Kirk-Othmer Encyclopedia of Chemical Technology.
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REFRACTORY COATINGS

Refractory coatings denote metallic, refractory compound, ie, oxides, carbides (qv), and nitrides (qv), and metal-ceramic coatings associated with high temperature service as contrasted to coatings (qv) used for decorative or corrosion-resistant applications. Coatings of high melting materials that are used in other than high temperature applications are also considered to be refractory. A coating may be defined as a near-surface region having properties that differ significantly from the bulk of the substrate (see Ceramics; Metallic coatings; Metal surface treatments).

The highest melting refractory metals are tungsten, tantalum, molybdenum, and niobium, although titanium, hafnium, zirconium, chromium, vanadium, platinum, rhodium, ruthenium, iridium, osmium, and rhenium may be included (see Refractories). Many of these metals do not resist air oxidation. Hence, very few, if any, are used in elemental form for high temperature protection. However, bulk alloys based on nickel, iron, and cobalt and alloying elements such as chromium, titanium, aluminum, vanadium, tantalum, molybdenum, silicon, and tungsten are used extensively in high temperature service. Some modern high temperature oxidation- and corrosion-resistant coatings have compositions similar to the high temperature bulk alloys (see High temperature alloys) and are applied by thermal spraying, evaporation, or sputtering. The protection mechanism for these high temperature alloy coatings is based on adherent impervious surface films of Al_2O_3, SiO_2, CrO_2, or a spinel-type material that grow upon high temperature exposure to air.

Refractory coatings also include materials having high melting points, eg, silicides, borides, carbides, nitrides, or oxides, and combinations such as oxycarbides, etc. In addition, mixtures of metals and refractory compounds, sometimes called metallides, of various microstructural configurations, ie, laminates, dispersed phases, etc, can also be classified as refractory coatings. Other terms used to describe such multiphase coatings are multilayer coating, multicoating, composite coating, reinforced coating, and the like.

In some cases, a coating is a new material that is deposited onto the substrate by a variety of methods. It is then called a deposited or overlay coating. In other cases, the coating may be produced by altering the surface material to produce a surface layer composed of both the added and substrate materials. This is called a conversion coating, cementation coating, diffusion coating, or chemical-conversion coating when chemical changes in the surface are involved. Coatings may also be formed by altering the properties of the surface by melting and quenching, mechanical deformation, or other processes that change the properties without changing the composition.

Coating technology has developed extensively since the 1980s. In this article, emphasis is given to those processes which have proven to be commercially viable or to processes that have undergone extensive development in the 1990s.

All coating methods consist of three basic steps: synthesis or generation of the coating species or precursor at the source, transport from the source to the substrate, and nucleation, growth, or buildup of the coating on the substrate. These steps can be completely independent of each other or may be superimposed on each other, depending on the coating process (see Coating processes). A process in which the steps can be both varied independently and controlled offers great flexibility, enabling a larger variety of materials to be deposited.

Numerous schemes can be devised to classify deposition processes. The scheme used herein is based on the dimensions of the depositing species, ie, atoms and molecules, softened particles, liquid droplets, bulk quantities, or the use of a surface-modification process (1, 2). Coating methods are as follow (2):

Atomistic deposition

- electrolytic environment
  - electroplating
  - electroless plating
  - fused-salt electrolysis
  - chemical displacement
- vacuum environment
  - vacuum evaporation
  - ion beam deposition
  - molecular beam epitaxy
- plasma environment
  - sputter deposition
  - activated reactive evaporation
  - plasma polymerization
  - ion plating
- chemical vapor environment
  - chemical vapor deposition
    - reduction
    - decomposition
    - plasma enhanced
  - spray pyrolysis

Particulate deposition

- thermal spraying
  - plasma spraying (at 50 kW)
  - high power plasma spraying (at 250 kW)
  - D-gun
  - flame spraying
  - arc wire
  - HVOF
- fusion coatings
  - thick-film ink
  - enameling
  - electrophoretic
- impact plating

Bulk coatings

- wetting processes
  - painting
  - dip coating
- electrostatic spraying
  - printing
  - spin coating
- cladding
  - explosive
  - roll bonding
- overlaying
- weld coating
- liquid-phase epitaxy

Surface modification

chemical conversion

- electrolytic
  - anodization (oxides)
  - fused salts
- chemical–liquid
- chemical–vapor
  - thermal
  - plasma
- leaching
- mechanical
  - shot peening
- thermal
- surface enrichment diffusion from bulk
- sputtering
- ion implantation

The coating has to adhere to the substrate. In older thermal spray technology, the bonding may be mechanical as a result of the interlocking between the asperities on the surface and the coating. In this case the surface roughness, ie, the average distance between asperities, must be equal to or larger than the dimensions of the depositing particles. These sprayed coatings internally do not adhere to a polished metal surface. In such cases the substrate surface has to be coarsened by techniques such as grit blasting that not only provide an anchor, but also clean the surface by removing oxide layers and scales, and provide high energy sites for a denser nucleation of coating crystallites and, to some extent, increase the real interfacial area. High velocity processes such as D-gun, high velocity oxy fuel (HVOF), and high powered plasma, eg, PlazJet (TAFA Inc. (Concord, New Hampshire)), propel particles at 4–10 times the impact velocity of other spray devices and provide coating bonds two to three times that of older spray processes, in many cases on clean, ground substrates (see Plasma technology). These particular processes also provide denser and in many cases pore-free coatings having thicknesses in the range of 325–1000 μm.

In diffusion or chemical bonding, the substrate and the coating material interdiffuse at the interface. The latter depends on the equilibrium between the two materials at the effective temperature of deposition. If the two materials have no solid solubility, a sharp or abrupt interface forms. The bond strength depends on the affinity between the materials and increases with the degree of wetting of the substrate with the coated material. If the two materials exhibit extensive solid solubility, the interface is a solid solution. If intermetallic phases are indicated on the equilibrium diagram, these may also form at the interface as may gas–metal compounds, depending on the degree of contamination present on the substrate or arriving at the substrate from the environment.

Residual stresses, which are always present in coatings, arise from thermal expansion mismatch between coating and substrate, or growth stresses caused by imperfections in the coating that are built-in during the process of film growth. Growth stresses are usually significant for coating processes carried out near room temperature. Failure or debonding of the coating may be caused by the residual stresses in the coating and substrate. The location of the failure may be in the substrate, at the interface, or in the coating, depending on plastic deformation and resistance to nucleation and growth of cracks, ie, fracture toughness. For example, a coating may fail at the interface because of crack propagation caused by a brittle intermetallic phase. A post-failure surface analysis of the substrate and the coating is recommended; the use of surface chemical analysis techniques, eg, scanning electron microscopy (sem) having energy-dispersive x-ray analysis (edax) capabilities, Auger spectroscopy, or esca analysis can determine the chemical composition at the failed interfaces and deduce its cause (see Surface and interface analysis ( ).

Newer high velocity thermal spray coating processes produce coatings in compression rather than tension because of the shot peening effect of the supersonic particles on impact. This has permitted coating as thick as 12,500 μm without delamination as compared to older processes limited to 1,250 μm. The reduced residence time of particles at temperature minimizes decomposition of carbides present in conventional d-c plasma. This improves wear and hardness (qv) properties.

Coatings may be permeable either to the atmosphere or the substrate material. Diffusion of oxygen through a coating can result in gaseous products that may rupture the coating. Even if the gas can escape through the substrate, as for graphite, the substrate can be consumed and the bond weakened. Coatings permeable to the substrate material by outward diffusion can suffer similarly, as oxidation of the diffused species may occur at the atmosphere–coating interface.

The design of a coating that might equilibrate with its substrate during use is based on the phase diagram of the system. Extensive regions of solid solubility may indicate that rapid interdiffusion can be expected. For multicomponent coatings on multicomponent substrates, a large number of possibilities exists for formation of intermetallic compounds. Limited compound formation at the coating–substrate interface may be preferred if it decreases the permeability of the coating. Wetting or, more strictly speaking, high affinity between coating and substrate is conducive to high temperature service.

A reasonably close match of thermal expansion of the coating and substrate over a wide temperature range to limit failure caused by residual stresses is desired for coatings. Because temperature gradients cause stress even in a well-matched system, the mechanical properties, strength, and ductility of the coating as well as the interfacial strength must be considered.

The simple case of protecting tungsten or molybdenum by using platinum illustrates the above point. A wide range of solid solubility exists that contributes to interdiffusion between coating and base metal to form brittle intermetallic compounds. Both solutions and compounds oxidize preferentially, losing tungsten or molybdenum. Platinum is also somewhat permeable to oxygen, which permits subcoating oxidation. A thermal expansion mismatch exists between platinum and these intermetallic compounds and adds another complication where thermal cycling is required. Silicides and beryllides exhibit sufficient conductivity to be electroplated and could well be used as diffusion barriers. However, the bond strengths and mechanical compatibility of two layers instead of one must be considered.

1. Atomic Deposition Processes

1.1. Electrodeposition

1.1.1. Aqueous Electrodeposition

The theory of electrodeposition is well known (see Electroplating). Of the numerous metals used in electrodeposition, only 10 have been reduced to large-scale commercial practice. The most commonly plated metals are chromium, nickel, copper, zinc, rhodium, silver, cadmium, tin, and gold, followed by the less frequently plated metals iron, cesium, platinum, and palladium, and the infrequently plated metals iridium, ruthenium, and rhenium. Of these, only platinum, rhodium, iridium, and rhenium are refractory.

The electrodeposition of tungsten alloys of iron, nickel, and cobalt is commercially feasible but has remained largely experimental. The properties of these alloys should, however, be of sufficient interest for engineering applications.

Cermets, ie, materials containing both ceramic and metal, eg, TiC–Ni and Al_2O_3–Cr, can be deposited from plating baths if the particulate matter is suspended by air agitation or stirring (see Ceramics; Composite materials, ceramic-matrix). Particle sizes from 1 to 50 μm may be deposited to concentrations over 20%. Chromium-based cermets containing zirconium and tungsten borides, zirconium nitride, and molybdenum carbide can be plated on refractory metals and graphite. However, at 1650°C, protection is afforded only for a few minutes. Cermets also suffer from porosity. Therefore, such coatings find application where exposure times are short and erosion conditions severe, and where they can be used to bridge the expansion mismatch between a metallic substrate and a ceramic coating.

1.1.2. Fused-Salt Electrodeposition

Molten salt electrolysis has been used since Davy's and Faraday's pioneering experiments, but application as a method for coating metals has remained of academic interest. Fused-salt baths may be used to plate ruthenium, platinum, and iridium with improved coating soundness. Developments in this technology may lead to commercial plating of other refractory metals, such as zirconium, hafnium, vanadium, niobium, tantalum, molybdenum, and tungsten. Molten salt electrolysis is based on the same principles as aqueous electrolysis processes, but the vehicle, ie, the bath, is a molten salt. The coating material deposits as a layer on the substrate.

1.2. Electroless Deposition

Electroless plating (qv) is defined as a controlled, autocatalytic chemical reduction process for depositing metals. It resembles electroplating because it can be run continuously to build up a thick coating. Unlike displacement processes, it does not involve a chemical reaction with the substrate metal; and unlike the well-known silver reduction process (Tollens reaction) for the silvering of optical glass, it is selective, ie, deposits form only on a catalytic surface. The metals nickel, cobalt, platinum, palladium, and gold, and nickel–cobalt alloys can be deposited. Chromium, iron, and vanadium are often claimed, but electroless plating of active metals must be viewed with suspicion. Most such processes are of the displacement type.

1.3. Physical Vapor Deposition Processes

The three physical vapor deposition (PVD) processes are evaporation, ion plating, and sputtering (see Thin films, film formation techniques).

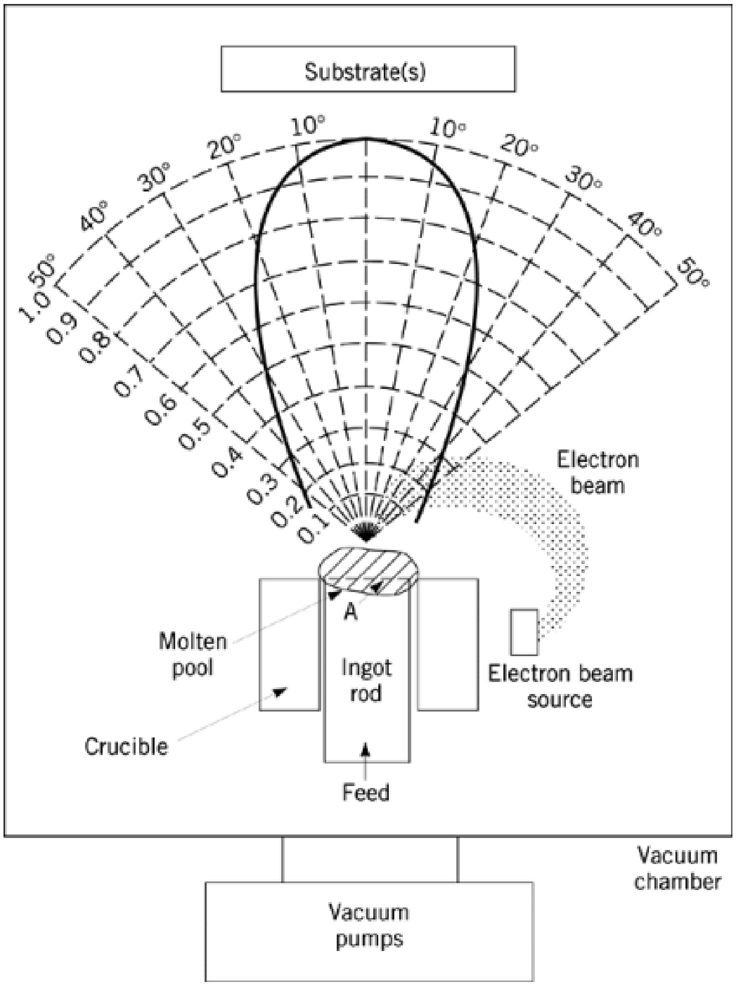

Fig. 1. Vacuum evaporation process with use of electron beam heating where A represents the material to be deposited. The flux profile (▬) is at a range of $1.0\ \text{m} \pm 50^\circ$ from perpendicular.

The materials deposited by PVD techniques include metals, semiconductors (qv), alloys, intermetallic compounds, refractory compounds, ie, oxides, carbides, nitrides, borides, etc, and mixtures thereof. The source material must be pure and free of gases and inclusions, otherwise spitting may occur.

1.3.1. Metals and Elemental Semiconductors

Evaporation of single elements can be carried out from various evaporation sources subject to the restrictions with regard to melting point, container reactions, deposition rate, etc. A typical arrangement is shown in Figure 1 for electron beam heating (3). This type of source is ideal for refractory coatings, because the material to be deposited is contained in a noncontaminating water-cooled copper crucible and the surface of the material can easily be heated to $>3000^\circ\text{C}$.

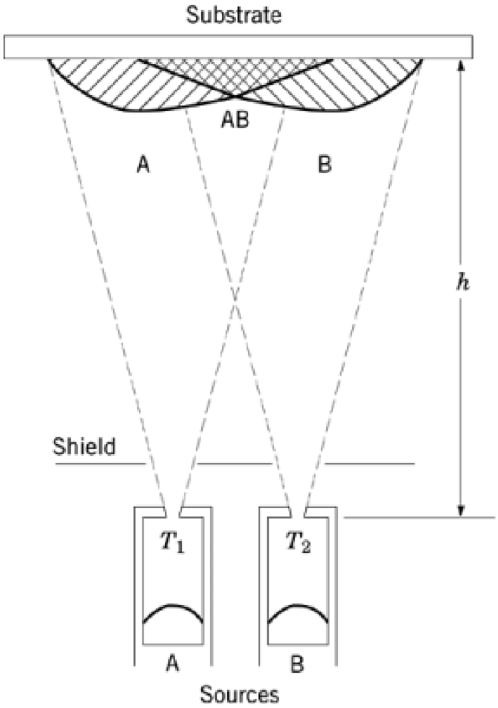

Fig. 2. Two-source evaporation at temperatures T_1 and T_2 defining the regions coated by materials A, B, and AB, where h represents height.

1.3.2. Alloys

Alloys consist of two or more elements of different vapor pressures and hence different evaporation rates. As a result, the vapor phase and therefore the deposit constantly vary in compositions. This problem can be solved by multiple sources or a single rod- or wire-fed electron beam source fed with the alloy. These solutions apply equally to evaporation or ion-plating processes.

1.3.3. Multiple Sources

Multiple sources offer a more versatile system. The number of sources evaporating simultaneously is equal to or less than the number of constituents in the alloy. The material evaporated from each source can be a metal, alloy, or compound. Thus, it is possible to synthesize a dispersion strengthened alloy, eg, Ni–ThO_2. However, the evaporation rate from each source has to be monitored and controlled separately. The source-to-substrate distance would have to be sufficiently large (38 cm for 5 cm dia sources) to blend the vapor streams prior to deposition, which decreases the deposition rate (Fig. 2). Moreover, if the density of two vapors differs greatly, it may be difficult to obtain a uniform composition across the width of the substrate because of scattering of the lighter vapor atoms. Evaporating each component sequentially produces a multilayered deposit that is homogenized by annealing. High deposition rates are difficult to obtain.

1.3.4. Single Rod-Fed Electron Beam Source

The disadvantages of multiple sources for alloy deposition can be avoided by using a single wire-fed or rod-fed source (Fig. 3) (3). A molten pool of limited depth is above the solid rod. If the equilibrium vapor pressures of the components of an alloy A_1B_1 are in the ratio of 10:1 and the composition of the molten pool is $A_{10}B_1$, under

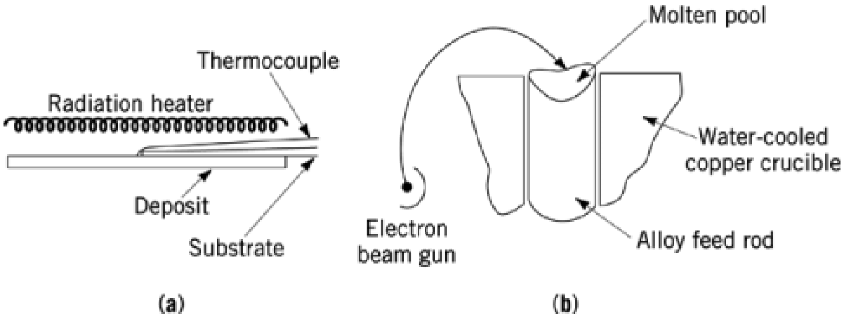

Fig. 3. Alloy evaporation from a single rod-fed source under steady-state conditions: $p^{\circ}=10p^{\circ}\mathrm{AB}$; feed rod, A_1B_1; molten pool, $A_{10}B_1$; and vapor and deposit, A_1B_1, where p°=the equilibrium vapor pressure of component BB, and p°=the equilibrium vapor pressure of component AA. Part (**a**) shows wire-fed, and (**b**) rod-fed sources.

steady-state conditions, the composition of the vapor is the same as that of the solid being fed into the molten pool. The procedure can be started with a pellet of appropriate composition $A_{10}B_1$ on top of a rod A_1B_1 to form the molten pool initially, or with a rod of alloy A_1B_1 to evaporate the molten pool until it reaches composition $A_{10}B_1$. The temperature and volume of the molten pool must be constant to obtain a constant vapor composition. A theoretical model has been developed and confirmed by experiment, and deposits of Ni–20 wt % Cr, Ti–6 wt % Al–4 wt % V, Ag–5 wt % Cu, Ag–10 wt % Cu, Ag–20 wt % Cu, Ag–30 wt % Cu, and Ni–Cr–yAl–zY alloy have been successfully prepared. This method can be used with a 5000-fold vapor pressure difference between components. It cannot be used when one of the alloy constituents is a compound, eg, Ni–ThO_2.

1.3.5. Sputtering

Sputtering deposits alloys by means of an alloy target. The surface composition of the target changes in the inverse ratio of the sputtering yields of the individual elements, as in the alloy evaporation from a single rod-fed electron beam source. Alternatively, the sputtering target can be made of strips of the components of the alloy with the respective surface areas inversely proportional to their sputtering yield.

1.3.6. Refractory Compounds

Refractory compounds resemble oxides, carbides, nitrides, borides, and sulfides in that they have a very high melting point. In some cases, they form extensive defect structures, ie, they exist over a wide stoichiometric range. For example, in TiC, the C:Ti ratio can vary from 0.5 to 1.0, which demonstrates a wide range of vacant carbon lattice sites.

In direction evaporation, the evaporant is the refractory compound itself, whereas in reactive or activated reactive evaporation (ARE), a metal or a low valency metal compound is evaporated in the presence of a partial pressure of a reactive gas to form a compound deposit, eg, Ti is evaporated in the presence of N_2 to form TiN, or Si or SiO is evaporated in the presence of O_2 to form SiO_2.

1.3.7. Direct Evaporation

Evaporation can occur with or without dissociation of the compound into fragments. The observed vapor species show that very few compounds evaporate without dissociation. Examples are MgF_2, B_2O_3, CaF_2, SiO, and other Group 14 (IV) divalent oxides, eg, SiO homologues such as GeO and SnO.

In general, when a compound is evaporated or sputtered, the material is not transformed to the vapor state as compound molecules but as fragments thereof. Subsequently, the fragments recombine, most probably on the substrate, to reconstitute the compound. Therefore, the stoichiometry (anion:cation ratio) of the deposit depends on the deposition rate, the ratios of the various molecular fragments, the impingement of other gases present in the environment, the surface mobility of the fragments which in turn depends on their kinetic energy and substrate temperature, the mean residence time of the fragments of the substrate, the reaction rate of the fragments on the substrate to reconstitute the compound, and the impurities present on the substrate. For example, direct evaporation of Al_2O_3 results in a deposit deficient in oxygen, ie, having the composition Al_2O_{3--x}. This O_2 deficiency could be compensated for by introducing O_2 at a low partial pressure into the environment.

1.3.8. Reactive Evaporation

In reactive evaporation (RE), metal or alloy vapors are produced in the presence of a partial pressure of reactive gas to form a compound either in the gas phase or on the substrate as a result of a reaction between the metal vapor and the gas atoms:

$$2\ \mathrm{Ti} + \mathrm{C_2H_2} \longrightarrow 2\ \mathrm{TiC} + \mathrm{H_2}$$

If the metal and gas atoms are activated or ionized in the vapor phase, which activates the reaction, the process is called the activated reactive process (ARE), as illustrated in Figure 4 (4). The metal is heated and melted by a high acceleration voltage electron beam. The melt has a thin plasma sheath on top from which low energy secondary electrons are pulled upward into the reaction zone by an electrode placed above the pool. The electrode is biased to a low positive d-c potential (20–100 V). These low energy electrons have a high ionization cross section, thus ionizing or activating the metal and gas atoms and increasing the reaction probability on collision. Titanium carbide was synthesized with this process by reaction of Ti metal vapor and C_2H_2 gas having a carbon:metal ratio approaching unity. Moreover, by varying the partial pressure of either reactant, the carbon:metal ratio of carbides could be varied at will. This process has also been applied to the synthesis of the five different Ti oxides (5). Using the ARE process, ie, with a plasma, as compared to the RE process, ie, without a plasma, a higher oxide formed for the same partial pressure of O_2, which demonstrates a better gas utilization in the presence of plasma (see Plasma technology).

1.3.9. Reactive-Ion Plating

In reactive-ion plating (RIP), as in the reactive evaporation process, the metal atoms and reactive gases form a compound aided by the presence of a plasma. Because the partial pressures on the gases are much higher (>1.3 Pa (10^{-2} mm Hg)) than in the ARE process (13 mPa (10^{-4} mm Hg)), the deposits may be porous or sooty. In the simple diode ion-plating process, the plasma cannot be supported at a lower pressure. Therefore, an auxiliary electrode adjusted to a positive low voltage, as originally conceived for the ARE process, is used to initiate and sustain the plasma at a low pressure (ca 0.13 Pa (10^{-3} mm Hg)), as shown in Figure 5 (6).

1.3.10. Reactive Sputtering

Reactive sputtering is similar to reactive evaporation and reactive-ion plating in that at least one coating species enters the system in the gas phase. Examples include sputtering Al in O_2 to form Al_2O_3, Ti in O_2 to form TiO_2, In–Sn in O_2 to form tin-doped In_2O_3, Nb in N_2 to form NbN, Cd in H_2S to form CdS, In in PH_3 to form InP, and Pb–Nb–Zr–Fe–Bi–La in O_2 to form a ferroelectric oxide.

By reactive sputtering, many complex compounds can be formed from relatively easy-to-fabricate metal targets, insulating compounds can be deposited using a d-c power supply, and graded compositions can be formed, as described. The process, however, is complicated.

1.4. Chemical Vapor Deposition and Plasma-Assisted Chemical Vapor Deposition

In chemical vapor deposition (CVD), thin films or bulk coatings up to 2.5 cm in thickness are deposited by means of a chemical reaction between gaseous reactants passing over a substrate. Temperatures can be anywhere

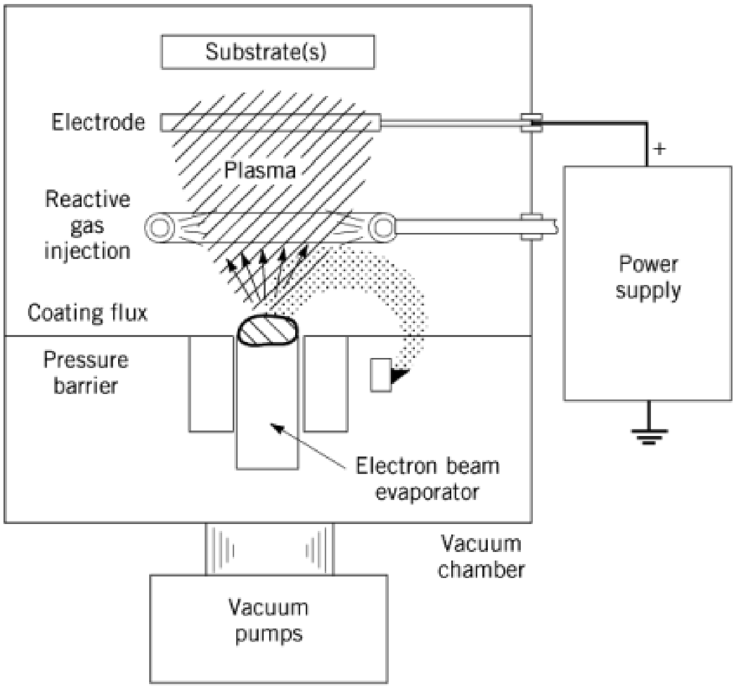

Fig. 4. Activated reactive evaporation process (4).

between 200 and 2200°C, but are usually between 500 and 1100°C. The optimum for a given reaction often lies within a very narrow range, and the process needs to be tailored to the substrate and the intended application. The substrate's melting point and susceptibility to chemical attack by the reacting gases or by their side products has to be considered. Coatings have application in a wide array of corrosion- and wear-resistant uses, but also in decorative layers, semiconductors, and magnetic and optical films (see Thin films, film formation techniques).

In most cases, CVD reactions are activated thermally, but in some cases, notably in exothermic chemical transport reactions, the substrate temperature is held below that of the feed material to obtain deposition. Other means of activation are available (7), eg, deposition at lower substrate temperatures is obtained by electric-discharge plasma activation. In some cases, unique materials are produced by plasma-assisted CVD (PACVD), such as amorphous silicon from silane where 10–35 mol % hydrogen remains bonded in the solid deposit. Except for the problem of large amounts of energy consumption in its formation, this material is of interest for thin-film solar cells. Passivating films of SiO_2 or SiO_2–Si_3N_4 deposited by PACVD are of interest in the semiconductor industry (see Semiconductors).

Plasma-assisted CVD processes use deposition temperatures lower than CVD processes. The desired deposition reaction is aided by the energy present in the plasma (8). The plasma greatly extends the utility of CVD processes, eg, the ability to deposit films on substrates that cannot withstand the temperature needed for the CVD process in reactions such as polymerization, anodization, nitriding, deposition of amorphous silicon, amorphous carbon (diamond-like carbon), etc. The films deposited by PACVD are generally more complex than their analogues deposited by normal CVD methods. For example, silicon nitride films have a composition $Si_xN_yH_z$ and may contain as much as 15 to 30 atomic % hydrogen as contrasted to the Si_3N_4 composition of the film deposited by the normal CVD process. Other advantages of PACVD are substrate surface etching and activation to produce good bonding at low deposition temperatures.

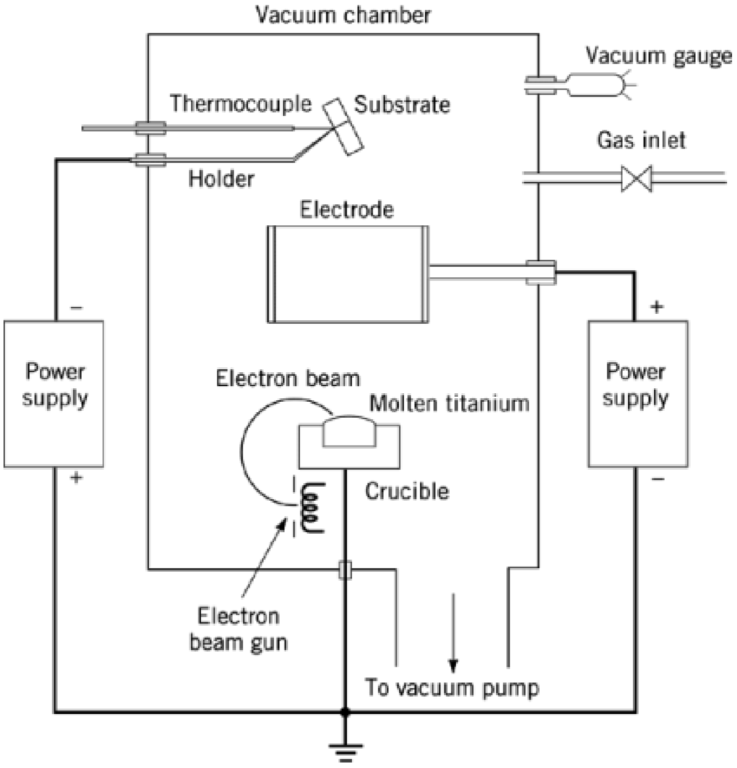

Fig. 5. Reactive-ion plating using auxiliary electrode for low pressure operation in deposition of compounds (6).(Courtesy of Kobayashi and Doi.)

1.5. Ion Implantation

High energy ion implantation (qv) is a highly successful process for doping semiconductors to precisely controlled concentrations. The part's surface is bombarded with high energy ions ($\sim$50 keV), which results in a layer of implanted ions at an approximate depth of 8 nm. The potential for producing refractory coatings by implantation of specific metal ions or by reactions within the substrate to form refractory compounds exists but has not been exploited to date.

2. Particulate Deposition Processes

2.1. Thermal Spraying

In thermal spraying, ie, particles heated or melted, a combustion flame or electric arc heats particles of the refractory-coating material to a temperature sufficient to achieve sintering or cohesive solidification when the particles impinge on a substrate. Penetration of the substrate rarely accompanies the coalescence. The techniques include flame plating (D-gun, HVOF), flame spraying, arc wire, d-c plasma spraying, and induction-plasma spraying. These processes generate considerable noise, and acoustical protection is needed.

Flame plating (D-gun) employs oxygen and fuel gas. In this method, developed by the Union Carbide Corporation, the gas mixture is detonated by an electric spark at four detonations per second. The powders, mixed with the gas, are fed under control into a chamber from which they are ejected when detonation occurs. The molten, 14–16-μm particles are sprayed at a velocity of 732 m/s at distances of 5.1–10.2 cm from the surface. The substrate is moved past the stationary gun.

A steady-state rocket-type combustion spray unit has been developed, called high velocity oxy fuel (HVOF), that creates a steady state, continuous, supersonic spray stream (1.2–3 mm dia) resembling a rocket motor exhaust. The portable device injects and accelerates the particles inside a barrel (rocket nozzle). It produces coating quality and particle velocities equal to the D-gun at 5–10 times the spray rate with significantly reduced coating costs.

Flame spraying is no longer the most widely used melt-spraying process. In the power-feed method, powders of relatively uniform size (<44 μm (325 mesh)) are fed at a controlled rate into the flame. The torch, which can be held by hand, is aimed a few cm from the surface. The particles remain in the flame envelope until impingement. Particle velocity is typically 46 m/s, and the particles become at least partially molten. Upon impingement, the particles cool rapidly and solidify to form a relatively porous, but coherent, polycrystalline layer. In the rod-feed system, the flame impinges on the tip of a rod made of the material to be sprayed. As the rod becomes molten, droplets of material leave the rod with the flame. The rod is fed into the flame at a rate commensurate with melt removal. The torch is held at a distance of ca 8 cm from the object to be coated; particle velocities are ca 185 m/s.

Arc-plasma spraying equipment has been commercially available since 1958. This process does not utilize a fully ionized gas (plasma). Uniform particles (<74 γm (-200 mesh)) are fed into the jet that emerges through the nozzle of a high pressure d-c arc. The particles are melted and ejected at controllable velocities of 30–210 m/s. The composition of the atmosphere can be varied over a wide range, ie, wet, dry, oxidizing, reducing ($\leq 80\%$), or inert. A 40–50 kW, 600 A d-c source supplies the average power requirements. The uv radiation generated during operations presents a safety hazard. During the early 1990s, high power (250 kW) d-c plasma spray systems (PlazJet) have been introduced. These can produce supersonic inert gas velocities, higher than those of HVOF, without combustion and the attendant oxygen. The coatings are significantly more dense, better bonded, and can be made to produce different, more desirable microstructures than conventional plasma.

Induction-plasma spraying is used in partial vacuum (ca 40 kPa (300 torr)) spraying of titanium aluminides for aerospace applications. A spark creates an ignition arc within the torch tube and coil to start the r-f power coupling to the levitated arc within the ceramic tube surrounded by the induction coil. This 5–8 cm egg-shaped plasma symmetrically fills the tube. Powders are fed into the plasma through a probe near the inlet of the plasma where the melted particle residence time can be varied over a greater range than in the d-c plasma process because gas velocity can be varied by adjusting the nozzle size and operating pressure. This apparatus is powered by a 100-kW, 450-kHz power source and cannot be held by hand. As in flame plating, the object is moved in the path of the gun.

Arc wire utilizes two continuously fed 1.6-mm dia intersecting wires with a d-c arc maintained between the wire tips as they meet. Compressed gas (usually air) strips the molten metal from the tips and forms a directional spray stream. This process is widely used to spray most metals. Arc wire is the most economical process because of the wire feedstock. Moreover, it utilizes $\sim 10\%$ of the thermal energy of the other spray processes (0.4 vs 6.6 kWh/kg using stainless steel) because of the direct arc heating of the wire tips.

Any refractory material that does not decompose or vaporize can be used for melt spraying. Particles do not coalesce within the spray. The temperature of the particles and the extent to which they melt depend on the flame temperature, which can be controlled by the fuel:oxidizer ratio or electrical input, gas flow rate, residence time of the particle in the heat zone, the particle-size distribution of the powders, and the melting point and thermal conductivity of the particle. Quenching rates are very high, and the time required for the molten particle to solidify after impingement is typically 10^{-4} to 10^{-2} s.

A broad range of materials can be handled by plasma spraying. However, each material requires some optimization of conditions, such as modification of carrier gas, power, particle-size distribution, and substrate. In some melt-spray processes, a preferential loss of material may occur that leads to a change in stoichiometry.

It can be compensated for by adding an appropriate additional gas to the gas stream. Thus, additions of oxygen can keep the reduction of TiO_2 and HfO_2 within acceptable limits, whereas methane reduces the loss of carbon from carbides. A wide selection of coating materials is available. Except for particle-velocity limitations, spray conditions are excellent because of the inert, clean carrier gases used. Inert atmospheres reduce the degradation or oxidation of the particles, preclude oxidation of the substrate, and diminish contamination of the sprayed material resulting from gas adsorption.

Arc wire, flame spraying, HVOF, and arc plasma spraying are the least expensive. Flame plating is more expensive. The adherence of melt-sprayed ceramic coatings onto metallic substrates varies widely from process to process and depends on procedure and substrate preparation (Table 1). The high strength of D-gun and HVOF coatings is a consequence of the higher particle velocity that results in penetration of the substrate surface. For other flame-spray processes, the substrate is usually roughened to provide a suitable surface. Chemical bonding contributes to adhesion but the mechanical bond is preferred. Advantages and disadvantages of flame-spray processes having porosities of 0.1–20.0% are as follow:

Advantages	Disadvantages
produces coatings on any substrate	undercuts, deep blind holes, and small internal diameters are difficult to coat
versatility in configuration size, shape, and structure	
good dimensional control, no shrinkage	properties are generally lower than wrought or pressed and sintered materials
mixed compositions	
fine grain size	
permits patching and repairing	nonstoichiometry may result
alternating layers	residual stresses can limit coating thickness
graded coatings	
by masking, localized areas can be coated	

Table 1. Tensile-Bond Test for Melt-Sprayed Al_2O_3

Method	Particle velocity, m/s	Bond strength, MPa[a]
flame spraying	46–83	3.4–13.8
HVOF[b]	700–800	60–80
arc-wire	15–30	30–70
high power dc	100–1000	15–80
flame plating	700–800	69
d-c plasma process	30–213	6.9–69
induction-plasma process	6–>300	3–15

[a] To convert MPa to psi, multiply by 145.

[b] HVOF = high velocity oxy fuel, particle velocity 700800 m/s

2.2. Electrophoretic Processes

Electrophoretic coatings are obtained through the migration of charged particles when a potential is applied to electrodes immersed in a suitable suspension of the particles. This process is particularly suited for applying uniform layers on complex bodies. Projecting edges become insulated and the current shifts to bare surfaces as the deposit builds up on them. Particles, not ions, are deposited. The early stages of coating are powdery and densification is required to produce adherence. Electrophoresis can be used to apply metals and alloys, ceramics, and cermets. The three steps are preparation of the dispersion, deposition and conversion, and bonding. In the preparation phase, particle size is critical and diameters may be from 1 to 50 μm; however, too small a size leads to cracking after thick coatings are dried and consolidated (see Electroseparations, electrophoresis).

Several suspension media having suitable viscosities, densities, conductivities, dielectric constants, and chemical stabilities are available. Binders improve the green strength of the coating. Deposition is effected rapidly using potentials of 50–1000 V dc. Simple d-c sources having no special filtering are sufficient. All inorganic materials are amenable to deposition and most are amenable to codeposition, even though they have different densities; for example, NiO (7.5 g/cm^3) and WC (15.7 g/cm^3) have been codeposited in the same ratio as they were dispersed. The practical limit of thickness is about 0.5 mm as set by shrinkage cracking. Conversion and bonding techniques vary with the type of coating. Hydrogen reduction, hydrostatic pressing, and sintering are used for most metal-base coatings. The oxides of iron, nickel, cobalt, molybdenum, and tungsten can be reduced in hydrogen at less than 600°C. For example, NiO–Cr green deposits are reduced in H_2 at 320°C to produce metallic nickel, with no particle sintering. After pressing at 69 MPa (10,000 psi), further densification is achieved by sintering to 90% of theoretical density at 1090°C. Vacuum sintering is preferred for titanium, zirconium, niobium, and tantalum. Glass and ceramic coatings can be either vitrified or fused.

3. Bulk Coating

In bulk coating processes, bulk materials are joined to the substrate either by a surface melt process or by attachment of the solid material. An example of the latter is the application of heat-resistant tiles of silica-type material to the aluminum alloy skin of a space shuttle vehicle, enabling the vehicle to withstand the reentry heat.

In cladding, one metal is coated with another by rolling or extruding the two metals in close contact to each other. Coherence of the two metals is induced by soldering, welding (qv), or casting one in contact with the other prior to the rolling operation. By this mechanical process, steel can be coated with copper, nickel, or aluminum. The coextrusion process, which is used for lightweight rifle barrels made of a steel core and titanium alloy wrap, is a good example of the cladding process.

Another familiar commercial method is the immersion or hot-dipping process. The article to be coated is immersed in a molten metal bath. Usually little else is done to change the properties of the coating, which adheres to the surface upon removal of the article from the bath. For a successful coating, an alloying action must take place between the components to some extent. Zinc and tin coatings are applied to sheet steel by hot-dipping.

Surface coatings are also applied by welding processes, such as manual arc welding (oxy–acetylene, gas–tungsten), gas–metal arc welding, submerged-arc welding, spray welding, plasma-arc welding, and electroslag welding (see Welding). Thin coatings (0.25–0.75 mm) are applied by spray welding. For heavier coatings in the range of 6 to 65 mm or more, other welding processes are used.

These welding processes are not suitable for the application of refractory coatings of reactive metals such as tungsten, tantalum, niobium, and chromium, although electroslag welding is being studied for this purpose. On the other hand, such refractory metal, alloy, and cermet coatings can be applied by electron beam melting to form thick coatings, because this process is carried out in vacuum.

A new cladding process permits brazing of carbides, nitrides, and metals and alloys to most metallic substrates. These thick coatings contain 95%+ metal ($<5\%$ braze component) and are metallurgically attached to the substrate. Another development in this area is the use of high power laser beams to surface melt refractory metal or cermet coatings onto substrates in a controlled atmosphere to prevent contamination of the reactive metals. This process is sometimes referred to as laser glazing (see Lasers). Significant surface stresses are produced but pore-free barriers often result.

Reaction spraying is also being widely explored. In this case new compositions or particle surface reactions providing enhanced coating properties, eg, nitrides for wear resistance, are achieved while the particle is in transit.

Enameling meets decorative as well as protective requirements. Ceramic enamels are mainly based on alkali borosilicate glasses. The part to be enameled is dipped into or sprayed with a slip, ie, a water suspension of glass fragments called frit. The slip coating is dried and fused in an enameling furnace under careful heat control (see Enamels, porcelain or vitreous).

Troweling and painting methods are used to apply thick protective coatings of a refractory paste or cermet onto a variety of substrates for high temperature service. Fiberfrax (The Carborundum Company) coating cements, composed of aluminosilicate fibers bonded with air-setting temperature-resistant inert binders, is commonly used as a coating for reducing the oxidation rate of graphite.

In the microelectronics industry, powdered metals and insulating materials that consist of nonnoble metals and oxides are deposited by screen printing in order to form coatings with high resistivities and low temperature coefficients of resistance. This technique may be useful in depositing oxide–metal refractory coatings.

4. Surface-Modification Processes

4.1. Cementation or Diffusion Coatings

Cementation is defined as the introduction of one or more elements into the outer portion of a metal object by means of diffusion at elevated temperatures. Cementation was first used to convert iron to steel, and copper to brass, but as of the mid-1990s it is considered only as a method of surface treatment. The coating produced by cementation is formed by an alloying or chemical combination of the diffusing elements and the substrate material. Cementation coatings enjoy wide metallurgical application. A prime example is the case hardening of steel whereby a soft, ductile, low carbon steel is heated to 810–900°C in a packing of carbonaceous material to produce a high carbon steel surface (see Metal surface treatments; Steel). The coating formed in this manner is limited to use at temperatures of about 600°C or lower. Truly refractory coatings are alloyed onto molybdenum, tantalum, niobium, and tungsten by cementation. Such coatings provide short-term protection at 1650°C or higher, and long-term protection at 1370°C.

Cementation coatings are produced at temperatures well below the melting points of either the coating or substrate material by means of a vapor-transport mechanism. The coating material and the substrate form definite chemical compounds, such as silicides, aluminides, beryllides, or chromides. On the other hand, some cementation coatings can be solid solutions of indefinite composition. Oxidation-resistant coatings act as diffusion barriers for both the inward diffusion of oxygen and the outward diffusion of the substrate. The diffusion of the coating components into the substrate is generally the rate-controlling step. Cementation coatings are applied by pack cementation, activated or nonactivated slurry processes, and the fluidized-bed technique.

In pack cementation, the part to be coated is placed in a retort and surrounded with a powdered pack consisting of the coating component and an activator; the latter reacts with the coating component to form the carrier vapor, usually a halide or an inert diluent, to prevent the pack from sintering together and to permit vapor transport of the alloying component through the pack.

The slurry process requires less coating component. The latter is suspended in a vehicle, eg, lacquer or water, and is painted onto the substrate. The coated part is heated in an alumina retort containing a layer of activator at the bottom. The coating component forms a halide and is deposited onto and diffused into the substrate. Slurry processes can be either activated or nonactivated. In the latter case, development of the coating relies purely on diffusion without the possible benefits of vapor deposition.

The fluidized-bed technique combines aspects of pack cementation and vapor deposition. A fluidized bed consists of a mass of finely divided solids contained in a column. The solids are brought into a fluidized state by the lifting action of a gas as it rises through the column. A vaporized halide may be carried by a gas into the bed, where it reacts with the fluidized coating powder to form the coating component halide, which then thermally decomposes and deposits on the substrate contained within the retort. Alternatively, the metal coating particles may be fluidized before entering the bed, whereby the halide gas permeates the fluidized particles to form the coating halide vapor. This vapor is carried into the bed of inert particles, where it thermally decomposes to deposit the coating (see Fluidization).

The chromizing of iron is described by three mechanisms:

$$\textit{Displacement} \qquad \mathrm{Fe\ (alloy) + CrCl_2\ (g) \longrightarrow FeCl_2\ (g) + Cr\ (alloy)}$$

$$\textit{Reduction} \qquad \mathrm{H_2\ (g) + CrCl_2\ (g) \longrightarrow 2\ HCl\ (g) + Cr\ (alloy)}$$

$$\textit{Thermal decomposition} \qquad \mathrm{CrCl_2\ (g) \longrightarrow Cl_2\ (g) + Cr\ (alloy)}$$

The displacement mechanism involves placing the iron alloy packed in chromium powder, NH_4Cl, and Al_2O_3 in a sealed retort, which is heated to promote vapor deposition and diffusion processes. The exact chemistry is not known, but the following steps probably occur:

$$\mathrm{NH_4Cl\ (g) \longrightarrow NH_3\ (g) + HCl\ (g)}$$

$$\mathrm{2\ NH_3\ (g) \longrightarrow N_2\ (g) + 3\ H_2\ (g)}$$

$$\mathrm{Cr\ (powder) + 2\ HCl\ (g) \longrightarrow CrCl_2\ (g) + H_2\ (g)}$$

$$\mathrm{CrCl_2\ (g) + 2\ Fe\ (alloy) \longrightarrow FeCl_2\ (g) + Fe{-\!\!-}Cr\ (alloy)}$$

Several thermodynamic and kinetic requirements must be fulfilled for the reactions to proceed as shown. First, the vapor pressure of the activators or carriers must be sufficiently high at the coating temperature for the reaction to proceed. The activator, ie, the chloride, should have a boiling point slightly above the temperature of the coating to provide a reservoir for reaction without volatizing too rapidly. The coating-component halide should have a boiling point below the coating temperature to saturate the pack. The volatility of the by-product of the coating reaction must be high; fast removal prevents the formation of a barrier to continued deposition of the coating element and also prevents contamination of the coating.

Another example is the silicidizing of tantalum, basically an oxidation– reduction reaction. The packing is sodium fluoride and silicon. After deposition, the coating diffuses continuously into the substrate, according to the following reactions:

$$6\ \mathrm{NaF}\ (g) + 2\ \mathrm{Si}\ (l) \longrightarrow \mathrm{Si_2F_6}\ (g) + 6\ \mathrm{Na}\ (g)$$

$$\mathrm{Ta} + 4\ \mathrm{Si_2F_6}\ (g) \longrightarrow 6\ \mathrm{SiF_4}\ (g) + \mathrm{TaSi_2}\ (\mathrm{alloy})$$

$$3\ \mathrm{SiF_4}\ (g) + \mathrm{Si}\ (l) \longrightarrow 2\ \mathrm{Si_2F_6}\ (g)$$

If the rules for volatiles and thermodynamics of the halides are followed, the reaction can be used for aluminizing, silicidizing, chromizing, and similar processing.

Silicide coatings of refractory metals may contain as much as three to five coating components other than silicon. A mixture of halide carriers is selected containing the best carrier for each component.

The outstanding characteristics of a fluidized bed are its high heat-transfer coefficient and its turbulence, which yield optimum temperature uniformity throughout the bed. These factors contribute to the successful treatment of large, complex objects, which might not be possible by other means.

Analogous to the carburization of steel is the nitrogen case-hardening of steel in which surfaces are hardened by heating the steel in the presence of nascent nitrogen. The nitrogen reacts with impurities or alloy constituents, eg, aluminum, chromium, vanadium, tungsten, etc, to form dispersed nitrides. Other examples of cementation coatings include the surface-hardening of steel by immersion in a molten sodium cyanide bath at 850–870°C to promote codiffusion of both carbon and nitrogen into the surface. Iron and steel are cemented with silicon at 800°C, and iron, nickel, and copper with tungsten at 800–1350°C. Similarly, iron and nickel are cemented with molybdenum by heating in ferromolybdenum. In the same temperature range, titanium coatings are obtained on ferrous metals by heating them for 1.5 h in a powdered mixture of sponge titanium containing 0.5–6.0% Fe at 800–1200°C. Boride coatings are produced by heating iron, cobalt, or nickel substrates in boron powder at 950°C in a vacuum of 67 mPa (5×10^{-4} mm Hg).

The most advanced cementation coatings are the intermetallic coatings, specifically silicides and aluminides, that protect refractory metals. The earliest and simplest of these is the molybdenum silicide coating developed for molybdenum substrates. It consists largely of $\mathrm{MoSi_2}$ but is modified by additions of boron, manganese, titanium, chromium, beryllium, etc, singly or in combinations. Coating systems for niobium are more complex, but oxidation-resistant coatings result by diffusing silicon, chromium, aluminum, boron, titanium, and beryllium singly or in combinations into the substrate. Diffusion coatings for tantalum are based on the formation of $\mathrm{TaAl_3}$, an oxidation-resistant material. Silicide coatings on tantalum also provide significant oxidation protection. Aluminum, boron, or manganese are often added as modifiers. Tungsten presents a more difficult problem, but various silicide coatings provide a measure of protection at temperatures as high as 1815°C. After 10 h at this temperature, $\mathrm{WSi_3}$ is converted to the glassy $\mathrm{W_5Si_4O_2}$ composition.

An activated slurry process can be used to place impervious silicon carbide coatings on graphite. A slurry of silicon carbide, carbon, and appropriate organic binders is applied to the surface of the graphite by spraying, dipping, or painting. After a low temperature treatment to drive off the binder, the coated substance is heated in the presence of silicon vapor, which diffuses into the surface to form a SiC layer on the graphite. The coating composition can vary from self-bonded silicon carbide containing only a few percent of uncombined silicon to SiC crystals bonded with a continuous silicon matrix. Successful SiC coatings on complex graphite shapes have been obtained with isotropic graphite substrates possessing compatible thermal expansion coefficients. Resistance to oxidation at 1400°C for 100 h or more has been accompanied by successful service in nuclear reactor environments. Coatings of SiC on graphite fail under compressive loads or impact at levels that do not damage uncoated graphite. This occurs because the graphite is less brittle and deforms under load, whereas the thin, more rigid SiC coating does not.

Aluminide and silicide cementation coatings such as $TaAl_3$ on tantalum and $MoSi_2$ on molybdenum oxidize at slow rates and possess some inherent self-repair characteristics. Fine cracks that appear and are common to these coatings can be tolerated because stable, protective oxides form within the cracks and seal them. Thermal cycling, however, accelerates failure because of thermal expansion mismatch that ultimately disrupts the protective oxide coating.

An important application is the aluminizing of air foils of gas-turbine engines made of high temperature Ni- or Co-base alloys. The aluminizing can be carried out either in a pack process or in an out-of-the-pack process.

Cementation coatings rely on diffusion to develop the desired surface alloy layer. Not only does the coating continue to diffuse into the substrate during service, thereby depleting the surface coating, but often the substrate material diffuses into the surface where it can be oxidized. Because the diffusion rate is temperature dependent, this may occur slowly at lower service temperatures.

The substrate has to be prepared for cementation. The surface must be clean and free of oxide. Corners and edges are particularly important in diffusion-type coatings; sharp edges are usually detrimental. Barrel finishing, ie, tumbling in a barrel with abrasive media, may result in the desired shape.

The quality of cementation coatings does not necessarily equal that produced by other techniques. There are cases, however, where a moderate degree of corrosion resistance is useful and where other requirements are best met by the application of cementation. Using other processes, it may be difficult to coat porous surfaces or preserve the contour of machined surfaces. Cementation may then be the method of choice. Coatings for molybdenum, niobium, tantalum, and tungsten not easily obtained by other means can be achieved by this method. Coated refractory metal systems have been applied to leading edges, skins, and structural members of space vehicles, rocket combustion chambers, nozzle inserts, extension skirts, and to vanes or blades for advanced gas-turbine engines.

4.2. Metalliding

Metalliding, a General Electric Company process (9), is a high temperature electrolytic technique in which an anode and a cathode are suspended in a molten fluoride salt bath. As a direct current is passed from the anode to the cathode, the anode material diffuses into the surface of the cathode, which produces a uniform, pore-free alloy rather than the typical plate usually associated with electrolytic processes. The process is called metalliding because it encompasses the interaction, mostly in the solid state, of many metals and metalloids ranging from beryllium to uranium. It is operated at 500–1200°C in an inert atmosphere and a metal vessel; the coulombic yields are usually quantitative, and processing times are short; controlled uniform coatings from a few to many μm are obtained, many of which are unavailable by other techniques. Diffusion rates are high and the process can be run continuously. Boron and silicon anodes can be diffused into most metals of Groups 5–11 (VB, VIB, VIIB, VIII, and IB) of the Periodic Table.

The borides are extremely hard (9.8–29 GPa (1000–3000 kgf/mm^2) Knoop) and, in the case of molybdenum, $>$39 GPa (4000 kfg/mm^2) (see Hardness). However, oxidation resistance is usually poor unless a subsequent coating is formed, such as silicidizing or chromizing, which imparts oxidation resistance. Silicides are generally very oxidation resistant, but not as hard as borides. Silicide coatings formed on molybdenum (51 μm in 3 h) at 675°C have superior oxidation resistance. At these low temperatures, the molybdenum substrate does not embrittle and the coatings are quite flexible.

The metals that can be aluminized act similarly with boron, as do the metals in Group 4 (IVB). Resistance to oxidation is the principal benefit. Titanizing and zirconizing are extremely sensitive to oxygen impurities, and when the salts are completely free of oxides and blanketed by high purity argon, excellent diffusion coatings can be formed in LiF at 900–1100°C. The most promising area for applications appears to be with nickel- and iron-based alloys where intermetallic compound formation gives rise to many unique coatings that are tough and oxidation resistant. Beryllide coatings can be formed on approximately 40 metals ranging from titanium to uranium and with compositions such as $TiBe_{12}$, Ni_5Be_{21}, and UBe_{13}. They are very hard, usually oxidation resistant, and easily formed up to several mils in thickness.

Moving further to the right in the Periodic Table, the scope of the metalliding processes becomes much more limited. Iron, cobalt, and nickel are restricted to approximately 12 metals into which they can be diffused. Iron can be diffused into cobalt and nickel with very good results, but the reverse is unsuccessful. The diffusion of nickel into molybdenum, tungsten, and copper has been successful. Germanium occupies a slightly higher position in the electromotive series than nickel and therefore diffuses into nickel; it is below cobalt and iron, however, as determined by voltage measurements in the salts, and cannot be diffused into either of these metals, even at high voltages and current densities. It is readily diffused into molybdenum, palladium, copper, platinum, gold, and Monel.

5. Microstructure of Coatings

The microstructure of bulk coatings resembles the normal microstructure of metals and alloys produced by melt solidification. The microstructure of particulate-deposited materials resembles a cross between rapidly solidified bulk materials having severe deformation and powder compacts produced by pressing and sintering. A special feature of particulate coatings is a significant degree (ca 2–20 vol %) of porosity that strongly affects the properties of the deposit.

The microstructure and imperfection content of coatings produced by atomistic deposition processes can be varied over a very wide range to produce structures and properties similar to or totally different from bulk processed materials. In the latter case, the deposited materials may have high intrinsic stress, high point-defect concentration, extremely fine grain size, oriented microstructure, metastable phases, incorporated impurities, and macro- and microporosity. All of these may affect the physical, chemical, and mechanical properties of the coating.

5.1. PVD Condensates

Physical vapor deposition condensates can deposit as single-crystal films on certain crystal planes of single-crystal substrates, ie, by epitaxial growth or, in the more general case, the deposits are polycrystalline. In the case of films deposited by evaporation techniques, the main variables are the nature of the substrates; the temperature of the substrate during deposition; the rate of deposition; and the deposit thickness. Contrary to what might be expected, the deposit does not initially form a continuous film of one monolayer and grow. Instead, three-dimensional nuclei are formed on favored sites on the substrates, such as cleavage steps on a single-crystal substrate. These nuclei grow laterally and in thickness (growth state), ultimately impinging on each other to form a continuous film. The average thickness at which a continuous film forms depends on the nucleation density and the deposition temperature and rate; both influence the surface mobility of the adatom. This thickness varies from 1 nm for Ni condensed at 15 K to 100 nm for Au condensed at 600 K.

The microstructure and morphology of thick single-phase films have been extensively studied for a wide variety of metals, alloys, and refractory compounds. The structure model first proposed is shown in Figure 6 (10). It was subsequently modified as shown in Figure 7 (10, 11).

At low temperatures, the surface mobility of the atoms is limited and the structure grows as tapered crystallites from a limited number of nuclei. It is not a full density structure but contains longitudinal porosity on the order of a few tens of nm width between the tapered crystallites. It also contains numerous dislocations with a high level of residual stress. Such a structure has also been called botryoidal and corresponds to Zone 1 in Figures 6 and 7.

	Zone 1	Zone 2	Zone 3
metals	$<0.3\ T_m$	$0.3–0.45\ T_{\mathrm{m}}$	$>0.45\ T_m$
oxides	$<0.26\ T_m$	$0.26–0.45\ T_{\mathrm{m}}$	$>0.45\ T_m$

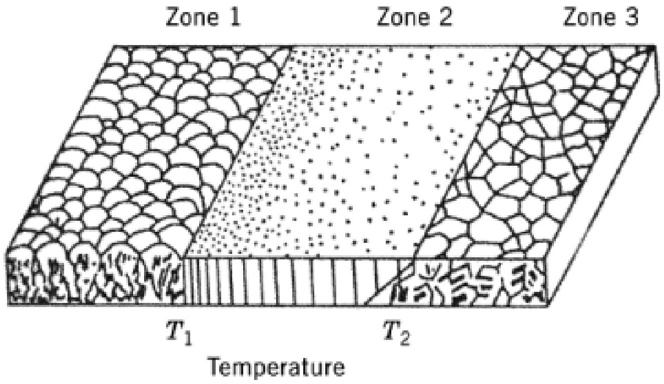

Fig. 6. Structural zones in condensates at various substrate temperatures. When T_{m} is the melting point (10):

As the substrate temperature increases, the surface mobility increases and the structural morphology first transforms to that of Zone T, ie, tightly packed fibrous grains having weak grain boundaries, and then to a full density columnar morphology corresponding to Zone 2 (see Fig. 7).

The size of the columnar grains increases as the condensation temperature increases. Finally, at still higher temperatures, the structure shows an equiaxed grain morphology, Zone 3. For pure metals and single-phase alloys, T_1 is the transition temperature between Zone 1 and Zone 2 and T_2 is the transition temperature between Zone 2 and Zone 3. According to the original model (10), T_1 is 0.3 T_{m} for metals and 0.22–0.26 T_{m} for oxides, whereas T_2 is 0.4–0.45 T_{m} for both (T_{m} is the melting point in K) (see Fig. 6).

The modification shows that the transition temperature may vary significantly from those stated above and in general shift to higher temperatures as the gas pressure in the synthesis process increases. The transition from one zone to the next is not abrupt, but smooth. Hence, the transition temperatures should not be considered as absolute but as guidelines. Furthermore, not all zones are found in all types of deposit. For example, Zone T (see Fig. 7) is not prominent in pure metals, but becomes more pronounced in complex alloys, compounds, or in deposits produced at higher gas pressures. Zone 3 is not often seen in materials with high melting points.

5.2. CVD Coatings

As in PVD, the structure of the deposited material depends on the temperature and supersaturation, roughly as pictured in Figure 8 (12). In the case of CVD, however, the effective supersaturation, ie, the local effective concentration in the gas phase of the materials to be deposited, relative to its equilibrium concentration, depends not only on concentration, but on temperature. The reaction is thermally activated. Because the effective supersaturation for thermally activated reactions increases with temperature, the opposing tendencies can lead in some cases to a reversal of the sequence of crystalline forms listed in Figure 8, as temperature is increased (12).

Growth of columnar grains is characteristic of many materials in certain ranges of conditions. This structure results from uninterrupted growth toward the source of supply. Where growth in one crystallographic direction is preferred over others, grains having that orientation engulf those of other orientations.

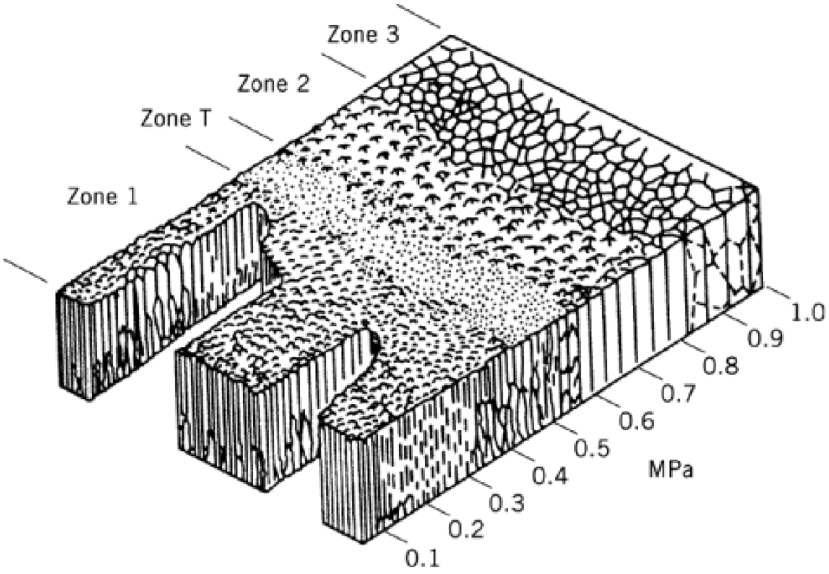

Fig. 7. Structural zones in condensates showing the effect of gas pressure. To convert MPa to psi, multiply by 145. See text.

Increasing supersaturation ↓

Epitaxial growth
Platelets
Whiskers
Dendrites
Polycrystals
Fine-grained polycrystals
Amorphous deposits
Gas-phase nucleated snow

↑ Increasing temperature

Fig. 8. Morphological effects of supersaturations and temperature on vapor deposited materials (12).

5.3. Electrodeposits

Columnar structures are characteristic of deposits from solutions, especially acid solutions, containing no additives, high metal-ion concentration solutions with high deposition rates, or from low metal-ion concentration solutions at low deposition rates. These usually exhibit lower tensile strength, elongation, and hardness than other structures, but are generally more ductile. Such deposits are usually of highest purity (high density) and low electrical resistivity.

Fibrous structures represent a grain refinement of columnar structure. Stress-relieving additives, eg, saccharin or coumarin, promote such refinement, as do high deposition rates. These may be considered intermediate in properties between columnar and fine-grained structures.

Fine-grained deposits are usually obtained from complex ion solutions, eg, cyanide, or using certain addition agents. These deposits are less pure, less dense, and exhibit higher electrical resistivities because of the presence of foreign material.

Banded structures are characteristic of some alloy deposits and of bright deposits resulting from brightening addition agents. Plating-current modifications (periodic reverse (PR), interrupted current (IC), pulse) favor the conversion of normal structure from a solution to a banded structure. These deposits generally possess higher tensile strength, hardness, and internal stress and lower ductility than the other structures.

Grain size varies widely, from 10 to 5000 nm. The grain size of fine-grained or banded deposits is usually 10–100 nm. Some metals, notably copper, nickel, cobalt and gold, can be deposited in all four types of grain structure, depending on the solution composition and plating conditions.

6. Characterization and Testing

Evaluation for high temperature service has been less reliable and less standardized than evaluations for conventional service. This is partly the result of the difficulty of reproducing in the laboratory the severe service conditions capable of yielding acceptable correlations. Test conditions do not necessarily simulate the geometrical and environmental conditions of the service. Nevertheless, screening tests yield primary behavioral parameters that usually define the limits of operation. Various tests are employed for the characterization of refractory coatings: optical and electron microscopy and metallographic and microscopic observation, which evaluate substrate and coating structures, coating thickness, bond characteristics, and detection of inclusions; electron microscope and scanning and transmission electron microscopy, which evaluate detection of injurious inclusions in the substrate or coating; x-ray diffraction (electron), which evaluates the effects of processing on coating composition, ie, composition of coating at various depths within the coating can be determined by controlled polishing followed by x-ray; chemical microscopy, eg, Auger electron spectroscopy, electron spectroscopy for chemical analysis, and secondary ion mass spectroscopy, which determine chemical analysis of surface and subsurface layers, ie, resolution can be as low as 5-nm segregation at imperfections; bend, tensile, and tensile bond tests, which determine adhesion, the ductility effect of coating or processing on base-material strength, ductility, and elongation; microhardness transverse and corrosion tests, which gauge the cross-sectional hardness of the coating and substrate, the effect of processing on the substrate, and ductility; fatigue tests, which show the effect of coating or coating process on the substrate, fatigue properties, and fatigue strength of a coated-metal system; thermal tests, eg, chemical oxidation and thermal cycling with sustained load in air, which evaluate oxidation and thermal shock resistance, the effect of coating on ductility of base and specimen creep on coating, integrity, and thermal shock and oxidation resistance; and the plasma or oxyacetylene torch test, which shows coating emissivity, thermal shock and oxidation resistance, and melting point.

Nondestructive tests for refractory coatings include the following: evaporgraph which detects residual moisture left behind in cracks, pores, or flaws, and evaluates discontinuities on flat panel surfaces; electromagnetic inspection, which evaluates pores, cracks, and pits; ultrasonic inspection, which shows surface and subsurface flaws, unsuitable for thin skins; fluorescent particle inspection, ie, finely divided, fluorescent-coated magnetic particles attracted to and outlining the pattern of any magnetic leakage fields created by discontinuities, which determine surface cracks, pits, and similar coating defects; red-dye penetrant, which shows surface flaws; radiographic inspection, which shows small coating flaws in assembled structures, although the sensitivity is difficult to control; and microscopy, which evaluates flaws by observation of oxidation and weakness in bond strength resulting from thermal shock. This test is very reliable after an exposure test. Many of these factors are unsuitable for corner or edge defects.

7. Selection Criteria

The selection of a particular deposition process depends on the material to be deposited and its availability; rate of deposition; limitations imposed by the substrate, eg, maximum deposition temperature; adhesion of deposit to substrate; throwing power; apparatus required; cost; and ecological considerations. Criteria for CVD, electrodeposition, and thermal spraying are given in Table 2 (13).

Table 2. Characteristics of Deposition Processes

Characteristic	Evaporation	Ion plating	Sputtering	Chemical vapor deposition	Electro- deposition	Thermal spraying
mechanism of production of depositing species	thermal energy	thermal energy	momentum transfer	chemical reaction	deposition from solution	from flames, arcs, or plasmas
deposition rate, nm/min	$\leq 75,000$	$\leq 25,000$	low except for pure metals[a]	moderate, eg, 20–2500	low to high	very high
depositing specie	atoms and ions	atoms and ions	atoms and ions	atoms	ions	droplets
throwing power						
for complex shaped object	poor line-of-sight coverage[b]	good[c]	good[c]	good	good	none
into small blind holes	poor	poor	poor	limited	limited	very limited
deposition of						
metal	positive	positive	positive	positive	positive but limited	positive
alloy	positive	positive	positive	limited	limited	positive
refractory compound	positive	positive	positive	positive	limited	positive
energy, depositing species, eV	ca 0.1–0.5	1–100	1–100	high for PACVD	can be high	can be high
bombardment of substrate and deposit by inert gas ions	normally not	yes	possible, depending on geometry	possible	none	positive
growth interface perturbation	normally not	yes	yes	yes, by rubbing	none	none
substrate heating by external means	normally yes	yes	generally not	no	none	normally not

[a] For copper, 1000 nm/min.

[b] Except by gas scattering.

[c] Thickness distributions may be nonuniform.

8. Applications

Coatings can be classified into six categories: chemically functional, mechanically functional, optically functional, electrically functional, biomedical, and decorative. In addition, there are some unique applications in the aerospace program, such as the ablative coatings of pyrolytic carbon and graphite- and silica-based materials for protection of nose cones and the space shuttle during reentry (see Ablative materials). Another unique energy-related application is the coating of low atomic number (low-Z) elements such as TiC for the first wall of thermonuclear reactors to minimize contamination of the plasma.

8.1. Chemically Functional

Refractory coatings are used for corrosion-resistant high temperature service in gas turbine and diesel engines, components such as crucibles, thermocouple protection tubing, valve parts, etc.

Blades and vanes used in the hot-end of a gas turbine are subject to high stresses in a highly corrosive environment of oxygen, sulfur, and chlorine-containing gases. A single or monolithic material such as a high temperature alloy cannot provide protection against both. A bulk alloy designed for its mechanical properties provides the corrosion resistance by means of an overlay coating of an M–Cr–Al–Y alloy where M stands for Ni, Co, or Fe or Ni $_+$ Co. In production, the coating is deposited by electron beam evaporation; in the laboratory, by sputtering or plasma spraying. These overlay coatings have several advantages over diffusion aluminide coatings. The latter lose their effectiveness at higher temperatures because of interactions with the substrate. The composition and properties of overlay coatings can be more easily tailored to the needs of specific applications. In addition, coatings of stabilized zirconia are used as thermal barriers in diesel engines and gas turbines to raise operating temperature of the engine and protect it from corrosive fuels.

Boron nitride and titanium diboride coatings are used on graphite for the evaporation of liquid aluminum.

8.2. Mechanically Functional

Refractory coatings are used in engine parts, landing gears, soft-film lubricants, and cutting and forming tools (see Tool materials).

A large and rapidly growing application is the coating of cutting and forming tools and industrial knives with carbides, nitrides, oxides, or multiple layers of these materials. These coatings are deposited by CVD and PVD methods and increase the tool life by factors ranging from 2 to 10, depending on the operating conditions. Cermet coatings such as TiB_2–Ni are also deposited electrolytically to provide wear resistance.

These coatings are also employed as solid lubricants in engine components. Refractory materials such as MoS_2 and WSe_2 are lamellar compounds and provide very effective solid-state lubrication in spacecraft bearings and components used in radiation environments where conventional organic liquid lubricants are not stable (see Lubrication and lubricants).

8.3. Optically Functional

Laser optics, layer architectural glass panels (up to 3×4.3 m), lenses, TV-camera optical elements, and similar applications require optically functional coatings.

A large and expanding operation is coatings on architectural glass panels used in buildings to alter the transmission and reflection properties of glass (qv) in various wavelength ranges and thus conserve energy usage. Furthermore, attractive visual effects, such as a bronze appearance, can be achieved. These coatings consist of multiple layers of oxides and metals (the precise compositions are proprietary) and are deposited in large in-line sputtering and evaporation systems. Future applications should utilize the selective transmission of coatings of nitrides, carbides, and borides in solar-thermal applications.

Another growing application that overlaps the electrically functional area is the use of transparent conductive coatings or tin oxide, indium–tin oxide, and similar materials in photovoltaic solar cells and various optic electronic applications (see Photovoltaic cells). These coatings are deposited by PVD techniques as well as by spray pyrolysis, which is a CVD process.

8.4. Electrically Functional

Refractory coatings are used in semiconductor devices, capacitors, resistors, magnetic tape, disk memories, superconductors, solar cells, and diffusion barriers to impurity contamination from the substrate to the active layer.

Thin-film capacitors and resistors contain such dielectric materials as silicon monoxide and dioxide, tantalum oxide, silicon nitride, and the like. These coatings are deposited by a variety of atomic deposition techniques (PVD, CVD) and thick-film methods. In some cases coatings, eg, SiO, are formed by thermal oxidation. An important application is the deposition of passivating layers of SiO_2 or SiO_2–Si_3N_4 by plasma-assisted CVD techniques. A newer area is insulation coatings for GaAs devices formed by plasma-assisted oxidation methods and the deposition of amorphous silicon by CVD techniques. The fabrication of tungsten-emitter elements for thermionic convertors by CVD is another application. Thermal sprayed coatings are used widely for thicker spot coatings (wire attachment) and current conductors, ie, on collectors (silicon solar cells). Typical products in use include polypropylene foil capacitors, material components, varistors, etc.

8.5. Biomedical

Heart-valve parts are fabricated from pyrolytic carbon, which is compatible with living tissue. Such parts are produced by high temperature pyrolysis of gases such as methane. Other potential biomedical applications are dental implants and other prostheses where a seal between the implant and the living biological surface is essential. Plasma and arc-wire sprayed coatings are used on prosthetic devices, eg, hip implants, to achieve better bone/tissue attachments (see Prosthetic and biomedical devices).

8.6. Decorative

Titanium nitride has a golden color and is used extensively to coat steel and cemented carbide substrates for watch cases, watch bands, eyeglass frames, etc. It provides excellent scratch resistance as well as the desired aesthetic appearance, and it replaces gold coatings used previously.

9. Economic Aspects

Diffusion aluminide and silicide coatings on external and internal surfaces for high temperature corrosion protection in parts such as gas-turbine blades is estimated at $\$40 \times 10^6$/yr in North America and about $\$50 \times 10^6$ worldwide.

Overlay coatings onto gas-turbine blades and vanes of M–Cr–Al–Y type alloys by electron beam evaporation is estimated at $\$10 \times 10^6$ to coat 200,000 parts at an average cost of $50 per part.

Hard facing of various components in the aircraft gas-turbine engine and in industrial applications for textile machinery parts, oil and gas machinery parts, paper-slitting knives, etc, is estimated at $\$1 \times 10^9$ in 1995 with an estimated growth rate of 5% annually. The mix is approximately 45% aerospace applications, 55% industrial applications. Additionally, repair coatings for gas-turbine blades and vanes is estimated at $\$500 \times 10^6$. These coatings are primarily deposited by plasma spray, arc-wire, HVOF, and detonation gun techniques.

Refractory compound coatings of carbides, nitrides, and oxides on cemented carbide cutting tools, mainly by the CVD process, are estimated at $\$300 \times 10^6$ annually worldwide.

Another application is the coating of complex-shaped high speed steel cutting tools such as drills, holes, gear-cutters, etc, using a titanium nitride coating deposited by the methods of plasma-aided reactive evaporation and ion plating. A very rough estimate of the add-on value of the coating is $\$(50) \times 10^6$ in 1995, but with a rapid growth rate of 100–300% expected into the year 2000. The same processes are also used to deposit gold-colored wear-resistant titanium nitride coatings on watch bezels, watchbands, and other decorative jewelry items. A very rough estimate is $\$20 \times 10^6$ annually. The last two applications are practiced principally in Japan, Europe, and the United States.

Refractory coatings extensively used in the semiconductor and optical materials industry have an annual add-on value exceeding $\$10^9$.

The thermal spraying industry had rapid, 30% annual growth from 1960–1989 because of the acceptance of this process by the aircraft gas-turbine industry. Over 300 separate coating areas were used in each engine as of 1995. This application area was 50% of the total thermal spraying market. A slump in this market niche reduced industry sales by 30% from 1990 to 1995. Growth has resumed owing to broader acceptance by other industry segments, such as the automotive industry. Significant merger activity in the early 1990s reduced ownership in this industry, formerly dominated by U.S. companies, to two principal players: Sulzer

Metco (Wohlen, Switzerland), which had annual sales in 1995 of \$120 × 10^6, and Eutetic Castolin (Lausanne, Switzerland), with \$80 × 10^6. In contrast, Praxair Materials (Indiana) had only \$60/yr.

There are job shops and applicators in the thermal spraying business and the annual value was about \$1 × 10^9 in 1995. Up to 65% of the total company sales represented materials prices from \$1–\$25/kg. Equipment prices for spray technology and the number of units sold per annum in the mid-1990s are given in Table 3.

Table 3. Spraying Processes Equipment Prices

Equipment type	Price, \$ × 10^3	Units sold/yr
	Spray equipment	
plasma	25–175	100
wire spray	10–30	1000
[a]	40–90	250
large combustion powder	5–50	300
	Automation equipment	
automated cells	100–2000	50
water jet coating strippers	100–1000	30

[a] HVOF = high velocity oxy fuel.

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