinc coating is sacrificial, dissolving preferentially before the iron. The most important feature of this process is that holes and breaks in the coating have little effect as long as there is some zinc within a centimeter or so of any exposed iron. The zinc and iron, in the presence of any moisture and electrolyte such as absorbed carbon dioxide or salt, form a battery where the zinc is the anode and steel the cathode. This active passivation

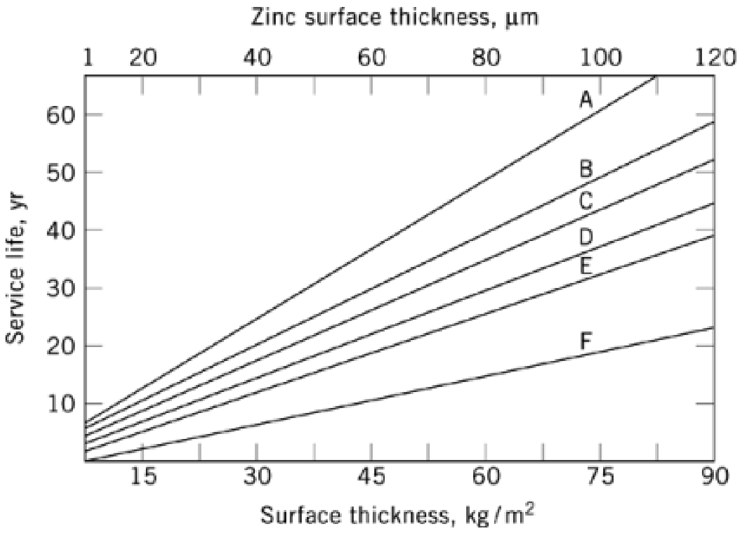

Fig. 1. Relationship between thickness of galvanized zinc surface and service life where service life is defined as the time to 5% rusting of the steel surface and A, use in a rural environment; B, tropical marine; C, temperate marine; D, suburban; E, moderately industrial; and F, heavy industrial. To convert kg/m^2 to oz/ft^2, multiply by 3.278.

lasts as long as there is metallic zinc to corrode within transfer range of electrons donated to the iron (19). Zinc coatings are therefore superior to coatings of gold or other insoluble metals more noble than steel. If steel is coated with gold a different type of battery forms at every pinhole and break in the coating where gold is the cathode. Then the large cathode-to-anode ratio leads to extremely rapid steel corrosion at every pore.

The essential protective film on the zinc surface is that of basic zinc carbonate, which forms in air in the presence of carbon dioxide and moisture (Fig. 1). If wet conditions predominate the normally formed zinc oxide and zinc hydroxide, called white rust, do not transform into a dense protective layer of adhesive basic zinc carbonate. Rather the continuous growth of porous loosely adherent white rust consumes the zinc then the steel rusts.

Fresh zinc surfaces cannot be painted because of the activity of pure zinc. Diffusion of moisture and oxygen through a paint film results in a reaction with the fresh zinc to form hydroxide ions, which causes the paint to blister and delaminate. Zinc surfaces must be allowed to age before painting to form a protective layer of basic zinc carbonate, or passivation treatments such as phosphating and chromating must be used (see Metal surface treatments). Painting can also give protection against electrolytic corrosion caused by contact with more noble metals or alloys such as stainless steel, copper, and brass, as long as the nonconductive paint separates the metals.

Dry galvanizing, developed in Europe, and wet galvanizing, more commonly used in North America, are two types of conventional batch galvanizing in wide use. In the dry galvanizing process the material is degreased, acid pickled, immersed in an aqueous flux solution, and dried before immersion into molten zinc. Wet galvanized parts are not prefluxed after cleaning and pickling, but are placed into the molten zinc through a top flux blanket on the kettle. The purpose of the flux blanket is to remove the small amounts of impurities left on the surface after degreasing and pickling. The usual operating temperature of the molten zinc bath is 445–465°C, but higher (550°C) temperatures are used for high silicon steels. Whereas the immersion time controls the alloy layer coating thickness, the immersion speed influences coating uniformity. The rate of withdrawal determines the thickness of the unalloyed zinc layer which is left on the parts. When a low rate of withdrawal to decrease the thickness of the zinc layer is not practical, the parts can be spun or blown using

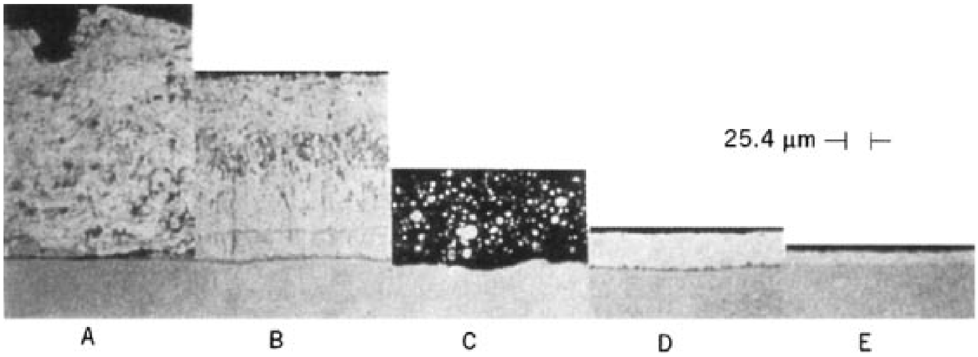

Fig. 2. Microstructure of various zinc coatings where A is metallized; B, hot dip galvanized; C, zinc-rich paint; D, galvanized sheet; and E, electroplated.

live steam. Compressed air is normally used on continuous coil galvanizing at speeds up to about 200 m/min. Various feedback controls are used to maintain the desired coating thickness.

The surface of galvanized steel is characteristically rough and irregular. Various surface finishes are also available on continuous sheet galvanized steel, from full spangle, ie, large zinc crystals, to minimum spangle, ie, small crystals, to wire brushed smooth surfaces. The spangle, or zinc crystal size, results from the rapid crystallization of the molten zinc, and from the condition of the bare steel. Minor additions to the molten zinc can lower the melting point of the zinc, and decrease the spangle size. One-side galvanized steel is made by coating one side of the sheet with a sodium silicate solution which is nonwettable in molten zinc. The silicate is then removed with a hydrofluoric acid-based etchant (see Fluorine compounds, inorganic). Galvanized steel coatings contain globules of lead (qv), forced to the surface during zinc crystallization. The lead is an impurity in the zinc, usually at $<0.5\%$. Lead does not form an alloy with zinc so it segregates upon cooling. Another process, galvannealing, is used to heat treat the zinc coating on-line to convert the whole coating to an iron–zinc intermetallic compound for better paintability. Numerous commercial grades of galvanized thicknesses are available, from thinner than the standard commercial-grade of 0.275 kg/m^2 (0.19 μm thickness per side) to coatings three times as thick.

Over half of the total tonnage of metallic coated parts is produced by galvanizing of steel strip. The majority of this is produced on continuous high speed coil coating lines, often operating at up to 15 km/h or more. An additional large quantity of electrogalvanized steel coil is produced by electroplating from aqueous zinc sulfate or chloride baths. This thinner but smoother zinc coating is used where a higher quality or painted finish is necessary, and where lesser corrosion resistance is tolerable (Fig. 2). Electroplated steel strip is preferred when used as prefinished, fully painted strip stock sold for final forming into finished parts by the fabricator. The automotive industry consumes a large amount of these materials. Newer developments in electrogalvanized steel are the use of more corrosion-resistant sacrificial zinc alloys such as those containing iron, nickel, and cobalt.

1.2. Hot Dipping Using Other Metals

1.2.1. Coating with Aluminum

The numerous methods of applying aluminum coatings include continuous and batch hot dipping, pack diffusion, slurry processes, thermal spraying, and cladding, as well as vacuum, chemical, and ion-vapor deposition. Regardless of method, the essential factor for successful coating is proper preparation of the steel surface. The iron oxide scale, as well as adsorbed moisture and gas, must be removed.

Hot dipping of aluminum is normally applied only to steel. Aluminum coatings are harder and more durable than zinc coatings and give some galvanic protection, but must be about twice the thickness of zinc for acceptable performance. The high melting point of aluminum compared to that of zinc can give more softening of cold worked steel when hot dipped (12, 14).

The most widely used method for continuous hot dip coating is the Sendzimir process, which consists of oxidizing the cleaned steel surface, reducing the surface oxide in a reducing atmosphere, and immersing the steel into molten aluminum or zinc. In this method no flux is needed, but the strip must be cooled and protected by hydrogen until it enters the molten metal. Other processes may also use a reducing atmosphere but without a preliminary oxidation to form a more uniform oxide. The Lundin process uses aqueous fluxes instead of a reducing atmosphere. Hot dip coatings decrease the tensile strength of cold drawn wires.

In batch hot dip coating, cleaning is achieved by hot alkaline cleaning, water rinsing, abrasive blasting, acid pickling, and drying. Cleaning is followed by fused salt fluxing, dipping into molten aluminum, centrifuging, and air blasting or shaking. Coatings consist of an intermetallic layer of iron–aluminum alloy phases, FeAl and Fe_3Al, and a pure aluminum overlay. The thickness of the intermetallic layer depends mainly on the immersion time, but also on the composition of the steel and the aluminum bath. The total coating thickness is determined by the viscosity of the aluminum bath and the speed of withdrawal. Aluminum hot dipping is difficult to control because the intermetallic layer can grow very quickly, even leading to spalling of the coating. Coating times are generally 2–15 seconds.

The corrosion protection of aluminum depends more on aluminum passivation than on sacrificial corrosion. Thus aluminum coatings are less effective than zinc in inhibiting red rusting around breaks in the coating. Aluminum coatings last appreciably longer than zinc ones and are easier to paint. Aluminum passivation results from formation of layers of various hydrous aluminum oxides and hydroxides giving an adherent protective layer which greatly reduces the corrosion rate of the aluminum. Aluminum can be given a chromate or phosphate plus chromate conversion coating to further decrease the corrosion rate and to give a better surface for painting.

1.2.2. Coating with 55% Aluminum–Zinc Alloy

A coating with a nominal composition of 55% aluminum, 43.4% zinc, and 1.6% silicon provides the durability and high temperature resistance of aluminum coatings, and the corrosion protection of zinc coatings. This coating is known as Galvalume or Zincalume. Silicon is added to control the growth of the intermetallic boundary layer. The alloy owes its superior corrosion protection to a particular dendritic microstructure which consists of 80 vol % aluminum, 22 wt % zinc-rich interdentritic aluminum–zinc eutectic alloy, and a few silicon-rich particles. The zinc-rich interdendritic material corrodes preferentially; the aluminum-rich dendrites act as a mechanical trap to retain zinc corrosion products. The coating is bonded to steel by a layer of a quaternary Fe–Al–Zn–Si intermetallic compound, which comprises about 10% of the total coating thickness (20 μm). The coating process is similar to hot dip galvanizing, consisting of cleaning, heat treating, coating, and fast cooling. Heat treating achieves stress relief by recrystallization of steel, while forced air cooling is needed to produce the correct microstructure for maximum corrosion resistance.

Galvalume has been shown to have two to six times the life of an equivalent thickness of zinc, including marine atmospheres. For high temperature oxidation resistance up to 700°C, Galvalume is equivalent to pure aluminum.

1.2.3. Hot Dip Tin Coating of Steel and Cast Iron

Hot dipping of tin [7440-31-5] has been largely superseded by electrolytic coating techniques, especially for sheet. However, hot dipping can be the method of choice for complex and shaped parts. Very thin layers of tin are extensively used to passivate steel used for canned goods. Tin is essentially nontoxic, is nearly insoluble in almost all foods, and easily wets and completely covers steel with a pinhole-free coating.

Hot dip tinning applies a thin (3.8–18 μm) coating of molten tin to provide nontoxic protection for food handling, packaging, and dairy equipment. More than 90% of all tin-coated steel is used for food processing (qv). The tin coating facilitates soldering and assists with metal-to-metal bonding during can forming and lid attachment. Low carbon steels give the best results, but medium to high carbon steels work well given extra care in pickling. High alloy steels, especially high chromium stainless steels, are difficult to coat satisfactorily using molten tin. A wide range of compositions of cast irons tin easily, regardless of the total carbon, silicon, manganese, sulfur, and phosphorus analyses. Difficulties may be experienced when there are large quantities of graphite or buried silicon oxides. The actual interfacial coating is a thin intermetallic alloy of $FeSn_2$ [12023-01-7]. This alloy forms by diffusion so is limited to a practical thickness of about 0.5 μm. Pure tin comprises the remainder of the coating.

The metal parts must be cleaned, degreased, pickled, and fluxed prior to tinning. Iron and steel parts must be free of all surface contaminants such as oil, drawing lubricants, and scale. Abrasive blast cleaning is also used on castings to increase the surface area for better adhesion and retention of tin. Fluxing facilitates the reaction between molten tin and iron or steel by promoting the formation of iron–tin intermetallic compounds. These initial intermetallic layers provide a low energy surface which allows the molten tin to spread in an even, smooth film. The fluxes commonly consist of mixtures of zinc, ammonium, and sodium chlorides plus some free hydrochloric acid. Similar fluxes are used in almost all types of steel coating by hot dipping, and even in soldering of various alloys to copper and nickel. These fluxes may be applied from an aqueous dip tank, from a fused layer floating on top of the molten tin, or as a paste with tin powder.

Those coatings which do not require the highest quality finish or which are used prior to soldering or bonding are produced by single-pot tinning. Higher quality thick coatings are achievable by two-pot tinning in which the second bath is covered with a layer of high flash point oil or grease instead of flux. The flux residues from the first tinning are absorbed or displaced by the oil and the retained thin oil coating protects the items during shipment and storage. The final coating from a two-pot system is much more pure because no iron contaminates the surface.

1.2.4. Hot Dip Terne Coating

Terne coatings are lead or lead alloy coatings, usually containing 2–25% tin. Lead alone does not alloy with iron. Other elements must be added to form an adherent interfacial iron alloy. Tin and antimony are common additives. An iron–tin intermetallic layer provides an excellent metallurgical bond which adheres well to lead. Lead acts as a lubricant to facilitate forming and drawing of coated sheet, provides excellent solderability and weldability, and provides good corrosion resistance. Terne coatings cannot be used in any food handling items and are not recommended on general unpainted consumer parts, owing to the lead content. Terne coatings are used for gasoline tanks for cars, trucks, lawnmowers, and boats; oil filter cans, air filter holders; chassis for radios and other electrical equipment; roofing siding, gutters, and downspouts; and electrical hardware. Terne coatings are also commonly made by electroplating.

All parts must be given a thorough cleaning prior to dipping, including a final flux coating. Coating thickness is generally between 5–15 μm. It is controlled by the bath temperature (325–390°C), immersion time, and degree of shaking or centrifugation before coating solidification. Coating thickness is controlled to 2–5 μm for sheet or strip by an air knife system of high pressure jets of air or nitrogen against the molten coating.

1.2.5. Solder Coatings

Soldering, brazing, and welding (qv), are all used for joining metals (see also Solders and brazing filler metals). Two metallic objects are joined in a weld by making the interface molten, as by an electric current, friction, electron beams, etc. Brazing is a special type of welding in which various fluxes are used to help clean and bond the two surfaces. Discussions of brazing and welding are available (22).

Solder and other fusible lead and tin-based coatings are used for several applications in printed circuit production. The most commonly applied coating is a 63:37 tin–lead eutectic alloy, but 90:10, and other coatings can be used. Any alloy or metal which melts at a relatively low temperature and forms a bond with the underlying and overlying metals can be used as a solder. Alloys of tin, lead, bismuth, silver, and indium are the most common combinations. There is much interest in finding an economical substitute for lead-containing solders, in order to reduce environmental lead exposure, and many novel alloys have been introduced. A practical tin–lead solder substitute must possess a number of attributes, including reasonable cost, recyclability, good joint strength, heat and cold resistance to recrystallization, corrosion resistance, acceptable liquidus temperature, easy resolderability for rework purposes, and low toxicity. Thus pure tin is not an acceptable solder because it melts at too high a temperature, recrystallizes to form nonadherent crystals at low temperatures (tin pest), and grows conductive short-circuiting whiskers between active circuits on contaminated circuit boards at high humidities (23–27).

Solder is used either as the final coating allowing permanent bonding of electrical connectors to copper or nickel-coated copper parts, as a final protective layer on copper circuits to inhibit corrosion, or as a temporary etch-resistant coating when applied imagewise to the printed circuit board. In the last case solder or tin is usually applied by imagewise electrodeposition on the final circuit paths prior to photoresist removal. The photoresist is then stripped and the exposed copper is etched using ammoniacal copper etchant or sulfuric acid–hydrogen peroxide to make the final circuits. Finally the protective solder layer is chemically stripped from the copper to allow for final processing and inspection. Any future deposits of solder are made by hot dipping or direct soldering, not by electroplating (see Lithographic resists).

Bulk solder coatings are applied by immersion in fused solder. The surface or electrodeposited surfaces are smoothed and leveled by hot oil, hot air, or infrared reflow. There are cases where electroplating is used to give a functional tin–lead solder. The electrodeposited solder is normally heated to the liquidus temperature (reflowed) by one of the means described to give a smooth, pore-free surface. Several different tin–copper alloys form during reflow or hot dipping, and more slowly at room temperature. These alloys are important to give high wettability and bonding strength. Lead does not form an alloy with copper, so the bulk of the solder becomes enriched in lead.

Solder coatings are more difficult to apply to nickel than to other metals. Nickel passivates easily and quickly to form nickel oxides. The nickel oxides inhibit good bonding and need aggressive treatments for removal. Often a thin ($<0.1-0.5\ \mu$m) gold layer is used as a temporary protective layer on the nickel. Contact with molten solder instantly dissolves the gold, bringing the solder in contact with the clean, oxide-free nickel surface to which the solder bonds. The disadvantage of using gold is that a gold–tin intermetallic layer forms which weakens solder bonds. The cost of gold is so great that molten solder pots are recycled for their gold content when the gold comprises only a few tenths of a percent.

1.3. Electroplating

Many developments in electroplating (qv) have been driven by increased coating functionality and economy, others by environmental and legislative compliance. This field has expanded rapidly. Only some of the developments are discussed herein.

The most common electroplated metal is zinc, followed by nickel, copper, and chromium. Many other metals and metaloids can be electroplated, including manganese, iron, cobalt, gallium, germanium, arsenic, selenium, ruthenium, rhodium, palladium, silver, cadmium, indium, tin, lead, bismuth, mercury, antimony, gold, iridium, and platinum. Alloy deposition is common, although the choice of practical alloy coatings is generally somewhat limited to tin–lead, tin–nickel, zinc with cobalt, nickel, or iron, brass (copper–zinc), bronze (copper–tin–zinc), and numerous colored gold alloys. Many other alloys can be electrodeposited, but generally lack commercial utility as a surface coating (3, 6, 7, 15, 28, 29).

Microcracked and microporous chromiums are a unique way to increase the corrosion resistance of a combination of metals. The top coating is more corrosion resistant than the other metals. A totally pore-free chromium layer may be corrosion resistant, but impossible both to fabricate and to keep in this condition throughout the use of the product. The chromium baths contain additives which deposit this metal in a highly stressed condition, resulting in innumerable tiny pores or cracks in the thin (0.25–1 μm) chromium coating. These openings spread out the cathodic battery current from the passive chromium over a relatively large surface area of exposed metal such as nickel. The currents are either dissipated harmlessly or cause general uniform corrosion instead of pitting corrosion to the base metal.

Semibright and bright nickels are used in combination with chromium baths to increase the effective life of plated parts. The automotive industry has developed the Step test which allows measurement of the electrochemical potential of different nickel coatings. Nickel plating for all uses worldwide annually consumes 81,700 metric tons, about 11–12% of world production of nickel. Of this amount, about 80% is used for decorative plating and 20% for electroforming and engineering plating, such as electroless nickel (see Electroless plating).

Originally decorative chromium coatings consisted of an iron or other metal or plastic base, plated with copper, nickel, and pore-free chromium. Pitting corrosion was common and rapidly produced visible deposits of green copper and red iron corrosion products. As of this writing two separate nickel layers are used, plated from different bath chemistries. The top bright nickel coating is more electrochemically active than the lower layer. The top layer corrodes preferentially instead of the lower, less active semibright nickel layer. Thus the top nickel layer acts as a sacrificial coating whereas the bottom nickel layer continues to provide corrosion resistance.

1.3.1. Environmental Aspects

Chromium metal seems to be biologically harmless owing to inertness. Trivalent chromium Cr(III), one of the essential mineral nutrients (qv), has not been shown to be harmful. Hexavalent chromium, Cr(VI), found in chromic acid and used in electroplating baths, is very toxic as well as a suspected carcinogen. Two basic types of chromium are plated: hard chromium up to 100 μm or more, and decorative chromium at 0.25–1.0 μm. No replacement coating has been found for thick hard chromium deposits for wear resistance and parts salvage, although electroless nickel can partially substitute for chromium plating baths. Many decorative applications are being converted to Cr(III). Products from the newest Cr(III) baths are essentially equivalent to those from the older decorative Cr(VI) baths, although some cosmetic color differences exist which have prevented complete conversion to the Cr(III) baths.

Cyanide solutions were formerly ubiquitous in electroplating shops. The best cleaners contained sodium cyanide. Zinc, copper, cadmium, gold, silver, and other metals plated easily from cyanide solutions, which were simple to control and tolerant of impurities. The removal of cyanides (qv) from all plating baths has been a general goal since the latter 1980s. As of 1995 cyanide-containing cleaners are rare and used for special purposes. Copper cyanide strike baths are still needed for plating an initial copper layer on iron, zinc, and other active metals which cannot be directly plated in acid copper sulfate plating baths, but several noncyanide copper strike baths have been introduced. Many noncyanide gold baths are known, but often lack the necessary color, hardness (qv), or alloy composition possible using cyanide golds.

The greatest tonnage decrease in cyanide plating has occurred for zinc plating. As of this writing less than one-third of all zinc is plated from cyanide baths. The remainder is plated from alkaline noncyanide, zinc potassium chloride, and zinc ammonium chloride baths. Newer, slower corroding zinc alloys have been developed which plate from alkaline or acidic baths. These include zinc–iron, zinc–nickel, and zinc–cobalt coatings which are being used in the automotive industry.

Chlorinated and fluorinated cleaners have been widely used as degreasers during surface preparation prior to plating. Recognition of the role of many of these solvents as either global warming gases or ozone depletion agents has led to prohibitions in continued use (see Air pollution; Atmospheric modeling). Many new and improved cleaning systems are being developed, such as alcohol-based cleaners, emulsion cleaners, and cleaners based on natural bioproducts such as limonene. During this process a massive reformulation of many aqueous cleaners has also occurred. These changes are more profound than the simple removal of cyanide. The newer formulations are based on less toxic surfactants (qv) and fewer chelating and complexing agents that are difficult to treat as waste. Many cleaners are formulated to displace rather than emulsify oil, and are used with micro- or ultrafiltration (qv) to extend usage life.

Cadmium usage, illegal in most of Europe, is being discouraged elsewhere. The U.S. military has cadmium specifications for electronic, fastener, and marine equipment, which requires only cadmium. Tin is being substituted for tin–lead as a metallic etch resist during printed circuit board production.

1.3.2. Fused Salt Plating

Fused salt electrolysis has been used in mining and metallurgical technology since the 1800s, in order to win alkali and alkaline-earth metals as well as for the production of tantalum and aluminum. Win or winning is a classical term meaning production of metal at an electrode from its soluble salts. Interest in fused salt bath electroplating, ie, electrolytic deposition of metals from salt melts, has grown in the latter 1990s for the following reasons. (*1*) Certain technically important metals, eg, Nb, Ta, Ti, Zr, W, Mo, or Al, cannot be plated from aqueous electrolytes because of their great affinity for oxygen. (*2*) Metallic coatings from fused salt baths have properties such as high purity and ductility owing to the undisturbed crystal growth that results from low or no stress, as well as the capability of being deposited as thick films. (*3*) It is possible to achieve high deposition rates and high throwing power from salt melts because of the high conductivity of the carrier melts and the consequent low electrolytic voltages for deposition. (*4*) Diffusion layers can be produced whenever the temperature and the deposition rate are adjusted to the diffusion rate of the deposited metal into the basic raw material. Finally, (*5*) economic usage of expensive metals is feasible. This factor becomes more important as metals rise in price and fused salt technology progresses.

Fused salt electrodeposition of metals is used primarily for providing corrosion resistance, ie, protection from oxidation for the electrochemical activation of certain metals such as titanium. This technique offers a great deal of potential for galvanoplastic electroforming parts from metals and intermetallic compounds which as of this writing can only be formed mechanically with great difficulty, or not at all. This category includes the high temperature resistant metals which are also generally rather brittle, such as molybdenum, Mo, and tungsten, W, the platinum metals iridium, Ir, and rhodium, Rh, and intermetallic compounds such as zirconium diboride [12045-64-6], ZrB_2, and titanium diboride [12045-63-5], TiB_2 (see Refractories; Refractory coatings; Tool materials).

The most common fused salt baths are complex mixtures of alkali chlorides, rigorously purified and dried. Fused salt plating must be done under an inert atmosphere. Often argon is used because nitrogen can react with some metals. Inert anodes, eg, Pt-coated titanium or graphite, are used and the plating metal is supplied by additions of an appropriate metal salt.

Diffusion coatings of metals can be applied in the same type of fused salt bath, except without an electric current. The parts are suspended in the molten salt bath containing a metal salt. The metal ions react with the metal surface of the part, are reduced to metal, and diffuse into the bulk metal. One bath for chromizing uses a mixture of 40 mol % each of NaCl and KCl, and 20 mol % $CrCl_2$. Chromium carbides form in the same way as in pack diffusion chromizing. Many other molten baths have been tested or proposed, including baths based on borax, boric acid and other salts, molten calcium, and molten lead. In each case the coating metal has at least 0.1–1 wt % solubility in the molten bath in order to form rapid coatings (30).

1.3.3. Plating from Nonaqueous Solvents

Metals which are more electrochemically active than water usually cannot be plated from an aqueous solution. There are a few exceptions, such as zinc, where special factors allow plating. Aluminum has been the subject of the most research and application, although almost any metal could be plated from nonaqueous solutions. In general, aqueous solutions are both easier and cheaper to use if there is a choice. The solutions used for aluminum plating have to be oxygen free. These are usually mixtures of an aromatic molecule such as benzene or xylene, and anhydrous aluminum chloride as the metal source. Other chlorides such as ammonium or sodium chlorides are added to give sufficient electrical conductivity. The resultant coatings of aluminum are identical to other plated coatings. Hot dip and vapor or sputtered aluminum are less expensive, but electroplated aluminum may be useful for heat-sensitive or special substrates.

Nonaqueous electrolyte systems typically have a larger voltage window of solvent stability thus there is a greater flexibility in selecting cell operating voltages. Also, salts do not hydrolyze and solute selection is simpler. Nonaqueous electrolytes generally do not react with the substrates that react with water, and can be used when water-reactive metals need to be coated with metals normally deposited from aqueous solutions. The coating of uranium with zinc, tin, or nickel is an example of such an application. Even though aqueous electrolyte systems for electrodepositing these metals exist, the aqueous systems do not provide adequate adhesion.

Organic–solvent-based electrolytes have the advantage that a wide variety of complex ions can exist in solution. Metal–solvent complex formation should not be too strong, however, because although there is sufficient conductivity, deposition may not occur. Examples of generally unsuitable solvents, including those containing acidic hydrogen, are alcohols, ketones, acid anhydrides, amines, and amides.

Disadvantages associated with some organic solvents include toxicity; flammability and explosion hazards; sensitivity to moisture uptake, possibly leading to subsequent undesirable reactions with solutes; low electrical conductivity; relatively high cost; and limited solubility of many solutes. In addition, the electrolyte system can degrade under the influence of an electric field, yielding undesirable materials such as polymers, chars, and products that interfere with deposition of the metal or alloy.

Some inorganic nonaqueous solvents can be used in systems operable at near room temperature, eg, thionyl chloride; others, however, require special handling, eg, liquid ammonia, which must be used below its boiling point of -33°C in a thermally insulated container and in an inert atmosphere.

1.3.4. Brush Plating

A modified electroplating process, done without immersing the part in a plating tank, is called brush plating. Typically, the part is connected to a direct current source as the cathode. A highly concentrated, pH-buffered plating solution is soaked into a saturated pad attached to an insoluble anode. The pad is rubbed over the surface of the part, often while pumping additional solution over the contact area. Metal deposition occurs quickly owing to the concentrated solutions, high current densities, and high agitation at the contact area. Brush plating is useful in repairing nicks in printing press rollers or hydraulic cylinders without disassembling the machines. All platable metals can be applied by this process (3).

1.4. Electroless Plating

The metallizing process known as electroless plating (qv) is mainly used for deposition of copper on plastics and for nickel–phosphorus alloy on plastics and metals. A smaller amount of nickel–boron, nickel–copper–phosphorus, palladium–boron, palladium–phosphorus, silver, gold, and gold–boron alloys are deposited. Formaldehyde (qv) is the most common copper reducing agent, giving pure coatings. Sodium hypophosphite is the agent mainly used for electroless nickel. An unusual nickel–phosphorus alloy or solid solution is formed. Unlike electroplating, electroless plating can be used on almost any substrate, metallic or nonmetallic. Often electroless plating is used as the first coating to make glass (qv), ceramic, or plastic conductive, followed by conventional electrolytic plating (10, 31–34).

Improvements in this process include electrolytic regeneration for life extension of chromic–sulfuric acid baths used for etching plastics, and alkaline permanganate baths used for etching printed circuit board plastics prior to electroless plating. An initial immersion zinc coating called a zincating bath is used to prepare aluminum for electroless nickel plating. Noncyanide zincates are available. Specially formulated inexpensive electroless nickel strike baths are used to dissolve off the zincate layer and deposit an initial thin nickel layer. The rinsed parts are then placed in the full build electroless nickel bath, which has greater life and better deposit properties owing to elimination of zinc contamination. The inexpensive strike bath is replaced frequently. Newer electroless nickels have improved bath life, tolerance to impurities, and corrosion resistance. Electroless nickel composite coatings are becoming more common. Almost any particulate material can be incorporated into an electroless nickel coating, from fluoropolymers for increased lubricity, to silicon carbide for increased wear resistance. Electroless nickel is used to coat diamonds for better adherence to the bulk material when fabricated into grinding tools.

Many electroless coppers also have extended process lives. Bailout, the process solution that is removed and periodically replaced by liquid replenishment solution, must still be treated. Better waste treatment processes mean that removal of the copper from electroless copper complexes is easier. Methods have been developed to eliminate formaldehyde in wastewater, using hydrogen peroxide (qv) or other chemicals, or by electrochemical methods. Ion exchange (qv) and electrodialysis methods are available for bath life extension and waste minimization of electroless nickel plating baths (see Electroseparations, electrodialysis).

1.5. Immersion Plating

A simplified aqueous metal deposition process which does not use electric current, immersion plating, works only when a metal of higher electromotive force, such as copper, is deposited on a metal of lower electromotive force, such as iron or aluminum. The coatings are typically very thin and porous. This process is not often used for applications where durability is important unless the product is overcoated using a protective transparent film. One important application is immersion plating of copper from a copper sulfate bath onto steel wire, to use as a drawing agent. After drawing the steel wire, the copper is redissolved and reused. Zincate solutions are commonly used to apply an initial zinc layer on aluminum film prior to electroless nickel plating. These zinc coatings are dissolved by the electroless nickel plating solution, which immediately plates a thin nickel layer on the clean, oxide-free aluminum. This process gives improved adhesion and corrosion resistance of the electroless nickel deposit. Very thin immersion gold deposits are used for inexpensive jewelry (3).

1.6. Miscellaneous Techniques

Lasers (qv) have been used for both electroless and electrolytic plating. A semiconductor illuminated through a plating solution by a laser beam emits electrons which reduce dissolved metal ions to the metallic form. Whereas electroless plating solutions can also be illuminated, the heat of the laser beam alone can cause initiation of metal deposition by forming catalytic nuclei of the metal. High intensity light has, however, been used to inactivate electroless plating catalyst, to allow selective plating.

Selective dissolution has been used from ancient times to give the appearance of a thin plated coating of precious metal. A copper alloy containing some gold or silver can have part of the copper surface layer dissolved by weak acids, after which the item can be burnished or buffed to give a dense, rich appearing coating. More recent uses include pack aluminizing on nickel to form the NiAl [12003-78-0] intermetallic. The aluminum is then removed with caustic to form a very high surface area coating of nickel which can be used like Raney nickel in catalyst applications. The advantage is that foils or screens can be made and then partially converted to the catalyst.

Mercury layers plated onto the surface of analytical electrodes serve as liquid metal coatings. These function as analytical sensors (qv) because sodium and other metals can be electroplated into the amalgam, then deplated and measured (see Electroanalytical techniques). This is one of the few ways that sodium, potassium, calcium, and other active metals can be electroplated from aqueous solution. In one modification of this technique, a liquid sample can be purified of trace metals by extended electrolysis in the presence of a mercury coating (35).

2. Gas-Phase Metallizing Techniques

2.1. Metal or Thermal Spray Coatings

There are several ways to provide a metal film on a plastic part through the use of atomized metal at atmospheric pressure. Thermal spray, metal spray, or metallizing are common names for a group of processes for depositing metallic and nonmetallic coatings. These specific processes include plasma arc spray, flame spray, laser spray, and electric arc spray, depending on the energy input source. Rods, wires, and powders are used as coating material sources. Typically the coating material is melted, then atomized and forced onto the prepared substrate by a high velocity gas stream. Bonding is most often simply mechanical. The coating particles freeze interlocking on the roughened substrate surface. Some localized diffusion and alloying can also occur. Thermal spray metal and ceramic coatings have diverse properties suitable for numerous applications including corrosion resistance, eg, zinc and aluminum, especially against oxidation or salt water corrosion; high temperature oxidation, eg, nickel, cobalt, and chromium alloys; electrical conductivity, eg, radio frequency interference (RFI) shielding by zinc or tin on nonconductors; electrical resistance, eg, insulating layers in induction heating coils and high temperature strain gauges; wear resistance, eg, chromium–nickel–boron alloys and carbide-containing coatings; catalytic surfaces; nuclear moderators; and dimensional buildup for salvaging worn metal parts (17, 36–39).

A great advantage of zinc arc spray is that it can be applied to almost any plastic. The most common alternative technique, electroless plating, is normally only useful on plastics such as acrylonitrile–butadiene–styrene (ABS), polyphenylene oxide, epoxy, polycarbonate, and ABS–polycarbonate alloys, which can be chemically etched to improve the adhesion of deposited metals. Thermoset plastics rarely present a problem when spray metallization is used as long as the application temperature is below the heat-distortion temperature of the plastic. Excessive metal temperature can cause surface degradation, giving poor adhesion. Thermoplastic materials are more difficult to coat. The surface temperature should rise as little as possible to prevent warpage. Even sensitive thermoplastics such as foamed polystyrene can be acceptably coated with molten zinc using sufficient care. The adhesion of the zinc coating to the plastic surface is relatively poor. The plastic parts are sandblasted to provide a more adherent surface or are given a special primer coat that promotes adhesion.

Zinc arc spray, also suitable for prototypes and small lots of materials, is less suited for very small parts and parts having blind holes or complex interior surfaces, or where warpage is a problem. Zinc flame spray is normally applied to a thickness of 0.05–0.10 mm which can lead to appreciable weight gains on a large complex part such as a high speed printer or computer cabinet. Large numbers of parts and small parts are often best metallized by other processes because zinc arc spray is a slow, manual, serial coating process. The coating itself is brittle and can flake off when rubbed or bent. For RFI shielding, zinc coating is normally applied only to the part interior.

Application of an adhesion-promoting paint before metal spraying improves the coating. Color-coded paints, which indicate compatibility with specific plastics, can be applied at 20 times the rate of grit blasting, typically at 0.025-mm dry film thickness. The main test and control method is cross-hatch adhesion. Among the most common plastics coated with such paints are polycarbonate, poly(phenylene ether), polystyrene, ABS, poly(vinyl chloride), polyethylene, polyester, and polyetherimide.

2.1.1. Health and Safety

Zinc arc spraying or flame spray equipment is hardly more hazardous than a welding torch, and only safety goggles and gloves are required. Safety aspects emphasize reduction of noise and vapor inhalation. The gas flow through the jet is nearly at supersonic speed, and because of the high noise level, ear protection is required. The operator normally uses a positive-pressure fresh-air breathing helmet or a full-body protective covering having an integral air supply to eliminate exposure to toxic zinc fumes. Spraying must be done in a high velocity hood, ie, minimum 92 m/min. Metal dust is easily filtered out in a wet or dry collector to eliminate pollution.

Thermal spray processes can be used to give coatings of chromium carbide or nickel chromium for erosion resistance, copper nickel indium for fretting resistance, tungsten carbide cobalt for wear and abrasion resistance, and even aluminum silicon polyester mixtures for abradability.

2.1.2. Thermal or Flame Spray Process

The earliest experiments in metal spray used molten metal fed to a spray apparatus, where it was dispersed by a high speed air jet into tiny droplets and simultaneously blown onto the surface of the part to be covered. The metal solidified on contact. Modern processes use a more convenient source than premelted metal. Spray heads using a flame or an electrical arc to melt metal wires or powders directly are much more convenient. These are the only types used on a large scale in the United States.

Flame spray utilizes combustible gases such as propane, acetylene, and oxygen–hydrogen mixtures as the heat source to melt the coating material. The spray head contains orifices for the flammable gases in addition to the compressed gas used to blow the molten metal on the surface of the part. The sprayed materials can be used in either rod, wire, or powder form. Flame sprayed coatings exhibit lower bond strength, higher porosity, a narrower working range, and higher heat transmittal to the substrate than coatings obtained by other spray methods. However, this process also has low capital investment, high deposition rates, and high efficiency of deposition, plus relatively low costs of maintenance.

Surface cleanliness of the substrate is important for all thermal spray processes. Degreasing, which formerly often relied on freons or chlorinated hydrocarbons, is done with less environmentally harmful solvents and aqueous cleaners. Surface roughening, commonly used to increase adhesion, is done by rough threading and grit blasting using alumina, sand, crushed steel, or silicon carbide. Thorough cleaning to remove particulates follows grit blasting. The as-sprayed parts are usually rough and porous, requiring some type of finishing treatment which may consist of low viscosity epoxy coating, painting, machining, lapping, or polishing.

A modification of thermal spray processes is the flame spray and fuse in which the coating material is fusible and self-fluxing, requiring post-spray heat treatment. Fusible self-fluxing coatings are typically nickel or cobalt-based alloys which use boron, phosphorus, or silicon, singly or in combination, as melting point depressants and fluxing agents. Spraying is followed by fusing of the surface using flame or torch, induction, or vacuum, inert or hydrogen furnaces. Fusing is usually done between 1010 and 1175°C. These coatings can have very good wear resistance. The hardness can be as high as 65 HR_c (Rockwell hardness) and the wear resistance can be further improved by incorporating tungsten or chromium carbide particles into the alloy powders. These coatings are fully dense, have close-packed crystal lattice, and exhibit good metallurgical bonds. There is a limitation on the substrates to those which can tolerate the high fusing temperatures. The temperature of the part being coated is controlled by the application rate.

Another modification is the detonation gun process, in which mixtures of oxygen and acetylene are exploded in the combustion chamber. Metal powers are metered into the chamber. The shock wave of the supersonic explosion (2770 m/s) propels the powders to a speed of up to 770 m/s. The 3000°C combustion gases also heat the particles. Bond strength is exceptionally high with low porosities. Most coating materials are oxides or carbides (qv), plus bonding materials of Co and NiCr. Disadvantages of this process include line of sight coating, the danger of the high speed particles, and the explosions, which require soundproof enclosures and remote operation. The detonation gun process is one of the most expensive of the spray coating processes, but coating life can outlast conventionally sprayed coatings by up to eight times.

Flame spray metallizing is widely used for the protection of metal against corrosion, especially for *in situ* protection of structural members. The principal metal used for spraying of plastics is zinc. Aluminum

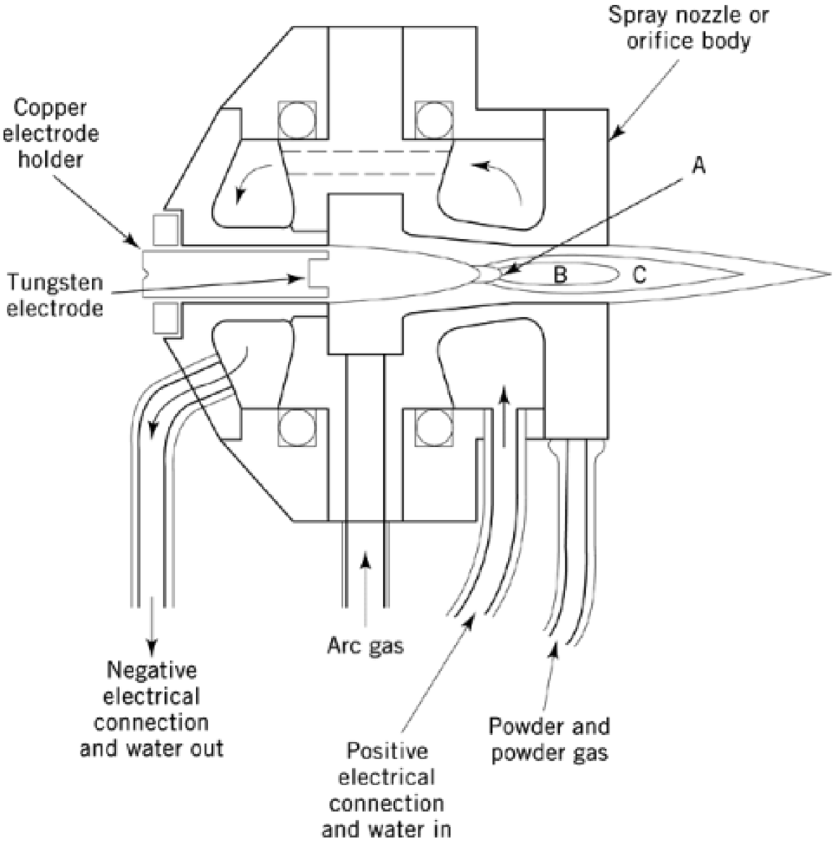

Fig. 3. A plasma arc spray gun where approximate plasma temperatures are A, 7,800°C; B, 10,000–13,000°C; and C, 7,800–10,000°C.

and copper are also used. If the distance from the part is too great, the zinc solidifies before it touches the part and adhesion is extremely poor. If the molten zinc oxidizes, conductivity and adhesion are poor. If the distance is too short, the zinc is too hot and the plastic warps or degrades. These coatings are not as dense as electrically deposited coatings because of numerous pores, oxide inclusions, and discontinuities where particles have incompletely coalesced.

2.1.3. Arc Spray Process

The least expensive among the thermal spray processes is the electric arc spray process which uses metal wires as spray materials. A plasma, an excited gas, consisting of equal amounts of free electrons and positive ions (see also Plasma technology) is formed by ionizing a primary gas, usually argon or nitrogen, using the electrical discharge from a high frequency arc starter. Two electrically isolated zinc or other metal wires connected to a high voltage transformer are slowly fed into a central chamber where an arc is formed at their intersection. A secondary gas such as nitrogen, helium, or hydrogen can be added to produce higher temperatures at lower power level. Once initiated, plasma can conduct currents as high as 2000 A d-c, at potentials of 30–80 V. A high velocity stream of compressed air simultaneously pushes the vaporized zinc out of the chamber and onto the surface of a part. A typical plasma arc spray gun is shown in Figure 3.

Process variables that must be controlled include the power level, pressure, and flow of the arc gases, and the rate of flow of powder and carrier gas. The spray gun position and gun to substrate distance are usually preset. Substrate temperature can be controlled by preheating and by limiting temperature increase during spraying by periodic interruptions of the spray.

Modified processes represent improvements in capability and quality in respect to the conventional process. By applying a secondary current through both the plasma and substrate, the transferred plasma arc process enables heating and melting of the substrate surface. This promotes improved metallurgical bonding, higher coating density, higher deposition rates, and higher coating thicknesses per pass. In another modification, inert atmosphere chamber spraying confines hazardous materials and restricts the formation of oxides which occur in open air spraying. Inert atmosphere spraying in a low pressure chamber has additional advantages including increase of the bond strength because higher substrate temperatures allow the coatings to diffuse into the substrate minimizing environmental problems such as dust and noise, created by the very high speed of the atomized coating materials. If an enclosed atmosphere is used, provision must be made for cooling and gas expansion. An alloy can be deposited by using alloy wires or two dissimilar wires, the only limitation being that ductile electrically conductive wires can be used. Among the advantages of this process are high bond strength, no need for an external heat source, low substrate heating, low electrical power requirements, and no need for expensive combustible gas. The operator should wear a protective suit with an independent breathing air supply.

Nickel–aluminum has been used for parts repair. Complex alloys of chromium, aluminum, yttrium, and another metal can be applied for oxidation and corrosion resistance. Before spraying, the part must be cleaned of oil and dirt. Standard aqueous or solvent cleaners are sufficient. Molded surfaces must be coated with a special paint to promote metal adhesion or blasted with fine aluminum oxide grit of 250–177 μm. Use of iron grit may lead to staining of the surface. Grit blasting is difficult to automate, and manual blasting may give quality control problems because there is little change in appearance after the operation. Arc spray coating must follow the grit blasting as soon as possible or blasting must be repeated.

Zinc arc spraying is an inexpensive process in terms of equipment and raw materials. Only 55–110 g/m^2 is required for a standard 0.05–0.10 mm Zn thickness. It is more labor intensive, however. Grit blasting is a slow process, at a rate of 4.5 m^2/h. Application of an adhesive paint layer is much quicker, 24 m^2/h, although the painted part must be baked or allowed to air dry. Arc sprayed zinc is applied at a rate of 9–36 m^2/h to maintain the plastic temperature below 65°C. The actual price of the product depends on part complexity, number of parts, and part size. A typical price in 1994 was in the range of \$10–32/m^2.

One large market for flame spray coatings on plastic is for radio frequency interference (RFI) shielding owing to concern expressed first in 1979 by the FCC for computerized equipment. Because of increasing pollution by or transmission of electromagnetic energy through the environment, insertion of a conductive shield between a part and the environment is often the cheapest and simplest way to eliminate RFI. Zinc arc spraying is an excellent method because of its high conductivity at normally applied thickness. Environmental pollution is minimal and only vaporized zinc particles need to be removed from the air.

2.1.4. Plasma Spray

The plasma spray is similar to arc spray coating, but the coatings of plasma spray are not limited to materials which can be fabricated as conductive wires. A controlled, low voltage arc is struck between a cooled tungsten cathode and a cooled copper anode. The plasma arc reaches temperatures up to 8000°C. The plasma consists of equal amounts of free electrons and positive ions. The plasma arc spray process produces the highest temperatures and particle velocities among the thermal spray processes. Argon, nitrogen, hydrogen, or other gases are fed through the arc, then past a powder feeder. Almost any powder, metallic or nonmetallic, can be used. The gas is so hot that tungsten, molybdenum, WC, and ceramics can be deposited. The porosity of these deposits may be high, but special techniques are available to increase particle velocity from 100–300 m/s up over 1200 m/s, giving denser deposits.

2.2. Carburizing and Nitriding

Several commonly used metallurgical surface treatments are applied by gas-phase reactions in a reducing atmosphere for carburizing, and in a nitrogen atmosphere for nitriding. These treatments are used to increase the surface hardness of ferrous alloys by diffusion of carbon and nitrogen at high temperature. As for all processes, good cleaning is necessary prior to treatment. Selective treatment can be done by electroplating cyanide copper onto the areas of the parts which are not to be hardened. The copper is an excellent barrier to carbon and nitrogen, and is easily removed after hardening (13, 14) (see Metal surface treatments, case hardening).

2.3. Pack Diffusion

Pack diffusion or cementation processes are similar to pack carburizing, and are used to coat iron, nickel, cobalt, and copper with chromium, boron, zinc (Sheradizing), aluminum, silicon, titanium, molybdenum, and other metals. It is possible to obtain a surface layer which contains 60% aluminum, but usual limits are 25% on iron-based alloys and 12% on nickel- or cobalt-based alloys. A pure aluminum overlay is never formed in this method, owing to the high temperature of the substrate, on which the deposited aluminum immediately alloys with the substrate. Aluminum is supplied in the pack diffusion process from pure aluminum powder or a ferroalloy powder, aluminum oxide, and an aluminum halide. Cleaned parts and the packing material react in a closed container at 820–1200°C, depending on the base metal, in a reducing atmosphere. The reaction deposits a high concentration of aluminum metal which subsequently diffuses deeply into the substrate. The concentration of aluminum is 50–60% immediately after coating, dropping to 12–25% after the diffusion cycle (18, 30).

Sheradizing is an old process which consists of heating cleaned iron parts in a mixture of zinc powder and zinc oxide diluent in a rotating furnace at 350–375°C for 3–12 hours. This diffused coating is $FeZn_7$ with some $FeZn_3$ at the higher temperature. Like most other diffusion coatings, the coating is microcracked but uniform providing excellent sacrificial corrosion protection of the steel. Sheradizing was formerly used widely on nuts, bolts, and washers, but has been largely replaced by electroplating and mechanical plating.

2.4. Chromizing and Related Diffusion Processes

Chromizing is similar to aluminizing. A thin corrosion and wear-resistant coating is applied to low cost steels such as mild steel, or to a nickel-based alloy. The pack contains chromium powder, alumina diluent, and an active transfer agent which gasifies at operating temperature, such as ammonium chloride. The pack is heated for about 24 hours at 950–1100°C to give a 150–200-μm thick chromized layer. If there is >0.3 wt% carbon in the steel, a chromium carbide coating forms on the surface. Chromizing is complicated because the Cr can diffuse rapidly in the grain boundaries, can form complex carbide phases, and can decarburize steel, changing its physical properties.

There is also a two-step process of chromizing followed by aluminizing. Above 900°C the chromizing begins to rediffuse and the protective oxide changes to Al_3O_3 from Cr_2O_3. Aluminum oxide is less volatile than chromium oxide and better for high temperature oxidation resistance above 1000°C.

In the related boronizing process, a thin boron alloy is produced for extreme hardness, wear, and corrosion resistance. The powder can be boron, boron carbide, or FeB. A chloride or fluoride salt is used as an activator, along with an inert diluent such as alumina or silicon carbide. The parts are heated to 800–900°C for 6–24 hours. Steel usually needs to be heat treated for strength after boronizing. FeB and Fe_2B form; the former is harder but more brittle. Most of the boronized layer is Fe_2B because of its lower solubility in iron. Plain steel achieves a boronized coating of up to 150 μm in 6 h, but alloy steels containing chromium or other refractory elements achieve only a 10-μm coating. Boronized coatings are much harder than nitrided or carburized coatings, and are unaffected by heating to 1000°C. The Vickers hardness of boronized coatings can be 1600–2000, compared to 600–900 for nitrided and 700–800 for carburized coatings (see Hardness).

Siliconizing is yet another process used especially for coating of the refractory metals Ti, Nb, Ta, Cr, Mo, and W (see Refractories). These metals form silicides which have a surface oxidation protection layer of SiO_2. Siliconizing is especially effective on molybdenum against air oxidation up to 1700°C.

2.5. Metals

Aircraft and space vehicles, turbine generators, and other such applications require high strength at high temperature along with excellent oxidation resistance. Superalloys, ie, complex nickel and cobalt-based alloys, and refractory metals, eg, niobium, tungsten, molybdenum, tantalum, and their alloys, are used for applications at temperatures above 1000°C. In many cases the coatings must be resistant both to oxidation and to hot corrosion by sulfidation from sulfur-bearing gases. Testing must be done to assure compatibility between the coatings and the substrate and to avoid undesirable solid-state reactions and interdiffusion, which can produce voids, cracks, and weak layers. Refractory metal coatings must be sufficiently ductile for the anticipated service and environmental pressures and stresses. All coatings must resist thermal cycling and mechanical forces without cracking (see also Refractory coatings) (22, 40).

Two types of coatings have been used for superalloys: diffusion coatings, in which a layer of nickel, cobalt, platinum, or palladium aluminide, ie, NiAl, CoAl, PtAl, or PdAl, is formed on the surface by diffusion; and overlay coatings, in which a complex coating material such as nickel–cobalt–chromium–aluminum–yttrium, NiCoCrAlY, is applied to the surface. Pack cementation is the most widely used process for applying diffusion coatings to superalloys, but brushing, dipping into, or spraying a prepared mixture of the coating elements followed by high temperature heating is also used. Physical and vapor deposition, plasma spraying, and sputtering are often used for applying the overlay coatings. Pack cementation, fluidized-bed deposition, and spray or dip-and-sinter processes are used for the application of silicide and aluminide diffusion coatings to refractory metals (40, 41).

2.6. Miscellaneous Methods

Powdered metals such as aluminum, chromium, nickel, and copper, along with various alloys, can be applied to parts by electrostatic deposition. The metal strip containing the attached powdered metal must be further processed by cold rolling and sintering to compact and bond the metal powder.

The laser spray process uses a high power carbon dioxide laser focused onto the surface of the part to be metallized. A carrier gas such as helium blows metal particles into the path of the laser and onto the part. The laser melted particles may fuse to the surface, or may be incorporated into an alloy in a molten surface up to 1-mm thick. The laser can be used for selective alloying of the surface, for production of amorphous coatings, or for laser hardening.

3. Vacuum-Phase Metallizing Techniques

Vacuum-phase metallizing techniques all depend on the use of a vacuum as part of the metallizing process (see Vacuum technology). The tonnage of metal deposited by these techniques is insignificant compared to hot dip galvanizing or plating, and the total surface area metallized is much less than that done by plating. However, the economic added value of vacuum metallizing probably exceeds either plating or galvanizing because of the extremely rapid growth and deep market penetration of semiconductor devices. In 1994, the growth rate for all of these devices was 10–15% and projections call for at least a 10% compounded annual growth rate into the twenty-first century. The state of the art in vacuum metallizing is in semiconductors (qv).

The largest value added industry which uses metallizing is by far the semiconductor industry. In terms of total metals usage, this industry is almost insignificant, but the effective value of the metals used is enormous. Almost all metals used in the semiconductor industry are small-volume, superpure, and extremely costly grades. One 200-mm silicon wafer, when fully utilized to fabricate a technologically demanding multilevel chip, such as the Pentium, may be worth up to $250,000. The total amount of metallic and nonmetallic elements used for metallizing the wafer is ca 0.25 grams.

Semiconductor manufacturing facilities are large and expensive. A modern plant doing 0.5-μm device manufacturing on 200-mm silicon wafers may cost > $1 billion to install. Semiconductor manufacturing uses a variety of vacuum deposition processes resulting in the semiconductor chip. Multiple layers of metal give a three-dimensional circuit in microscopic patterns. The next generation of semiconductor plants are expected to use 300–400-mm wafers at 0.35-μm device size and further shrinkage is in development (16, 42–45) (see Integrated circuits).

3.1. Thermal Evaporation

Thermal evaporation is done in a high vacuum to minimize chemical side reactions of the evaporated active metal. The vacuum is necessary because almost any metal reacts with oxygen, water vapor, or nitrogen to form brittle nonmetallic inclusions. Some metals even trap inert gases as the metal is deposited. The metal to be deposited is simply heated in a vacuum to a high temperature to increase its vapor pressure. The vapor deposits on any cold object in the chamber. The rate of deposition depends on the heat input but is normally faster than sputtering. The evaporated molecules travel in straight lines owing to the low pressure, so only line of sight coverage is achieved. This method is difficult to use on temperature-sensitive substrates such as plastics, except when formation of very thin films of metals is required. Adhesion can be marginal unless the object can be heated to about 400°C to remove residual moisture.

Thermal evaporation is inexpensive and efficient. It is used for low cost items such as aluminized plastic sheet and decorative Christmas tinsel, second surface coating of transparent plastic auto parts, and metallization of glass and ceramics (qv). Aluminum is the predominant metal used. Color effects such as gold or brass are achieved by applying a dyed translucent organic protective coating over the aluminum. Variants of this process use different methods to impart the thermal energy. These include electron beam vaporization and laser evaporation.

3.2. Sputtering or Glow Discharge

Sputtering can be done using both conductive and nonconductive items. A low pressure atmosphere of argon is used in the deposition vessel. The depositing metal becomes the cathode with a high potential; the metal item is the anode. Alternatively, specially designed anodes allow deposition on nonconductive plastics. Argon becomes ionized and is accelerated into the cathode at a high speed. The energy is transferred to the target metal atoms, which are sputtered off and deposit on the part to be coated. This method gives excellent coating adhesion and more consistent coatings than simple vacuum deposition. It can also be applied to a wider range of materials, including complex metal alloys and oxides. The equipment and operating costs are higher than vacuum deposition, and deposition rates are lower.

Reactive sputtering is a variation in which two or more deposition sources are used. This process can be used to give compounds such as silicon carbide on the surface. Titanium nitride [25583-20-4], TiN, can be applied to aluminum to increase wear resistance, especially sliding resistance. In a related process, a magnetron discharge is used to give higher deposition rates and less radiation damage. This is preferred for thermally sensitive substrates.

3.3. Chemical Vapor Deposition

This process is distinct from simple thermal evaporation because chemical vapor deposition (CVD) depends on a chemical reaction at the surface of the part and in that way is analogous to electroless plating. This process uses a gas of one or more chemical species, which react at a heated substrate to form an appropriate film. The film can be metallic, nonmetallic, single element, or compound. The reactions occur at 500–1500°C on the part to be coated, so temperature-sensitive materials cannot be used. Another variant is plasma-assisted chemical vapor deposition, which can use a lower processing temperature of near 300°C. The film-forming reactions can be disproportionation, reduction, displacement, or chemical reaction with formation of a compound. Among the coatings available are copper and aluminum conductors, diamond and tantalum oxide dielectrics, lead zirconium titanate piezoelectrics (qv), and bismuth strontium calcium cuprate superconductors (see also Electronics, coatings; Thin films, film formation techniques). Some of the largest applications are for coating TiC and TiN on cutting tools (2, 46).

3.4. Ion Implantation

Also known as ion plating, ion implantation (qv) is a high vacuum process for modifying the surface properties of any material. The equipment consists of an ion source, where an electrical discharge in a low pressure gas ionizes the chemical to be implanted. The ionized atoms are fed into a low pressure ion accelerator tube where they receive sufficient energy to penetrate the target item. The energy imparted to the ionized atoms can be closely controlled over a range of about $100 - >3000$ keV or 5–200 keV for semiconductor manufacturing, allowing penetration to a controlled and reproducible depth. Typical implantation of metal ions is to a depth of several tens of nanometers. This is a surface modification technique rather than a surface coating technique. Semiconductors are commonly modified using this technique, because ion implantation can be done using total or imagewise scanning of the beam over the surface. Nitrogen, chromium, and phosphorus can be used to harden metals and increase the corrosion resistance. Metastable alloys can be produced that are difficult to make by other processes. For example, niobium can be implanted into 316 stainless steel to improve its corrosion resistance (47–49).

3.5. Laser Hardening and Modification

Lasers are used to surface harden ductile steels and improve the toughness to a depth of 0.35 mm or more. The very rapid melting and freezing acts as an extremely quick quench process. Lasers can also be used to bond solid or powder coatings to a surface. The surface layer is melted and mixes with the substrate extremely quickly. Typical coatings are nickel or titanium carbide on iron, and nickel, cobalt, manganese, and titanium carbide [12070-08-5], TiC, on aluminum. Use of lasers with other specialized coating methods is common. Thermally sprayed coatings of Stellite, Co–Cr–WC, on stainless steel, 1 Cr–18 Ni–9 Ti, eliminate porosity, improve chemical homogeneity, increase the coating strength, and develop a better metallurgical bond.

3.6. Miscellaneous

Electron beams can be used to decompose a gas such as silver chloride and simultaneously deposit silver metal. An older technique is the thermal decomposition of volatile and extremely toxic gases such as nickel carbonyl [13463-39-3], $Ni(CO)_4$, to form dense deposits or dendritic coatings by modification of coating parameters.

In contrast to the older techniques, a newer method is to use a scanning tunneling electron microscope to deposit metal coatings in microscopic images as small as 0.001 μm. The ultimate surface metallization techniques allow deposition of metals atom by atom in controlled three-dimensional arrays.

4. Metallizing by Direct Physical or Thermal Bonding

Direct bonding techniques are among the oldest types of metallizing, and the most versatile. Applications for extremely thin films of gold foil range from ancient funerary decorations and medieval manuscripts to coatings of the roofs of many U.S. statehouses. Many methods depend on heat or pressure and an adhesive layer to glue the coating to the substrate. Methods for metallizing on a metallic surface often depend on removal or displacement of a preexisting surface oxide layer. Many metals form intermetallic alloys or self-diffuse into one another even at room temperature, but the surfaces in contact must be clean and oxide free.

4.1. Lamination

The most commonly used process for application of metals to nonmetals is that of lamination (see Laminated materials, plastics). One large-volume process involves the production of continuous lengths of copper foil by electrodeposition on a rotating polished cylindrical stainless steel mandrel. This gives one very smooth surface, and one surface which is microroughened for attachment to the substrate. The copper foil is the subject of numerous specialized treatments, some of which involve applying tin, bronze, or chromate treatments to one or both sides of the foil. A more recent development is the selective micronodularization of the exposed surface of the foil prior to removal from the cylinder. These foils are laminated under high pressure to epoxy–glass, polyimide–glass, or phenolic sheets to serve as the raw material for printed circuit boards, which can have as few as one layer, or greater than 40 layers of copper and insulator. Copper is also laminated to ceramics for high temperature printed circuit boards.

Die cut metal laminates are also applied to plastics for decorative effects, or for radio frequency interference shielding. These laminates are formed by vacuum deposition, or by attachment of foil to a plastic layer for easier handling. Multiple layer composites of plastic and aluminum are used for specialized packaging, especially for moisture or gas barriers.

Zinc foil coated with a conductive, pressure-sensitive adhesive is used for repair of other zinc coatings or for imparting corrosion resistance at field sites. The 0.08-mm zinc tape or sheet has a 0.025-mm conductive adhesive. The laminate is cut to size and pressed tightly to activate the adhesive. Conductive tape can be wrapped around pipe, especially around welds or connections. The corrosion resistance of this material is intermediate between galvanized or thermally sprayed coatings and zinc-filled paints (21, 50).

4.2. Mechanical Plating

Impact or peen plating is a mechanical process whereby the metal powder is compacted and welded to parts by mechanical energy. This process is limited to relatively small parts of no more than about one kilogram. The parts are placed in a specially designed barrel along with water, metal powder sized at 3–10 μm, glass impact beads of several sizes, and various promoter chemicals. The metal particles are plastically deformed by the impact of the glass beads, bonding to the continuously cleaned metal parts. Ductile metals and alloys can be applied by this process. Sequential layers of different metals can be prepared, and mixed co-deposits of metals difficult to prepare by other methods such as cadmium–zinc deposits can easily be made. Among the metals useful with this process are zinc, cadmium, lead, aluminum, silver, indium, gold, tin, copper, and brass. Rate of increase in coating thickness is almost independent of the plating time, but is governed by the amount of metal powder added. The coatings can be semibright but do not have the full brightness of electroplated coatings.

This process is especially suitable for high strength steels because there is no hydrogen embrittlement. The coating corrosion resistance can be as good as or better than that from hot dip galvanizing or electroplating (3).

4.3. Slurry Coatings

Many types of slurry coatings are used, including metal-filled paints and metal–glass frit compositions. Zinc-filled paints contain more metal powder by weight than organic binder so are electrically conductive. These are used as inexpensive sacrificial coatings in place of hot dip galvanizing. Aluminum, copper, stainless steel, and brass-filled paints are also common. Many of these paints are used in RFI shielding applications on plastic computer casings to reduce electrical interference (21, 51).

Metal powder–glass powder–binder mixtures are used to apply conductive (or resistive) coatings to ceramics or metals, especially for printed circuits and electronics parts on ceramic substrates, such as multichip modules. Multiple layers of aluminum nitride [24304-00-5], AlN, or aluminay ceramic are fused with copper sheet and other metals in powdered form. The mixtures are applied as a paste, paint, or slurry, then fired to fuse the metal and glass to the surface while burning off the binder. Copper, palladium, gold, silver, and many alloys are commonly used.

There are several types of slurry or powdered paint methods for coating high temperature processing equipment in the chemical and petroleum industry, and for turbine blades. These last are used for aircraft and power generation (qv) and are exposed to high temperature corrosive gases. The process consists of cleaning, sand blasting, and acid pickling parts, then applying a slurry by dipping or spraying. The parts are dried at 120°C and fired to 930–1200°C. The coating and blasting slurries are made of an aluminum source, eg, pure aluminum powder or 5–12% silicon–aluminum alloy; a vehicle, water or an organic solvent; a clay or gum binder; and an inert material such as alumina or a ceramic oxide. The thickness of the coating depends mostly on the substrate and the firing temperature, with a lesser effect from the time at temperature. For chromium stainless steels the thickness of the diffusion layer increases with the temperature. Nickel and cobalt alloys decrease the diffusion rate of aluminum in alloys owing to the stability of the intermetallic compounds NiAl, Ni_3Al, CoAl, and Co_3Al and the low solid solubility of aluminum in nickel and cobalt. This limits the attainable thickness of the diffusion layer in nickel and cobalt alloy steels.

Specialized alloys are used for high temperature applications on turbine blades, furnace parts, thermocouples, etc. These coatings can be as simple as iron–silicon–chromium or as exotic as chromium–aluminum–hafnium (36, 41, 52).

4.4. Roll Bonding or Strip Roll Welding

Roll bonding, also known as strip roll welding, was originally applied for fabrication of bimetallic strips for thermostats. It later found application in jewelry, cladding copper coins with cupronickel alloy, forming electrical contacts, conductive springs, cookware, electromagnetic shielding, underground cable wrappings, etc. An especially important application is in production of roll bonded heavy plate and sheet for process vessels in chemical plants, and in shipbuilding. The latter uses a 90:10 copper–nickel alloy cladding for resistance to fouling by marine organisms.

Clad strips are produced by continuous rolling, during which the bond is achieved by pressure welding. The process is relatively simple, but the requirements for surface preparation are strict. Wire brushing is the most commonly used method for surface preparation which is done just prior to rolling. Welding is usually accomplished in a single rolling pass. Subsequent heat treatment may be applied to the strips in order to improve mechanical properties and/or corrosion resistance. Almost all combinations of ductile metals and alloys can be clad by roll welding. However, oxides of some metals make the process difficult. Certain combinations of metals may suffer from formation of intermetallic compounds. The most common combinations of cladding by strip roll welding are copper to steel, nickel, and gold, aluminum to aluminum alloys, tin to copper and nickel, and gold to nickel.

Skiving is a variant in which the base metal surface oxides are mechanically removed followed immediately by pressure rolling of a precious metal or alloy strip. This is commonly used for inlays for electrical contacts and for jewelry fabrication. The common inlay materials include gold, silver, copper, brass, and solder. No heat is needed, and the coating is applied only to designated areas so there is little waste (3, 50).

4.5. Miscellaneous Processes

Metal strip for cladding can be produced by cold pressing metal powder into a low density green strip, followed by sintering to compact the powder. Alloy powders can be made into strip, along with specialized strip with one powder bonded to a different powder on the opposite side.

Explosive bonding uses the energy of an explosion to drive two metals together (see Metallic coatings, explosively clad). The energy dissipated at the juncture of the metals dissociates or disperses oxides and provides a clean metallurgical joint. This process is economically attractive because no expensive furnaces, presses, and other capital equipment is needed. This process is especially suitable for metals that are reactive with oxygen and/or nitrogen, such as titanium, tantalum, stainless steels, and aluminum. It can be done with metals having a wide difference in melting points, such as aluminum (660°C) and tantalum (2996°C). The metals to be bonded must not be brittle because these materials fracture during the explosion. As little as 5% tensile elongation can be sufficient.

5. Environmental Concerns

Each type of metallic coating process has some sort of hazard, whether it is thermal energy, the reactivity of molten salt or metal baths, particulates in the air from spray processes, poisonous gases from pack cementation and diffusion, or electrical hazards associated with arc spray or ion implantation. Vacuum or inert gas operations can produce flammable dusts or powders when opened for cleaning. Most of the hazards are confined to the operator and immediate environs in the operating plant. OSHA is the primary regulator of these hazards in the United States, although many local and state agencies, especially fire departments, also regulate coatings plants. Adequate training, documentation, and protective equipment are the minimum requirements. Many companies use worker–management teams, suggestion boxes, consultant surveys, supplier training sessions, and other methods to reduce risk of injuries (see Hazard analysis and risk assessment). The principal regulatory burden falls on wastes and discharges which leave the plant (3, 53, 54).

The U.S. EPA regards metallizers such as platers, surface finishers, and printed circuit board producers as among the most important point source polluters for metals. Whereas there has been some directed growth to inherently nonwater polluting processes such as vacuum metallizing, as of this writing most metal coatings are still applied by traditional processes. Much production of electroplated items has, however, shifted from the United States to less environmentally stringent countries.

The surviving U.S. plants have embraced all types of waste treatment processes (see Wastes treatment, hazardous waste; Wastes, industrial). The most desired pollution prevention processes are those which reduce the total amount of waste discharged. Treatment and disposal are less strongly emphasized options. Zero wastewater discharge facilities and water recycling processes are becoming more common (55, 56).

Some metals used as metallic coatings are considered nontoxic, such as aluminum, magnesium, iron, tin, indium, molybdenum, tungsten, titanium, tantalum, niobium, bismuth, and the precious metals such as gold, platinum, rhodium, and palladium. However, some of the most important pollutants are metallic contaminants of these metals. Metals that can be bioconcentrated to harmful levels, especially in predators at the top of

Table 1. EPA Pretreatment Standards for Aqueous Discharge[a], [b]

Material, mg/L	Existing source, PSES[c] 1 Day	Existing source, PSES[c] 30 Days	New source, PSNS[c] 1 Day	New source, PSNS[c] 30 Days
cadmium	0.69	0.26	0.11	0.07
chromium, total	2.77	1.71	2.77	1.71
copper	3.38	2.07	3.38	2.07
lead	0.69	0.43	0.69	0.43
nickel	3.98	2.38	3.98	2.38
silver	0.43	0.24	0.43	0.24
zinc	2.61	1.48	2.61	1.48
cyanide				
total	1.2	0.65	1.2	0.65
treatable	0.86	0.32	0.86	0.32
total toxic organics	2.13		2.13	

[a] Captive manufacturers performing metal finishing, including electroplating, discharging to POTWs (61).
[b] pH equals 6–10.
[c] Maximum value. PSES = pretreatment standards for existing sources; PSNS = pretreatment standards for new sources.

the food chain, such as mercury, cadmium, and lead are especially problematic. Other metals such as silver, copper, nickel, zinc, and chromium in the hexavalent oxidation state are highly toxic to aquatic life (37, 57–60).

Discharge limits vary between localities and among plants. Table 1 shows federal EPA maximum discharge limits for a number of metals for a new metal-finishing installation. These limits are for large captive manufacturers who discharge to a publicly owned treatment works (POTW). Limits vary according to the age and size of a plant and type of coating operation.

The waste discharge categories (Table 1) are regulated under the National Pollutant Discharger Elimination System (NPDES), a U.S. EPA program. Local municipalities are free to set more restrictive discharge limits. Typically mercury and arsenic are the most highly regulated, often at limits of 50 ppb for mercury and 150 ppb for arsenic, followed by lead, silver, and cadmium, which have discharge limits of <1 ppm (<1 mg/L). Hexavalent chromium, free and complexed cyanide, and copper are also highly regulated (3, 62).

Newer federal limits on metals content of sewage sludge combined with laws on fuller treatment of the sewage sludge and its allowed disposal methods have affected limits. The metallic content of sludges from municipal waste treatment facilities is becoming of great concern. High levels of cadmium and other metals may bioaccumulate when spread over cultivated fields. The U.S. EPA has put strict limits on the metals contents of such sludges, stating how much sludge may be added to fields, pastures, and forests. Zinc is being recognized as one of the most common nonpoint source metal pollutants. The great majority of this zinc comes from weathering of galvanized steel roofs, fences, and other items exposed to the atmosphere, although significant amounts may also come from zinc oxide pigments used in paints and tires. Copper is another common nonpoint source pollutant. Most comes from plumbing fixtures and piping.

Iron is commonly found as the toxic and difficult to treat ferrocyanide complex in plating waste streams, thus ancillary solution used to prepare surfaces or to complete the processes of metallizing surfaces can also be pollutants. Cleaners are significant sources of alkalinity, complexing agents, phosphates, grease and oils, particulates, surfactants, dissolved metals, suspended solids, chemical and biological oxygen demand, and total dissolved solids. Pickling solutions contribute strong acids and dissolved metals. Sandblasting, buffing, grinding, and polishing operations may produce a metal-laden hazardous solid waste. Passivating solutions contain chromates, dissolved metals, and acids. Fluxes often contain zinc and acids, plus dissolved or particulate lead, silver, and tin. Gaseous exhaust from flame spraying, sputtering, ion implantation, and other processes may be toxic, hazardous, flammable, or corrosive. Drosses from hot dipping, zinc or solder, may be a recyclable waste, but these are still hazardous. Even neutral salts can be of regulatory concern as more municipalities practice some type of sewage water recycle and reuse, especially for irrigation or groundwater replenishment (see also Groundwater monitoring).

Air pollution (qv) is recognized as a significant problem for coating facilities. Chromium emissions are tightly regulated to very low levels, based on the amount of electricity used. Hexavalent chromium is a known carcinogen. Trivalent and metallic chromium are of no special health concern. Many decorative chromium plating facilities have converted to the use of trivalent chromium plating baths, however there is no substitute for hexavalent chromium used for hard chrome plating applications.

Lead, a highly toxic and accumulative material, is also of concern especially with regard to children (53) (see Lead compounds, industrial toxicology). Lead, both from fume exposure during coating or melting, and from accidental ingestion from handling the metal or its salts, is problematic. Cadmium is another highly toxic and bioaccumulative metal that has been eliminated from use in many European countries. Its main continuing U.S. use is in military applications, aircraft electronics, and marine applications where it outperforms zinc coatings. Nickel can cause allergic reactions in many people, because the metal easily oxidizes to soluble salts.

The semiconductor industry uses significant quantities of metals combined in highly reactive and volatile compounds as sources for metallizing silicon wafers. These metals include organometallic or volatile inorganic compounds of aluminum, copper, lead, gallium, platinum, barium, strontium, titanium, tungsten, and the semimetals silicon, antimony, and arsenic. The waste gases from ion implantation, sputtering, evaporation, and other vacuum processes must be appropriately treated. Small chemical reactors are available to decompose some gases as these are discharged. The remaining metallic waste is then recycled or the appropriate legal disposal made.

Buffing, polishing, sandblasting, and grinding operations generate both airborne and solid wastes. Personnel exposed to these processes must use adequate protective equipment. Many states such as California require that solid wastes from these processes be tested and certified as to the toxic metals content to allow for appropriate disposal. Trivalent chromium oxides are commonly used in polishing compounds. Care must be taken to keep such wastes separate from oxidizing materials to avoid formation of carcinogenic hexavalent chromium.

Vapor degreasing by means of chlorinated hydrocarbons, freons, and other inert compounds used to be a universal practice. Many of these compounds are prohibited by the Montreal protocol, or are being taxed at progressively higher rates. These gases are often ozone (qv) depletion agents or greenhouse gases which contribute to global warming. New and improved aqueous cleaning processes have been developed as replacements, many based on emulsion chemistries of citrus derivatives or terpenes. Alcohol-based processes can be used for critical processes, including electronic assembly cleaning (3, 63).

Flame and other sprayed coatings generate large amounts of potentially toxic fumes. Zinc spraying can expose personnel to fumes, but the workers develop a tolerance to this exposure which disappears quickly once exposure stops. Excess zinc is rapidly excreted from the body. Silicon-containing materials, especially when used for abrasive blasting, have the potential to cause silicosis of the lungs after long exposure.

Both materials and process substitutions have been used to try to limit wastes while providing favorable performance and costs. One problem is that most of the vacuum or controlled atmosphere deposition methods have much higher equipment and operating costs than do electroplating or hot dipping. Moreover, electroplating gives better coverage on complex-shaped parts, and usually is much faster. The focus of most electroplating processes has been to eliminate the use of the most toxic compounds such as cyanides. Cleaners in general have undergone extensive transformations, with emphasis on formulations having smaller amounts of chelating agents (qv) to improve ease of waste treatment. Other cleaners are designed with surfactants (qv) which displace oil for removal by filters or overflow, rather than surfactants for emulsification of oil. Longer cleaner life and a higher oil content waste for energy recovery has resulted.

Electroplating processes in general have moved away from cyanide-based deposition baths. The majority of electroplated zinc is done from zinc sulfate, zinc potassium chloride, zinc ammonium chloride, or alkaline noncyanide zinc processes. Newer baths based on nontoxic chelating agents are replacing copper cyanide strike baths. Noncyanide zincate immersion baths are used for treating aluminum prior to electroless nickel plating. The electroplated metals are also being changed. Zinc–nickel alloy has been suggested as a substitute for toxic cadmium. Plated tin coatings are being used in place of tin–lead in the printed circuit industry, as temporary metallic etch resists (see Resists Lithographic).

Many types of waste treatment and waste minimization processes are in common use in the metallization industry. Air scrubbers are commonly required, even for general acid fume removal from plating shops. Additionally, many newer technologies have been adapted for use in metallizing operations. These include air stripping, antimisting agents, biological destruction, carbon absorption, countercurrent rinsing, crystallization (qv), distillation (qv), Donnan dialysis, electrodialysis, electrowinning, evaporation (qv), filtration (qv), flotation (qv), flocculation, hydrolysis, incineration (see Incinerators), ion exchange (qv), metallic replacement, neutralization, oxidation, pH adjustment (see Hydrogen–ion activity), photolysis, precipitation, process modification, reduction, reverse osmosis (qv), salt splitting, sedimentation (qv), solidification, and spray rinsing.

Whereas many of these technologies are not really new, they have never had the regulatory and economic justification for their use in metallizing. Each of these general methods has many variants. Some may be directed to waste treatment, some to recycle, and some to reclaim. An example is filtration, used to prevent release to air of zinc particles from flame spraying, microfiltration of cleaners to extend life, in combination with chemical precipitation to remove metal particles from wastewater, and many other uses.

BIBLIOGRAPHY

"Metallic Coatings" in *ECT* 1st ed., Vol. 8, pp. 898–922, by W. W. Bradley, Bell Telephone Laboratories, Inc.; in *ECT* 2nd ed., Vol. 13, pp. 249–284, by W. B. Harding, The Bendix Corp.; "Survey" under "Metallic Coatings" in *ECT* 3rd ed., Vol. 15, pp. 241–274, by R. C. Krutenat, Exxon Research and Engineering Co.

Cited Publications

1. E. A. Brandes, ed., *Smithells Metals Reference Book*, 6th ed., Butterworths, New York, 1983.
2. K. G. Budinski, *Surface Engineering for Wear Resistance*, Prentice Hall, Englewood Cliffs, N.J., 1988.
3. *Metal Finishing Guidebook and Directory*, Vol. **92**, No. 1A, Elsevier Publishing, New York, 1944; collected vols., Publications, Inc., Hackensack, N.J., updated yearly.
4. P. Schweitzer, *Corrosion Resistance Tables: Metals, Non-Metals, Coatings, Mortars, Plastics, Elastomers and Linings, and Fabrics*, 3rd ed., Marcel Dekker, New York, 1992.
5. *The Industrial Revolution*, in C. Singer and co-eds., *History of Technology*, Vol. **4**, Oxford University Press, New York, 1958.
6. J. W. Dini, *Electrodeposition: The Materials Science of Coatings and Substrates*, Noyes Data Corp., Park Ridge, N.J., 1993.
7. D. R. Gabe, *Principles of Metal Surface Treatment and Protection*, 2nd ed., Pergamon Press, Inc., Elmsford, N.Y., 1978.
8. "Properties and Selection of Nonferrous Alloys and Pure Metals" in *Metals Handbook*, 10th ed., American Society for Metals, Metals Park, Ohio, 1990.
9. H. H. Uhlig, *Corrosion Handbook*, John Wiley & Sons, Inc., New York, 1948.
10. *The Engineering Properties of Electroless Nickel Deposits*, International Nickel Co., New York, 1977.
11. G. Mann, *Fabricator* (Mar. 1992).
12. K. N. Strafford, P. K. Datta, and G. G. Googan, eds., *Coatings and Surface Treatment for Corrosion and Wear Resistance*, Halstead Press, New York, 1984.
13. *Surface Modification Technologies II: Proceedings of the 2nd International Conference on Surface Modification Techniques*, Minerals, Metals, and Materials Society, Warrendale, Mich., 1989.

14. R. B. Waterhouse and A. Niku-Lari, *Metal Treatments Against Wear, Corrosion, Fretting, and Fatigue*, Vol. **6**, Pergamon Press, New York, 1988.
15. D. R. Gabe, *Electrochimica Acta* **39**, 1115–1121 (1994).
16. R. F. Bunshak, *Handbook of Deposition Technologies for Films and Coatings*, 2nd ed., Noyes Data Corp., Park Ridge, N.J., 1994.
17. G. E. McGuire, D. C. McIntyre, and S. Hoffman, eds., *18th International Conference on Metallurgical Coatings and Thin Films*, Apr. 22–26, 1991, San Diego, Calif., Elsevier Sequoia, Lausanne, Switzerland, 1991.
18. V. Sedlacek, *Metallic Surfaces, Films, and Coatings*, Elsevier, New York, 1992.
19. *Surface Engineering*, Vol. **5**, American Society of Metals, Metals Park, Ohio, 1994.
20. *International Conference on Zinc and Zinc Alloy Coated Steel Sheet*, Sept. 5–7, 1989, Tokyo, Iron and Steel Institute of Japan, 1989.
21. F. C. Porter, *Zinc Handbook: Properties, Processing, and Use in Design*, International Lead Zinc Research Organization, Marcel Dekker, New York, 1991.
22. "Advanced Joining of Aerospace Metallic Materials," *61st Meeting of Structures and Materials Panel of AGARD, Oberammergau, Germany, Sept. 11–13, 1985*, AGARD #398, Nato Advisory Group for Aerospace Research and Development, Neuilly-sur-Seine, France.
23. R. J. Klein-Wassink, *Soldering in Electronics*, 2nd ed., Electrochemical Publications Ltd., Ayr, Scotland, 1989.
24. H. H. Manko, *Solders and Soldering*, 3rd ed., McGraw-Hill Book Publishing Co., Inc., New York, 1992.
25. M. C. Pecht, ed., *Soldering Processes and Equipment*, John Wiley & Sons, Inc., New York, 1992.
26. A. C. Tan, *Tin and Solder Plating in the Electronic and Semiconductor Industry*, Chapman & Hall, New York, 1993.
27. F. G. Yost, R. M. Hosking, and D. R. Frean, eds., *The Mechanics of Solder Alloy Wetting and Spreading*, Van Nostrand Reinhold, New York, 1993.
28. L. J. Durney, ed., *Electroplating Engineering Handbook*, 4th ed., Van Nostrand Reinhold Co., Inc., New York, 1984.
29. W. H. Safranek, *The Properties of Electrodeposited Metals and Alloys*, 2nd ed., American Electroplaters and Surface Finishers Society, Orlando, Fla., 1986.
30. S. Lyakhovich, ed., *Multicomponent Diffusion Coatings*, Oxonian Press Pvt., New Delhi, India, 1987.
31. *American Society of Electroplated Plastics*, *Standards and Guidelines for Electroplated Plastics*, 3rd ed., Prentice-Hall, Inc., Englewood Cliffs, N.J., 1984.
32. G. G. Gawrilov, *Chemical (Electroless) Nickel-Plating*, Portcullis Press, Redhill, U.K., 1979.
33. J. Hajdu and G. Mallory, *Electroless Plating: Fundamental and Applications*, American Plating and Surface Finishing Society, Orlando, Fla., 1990.
34. R. Suchentrunch, *Metallization of Plastics*, Finishing Publications Ltd., Herts, U.K., 1993.
35. M. Fleischmann, S. Pons, D. R. Rolison, and P. P. Schmidt, *Ultramicroelectrodes*, Datatech Systems, Inc., Morgantown, N.C., 1987.
36. *Fifth National Conference on Thermal Spray*, June 7–11, 1993, Anaheim, Calif., American Society for Metals, Metals Park, Ohio, 1993.
37. *"Lead–Zinc '90: Proceedings of a World Symposium on Metallurgy and Environmental Control" 119th TMS Annual Meeting, Feb, 18–21, 1990, Warrington, Pa.*, TMS Lead, Zinc, and Tin Committee.
38. R. Manory and A. Grill, *Protective Coatings of Metal Surfaces by Cold Plasma Treatments*, NASA Technical Memorandum 87152, National Technical Information Service, Springfield, Va., 1985.
39. H. S. Savage and R. G. McCormack, *Arc Sprayed Coatings for Electromagnetic Pulse Protection*, USA-CERL Technical Report M-89/15, U.S. Army Corps of Engineers, Washington, D.C., 1989.
40. *"Advanced Materials and Coatings for Combustion Turbines," ASM Congress Week, Oct. 17–21, 1993*, American Society for Metals, Metals Park, Ohio, 1994.
41. N. Birks and G. H. Meir, *Introduction to High Temperature Oxidation of Metals*, E. Arnold, London, 1983.
42. *Advanced Metallization for ULSI Applications*, Oct. 20–22, 1992 Tempe, Ariz., Materials Research Society, Pittsburgh, Pa., 1993.
43. S. P. Murarka, *Metallization: Theory and Practice for VLSI and ULSI*, Butterworth-Heineman, Boston, Mass., 1993.
44. Technical data, SEMATECH, Austin, Tex.
45. S. R. Wilson, C. J. Tracy, and J. Freeman, eds., *Handbook of Multilevel Metallizations for Integrated Circuits*, Noyes Data Corp., Park Ridge, N.J., 1993.
46. H. K. Pulker, ed., *Wear and Corrosion Resistant Coatings by CVD and PVD*, Halstead Press, New York, 1989.

47. R. Iscoff, *Semiconductor Int.* **17**, 65–72 (Oct. 1994).
48. F. F. Lomarov, *Ion Beam Modification of Metals*, Gordon and Breach Science Publishers, Philadelphia, Pa., 1992.
49. P. D. Prewett and G. L. R. Mair, *Focused Ion Beams from Liquid Metals Ion Sources*, John Wiley & Sons, Inc., New York, 1991.
50. J. A. Mock, *Introduction to Prefinished Metals*, Technomic Publishing Co., Lancaster, Pa., 1983.
51. C. W. Hoppesch, *A Method for Predicting Service Life of Zinc Rich Primers on Carbon Steel*, NASA technical memorandum #93101, Kennedy Space Center, Fla., 1986.
52. *Life Prediction for High Temperature Gas Turbine Materials, Aug, 27–30, 1985, Syracuse, N.Y.*, Syracuse University, 1986.
53. *Air Quality Criteria for Lead: Supplement to the 1986 Addendum*, U.S. EPA, Environmental Criteria and Assessment Office, Washington, D.C., 1990.
54. *Technical Support Document to Proposed Airborne Toxic Control Measure for Emissions of Toxic Metals from Non-Ferrous Metal Melting*, State of California Air Resources Board, Stationary Source Division, Sacramento, Calif., 1992.
55. C. S. Brooks, *Metal Recovery from Industrial Waste*, Lewis Publishers, Chelsea, Mich., 1991.
56. *Hazardous Waste Reduction Checklist and Assessment Manual for the Metal Finishing Industry*, California Department of Health Services, Alternative Technology Division, Toxic Substances Control Program, Sacramento, Calif., 1990.
57. B. L. Carson, H. V. Ellis, and J. L. McCann, *Toxicology and Biological Monitoring of Metals in Humans*, Lewis Publishers, Chelsea, Mich., 1986.
58. T. W. Clarkson, ed., *Biological Monitoring of Toxic Metals*, Plenum Press, New York, 1988.
59. H. K. Dillon and M. H. Ho, *Biological Monitoring of Exposure to Chemicals: Metals*, John Wiley & Sons, Inc., New York, 1991.
60. E. C. Foulkes, ed., *Biological Effects of Heavy Metal*, Vols. **1–2**, CRC Press, Boca Raton, Fla., 1990.
61. *Code of Federal Regulations*, Vol. 40, part 433, Washington, D.C.
62. *Eleventh AESF/EPA Conference on Environmental Control for the Surface Finishing Industry, Feb. 5–7, 1990*, American Electroplaters and Surface Finishers Society, Orlando, Fla., 1990; *Environmental Aspects of the Metal Finishing Industry*, United Nations Environmental Program, Technical Report Service No. 1, Industry and Environmental Office, Paris, 1989.
63. L. M. Brown, J. Springer, and M. Bower, *Chemical Substitution for 1,1,1-Trichloroethane and Methanol in an Industrial Cleaning Operation*, U.S. EPA, Cincinnati, Ohio; National Technical Information Service, Springfield, Va., 1992.

General References

64. *Plating and Surface Finishing, Semiconductor International*, and *Metal Finishing* provide some of the best information on innovative metallizing methods.

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