Applications of metallurgical coatings

The surface of a coated material can possess structure and properties quite different from those of the bulk material, thus allowing components to be individually tailored for specialized needs.

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What do we mean by a "metallurgical coating?" A *coating* may be defined as a near-surface region having properties differing from the bulk of the material, and coatings may be desirable or even necessary for a variety of reasons including economics, unique properties or the engineering and design flexibility that can be obtained by separating the surface properties from the structural requirements. *Metallurgy*, of course, is the art and science of procuring, shaping, treating and use of metals; but when we study metallurgical coatings we are concerned not only with the physical and mechanical properties of the materials themselves but also with the interaction of materials with their environments and the substrates. Thus "metallurgical coatings" involves us with a broad spectrum of problems ranging from deformation properties, to chemical interactions, to solid-state properties.

In some cases, a coating is a new material deposited onto the substrate by any of a variety of methods and 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 added material and the substrate material. This is called a "conversion" coating, or a "chemical conversion" coating when chemical changes are involved. So-called "coatings" may also be formed by altering the properties of the surface by melting and quenching, by mechanical deformation, or by other processes that change the properties without changing the composition (as in figure 1, for example).

Coatings are a fact of life in many materials used in modern technology, because there is frequently a requirement that the material possess a number of different properties a single (or "monolithic") material cannot supply. Turbine blades and vanes in gas-turbine engines, for example, operate at very high temperatures in a highly corrosive environment. Their high-temperature strength is provided by the nickel- or cobalt-base bulk alloy, whereas their corrosion resistance is enhanced by an alloy coating (Ni-Co-Cr-Al-Y) deposited onto the blades or vane. Another example is the coating of architectural glass to control the energy throughput or losses. A very recent application is the deposition of chromium onto plastic automobile bumpers and grilles for decorative and weight-saving reasons. (See figure 2, page 28, in the article by John Vossen in this issue of PHYSICS TODAY.)

Coatings may be composed of one or more layers of a metal, alloy, intermetallic compound, ceramic material or a polymeric material. They are produced by a variety of techniques. An example is shown in figure 2, which illustrates the development of an ultrafine neurological electrode to be used in the diagnosis of chronic epilepsy.[1] It is a coaxial wire with a total diameter of 150–180 microns, high stiffness (elastic modulus 60×10^6 psi), significant ductility for resistance to brittle fracture and biocompatibility. The successive layers consist of a central core of tungsten alloy wire, with a SiO_x insulator coating produced by chemical vapor deposition, a titanium conducting layer deposited by evaporation and an outer polymeric coating produced by a chemical reaction. The probe has been developed to replace a 750-micron diameter coaxial cable currently being used and will lessen patient trauma and related problems.

The table on page 54 categorizes the wide variety of ways by which coatings may be fabricated.

In atomistic deposition processes, the atoms form a structure by condensing on the substrate and migrating to sites where nucleation occurs. Further adatoms cause the nuclei to grow and coalesce. Additional adatoms increase the film thickness. Under many deposition conditions, the adatoms do not achieve their lowest energy configurations, and the resulting structure contains high concentrations of structural imperfections. Often the depositing atoms react with the substrate material to form a complex interfacial region.

Particulate deposition processes involve molten or solid particles, and the resulting microstructure of the deposit depends on the solidification or sintering of the particles. **Bulk coatings** involve the application of large amounts of coating material to the surface at one time, as in painting, for example. **Surface modification** involves ion, thermal, mechanical, or chemical treatments, which alter the surface composition or properties (figure 1). All of these techniques are widely used to form coatings for special applications.

In the remainder of this article we will discuss coatings formed by atomistic deposition processes. The sources of atoms for these deposition processes can be thermal vaporization (vacuum deposition) or sputtering (sputter deposition) in a vacuum, vaporized chemical species in a carrier gas (chemical vapor deposition), or ionic species in an electrolyte (electrodeposition). In low-energy atomistic deposition processes, the depositing species impinge on the sur-

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0031-9228 / 80 / 050050-05/ $00.50

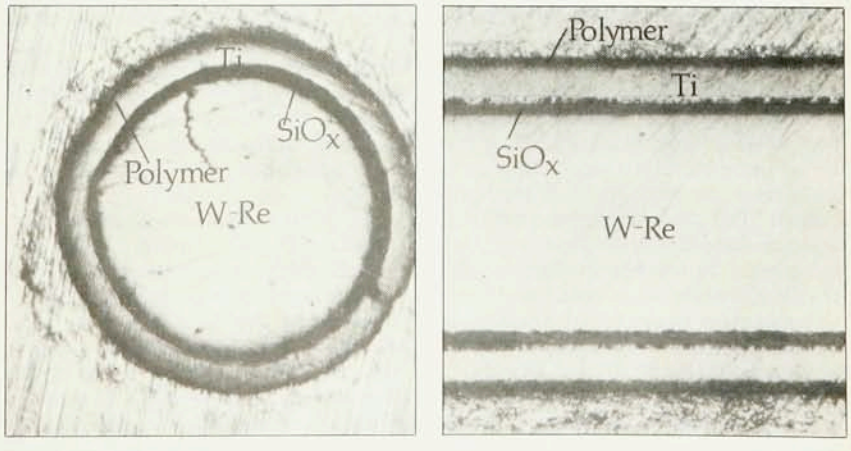
face, migrate over the surface to a nucleation site where they condense and grow into a coating. The nucleation and growth modes of the condensing species determine the crystallography and microstructure of the coating. For high-energy deposition processes, the depositing particles react with or penetrate into the substrate surface.

Microstructure and properties

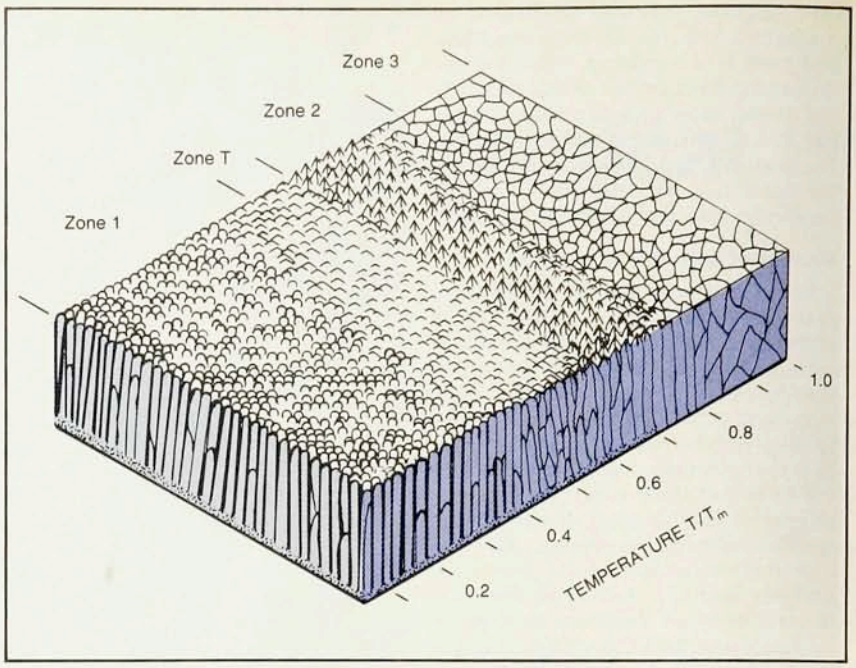
In electrodeposition, the growth process typically involves condensation of atoms at a kink site on the substrate surface, followed by layered growth of the deposit. Adatom mobility may vary with crystal orientation. From field-ion-microscopy stripping studies of copper electrodeposited on tungsten one finds that there is surface rearrangement of the tungsten atoms during the electrodeposition process. Electrodeposited material does not grow in a uniform manner; rather it becomes faceted, develops dendrites and other surface discontinuities. Thus the microstructure of electrodeposited coatings may vary from relatively defect-free single crystals usually grown on single-crystal substrates to highly columnar and faceted structures. In the electroplating process, organic additives may be added to modify the nucleation process and to eliminate undesirable growth modes. This technique results in a microstructure more nearly that of bulk material formed by conventional metallurgical processes. Electrodeposition from a molten-salt electrolyte allows the deposition of many materials not available from aqueous electrolytes.

In vacuum processes, the depositing species may have energies ranging from thermal (a few tenths of an electron volt) for evaporation, to moderate energies (ten to hundreds of electron volts) for sputtered atoms, to high energies for accelerated species such as those used in ion implantation. These energies have an important but poorly understood effect on interfacial interaction, nucleation and growth. If the substrate atoms and the depositing atoms react chemically, and if diffusion is possible, the "diffusion" or "compound" interfacial region that forms consists of compounds and/or alloys that modify the effective surface upon which the deposit grows. Low-energy electron diffraction studies have shown that this interfacial reaction is very sensitive to surface condition and process parameters. If the coating and substrate materials are not chemically reactive and are insoluble, the interfacial region will be confined to an abrupt discontinuity in composition. This type of interface may be modified by bombardment with high-energy particles to give high defect concentrations and implantation of ions resulting in a

Columnar structures on a beryllium surface. These 500-nanometer-high features are examples of the complex surface morphology that can occur when materials are bombarded by ions at a flux of about 2×10^{21} ions cm^{-2}. (Sandia National Laboratories scanning-electron micrograph from a study conducted by J. K. G. Panitz, D. J. Sharp and J. T. Healey.) Figure 1



Multilayer neurological probe for use in the diagnosis of chronic epilepsy. The tungsten alloy central core is coated with an SiO_x insulator by chemical vapor deposition, a titanium conducting layer by evaporation and an outer polymeric coating by chemical reaction. Total diameter of the coaxial wire is 150–180 microns. (From reference 1.) Figure 2



Structural zone model for vacuum deposited films by B. A. Movchan and A. V. Demchishin (reference 2). The zones are determined by the ratio, T/T_m, of surface temperature to the melting point of the deposited material. "Zone T" is a transitional zone proposed by J. A. Thornton in Annual Review Material Science **7**, 239 (1977). Figure 3

"pseudodiffusion" type of interface. The type of interface formed will influence the properties of the deposited coating. In many circumstances, these interfacial regions are of very limited thickness and pose a challenge to those interested in compositional, phase, microstructural and property analysis.

The microstructure of the depositing coating in atomic deposition processes depends on how the adatoms are incorporated into the existing structure. Surface roughness and geometrical shadowing will lead to preferential growth of the elevated regions, giving a columnar type of microstructure to the deposits. This microstructure will be modified by substrate temperature, surface diffusion of the atoms, ion bombardment during deposition, impurity atom incorporation and angle of incidence of the depositing adatom flux. Figure 3 shows B. A. Movchan and A. V. Demchishin's[2] structural zone model for vacuum-deposited films. The model consists of three zones determined by the ratio of the surface temperature to the melting point of the deposited material. Zone 1 results when adatom diffusion is insufficient to overcome shadowing effects and gives a columnar fine grained microstructure with low density boundaries between columns. The individual columns are polycrystalline and are usually highly defected with very small grain size (50–1000 Å). Figure 4 shows the fracture surface of a thick deposit of aluminum with such a columnar structure. In Zone 2, adatom diffusion dominates and the columnar structure consists of less defected and larger grains with higher density boundaries between columns. Figure 4 shows the fracture surface of a thick deposit of stainless steel with Zone 2 growth. In Zone 3, bulk diffusion and recrystallization dominate yielding material more closely resembling that of materials formed by melting processes. The nucleation and growth of vacuum-deposited films have been studied *in situ* by low-energy electron diffraction, transmission electron diffraction and other such analytic techniques where the deposition process is compatible with the analytical process.

In chemical vapor deposition, the chemical species containing the film atoms is generally reduced or decomposed on the substrate surface, often at high temperature. Care must be taken to control the interface reaction between coating and substrate and between the substrate and the gaseous reaction products. The coating microstructure that develops is very similar to that developed by the vacuum deposition processes, ranging from small-grained columnar structures to large-grained equiaxed or oriented structures.

Each of the atomistic deposition processes has the potential of depositing materials that vary significantly from the conventional metallurgically processed material. The deposited materials may have high intrinsic stresses, high point-defect concentration, extremely fine grain size, oriented microstructures, metastable phases, incorporated impurities, and macro and micro porosity. These properties may be reflected in the physical properties of the materials and by their response to applied stresses such as mechanical loads, chemical environments, thermal shock or fatigue loading. Among the metallurgical properties that may be affected are: elastic constants, tensile strength, fracture toughness, fatigue strength, hardness, diffusion rates, friction and wear properties, and corrosion resistance.

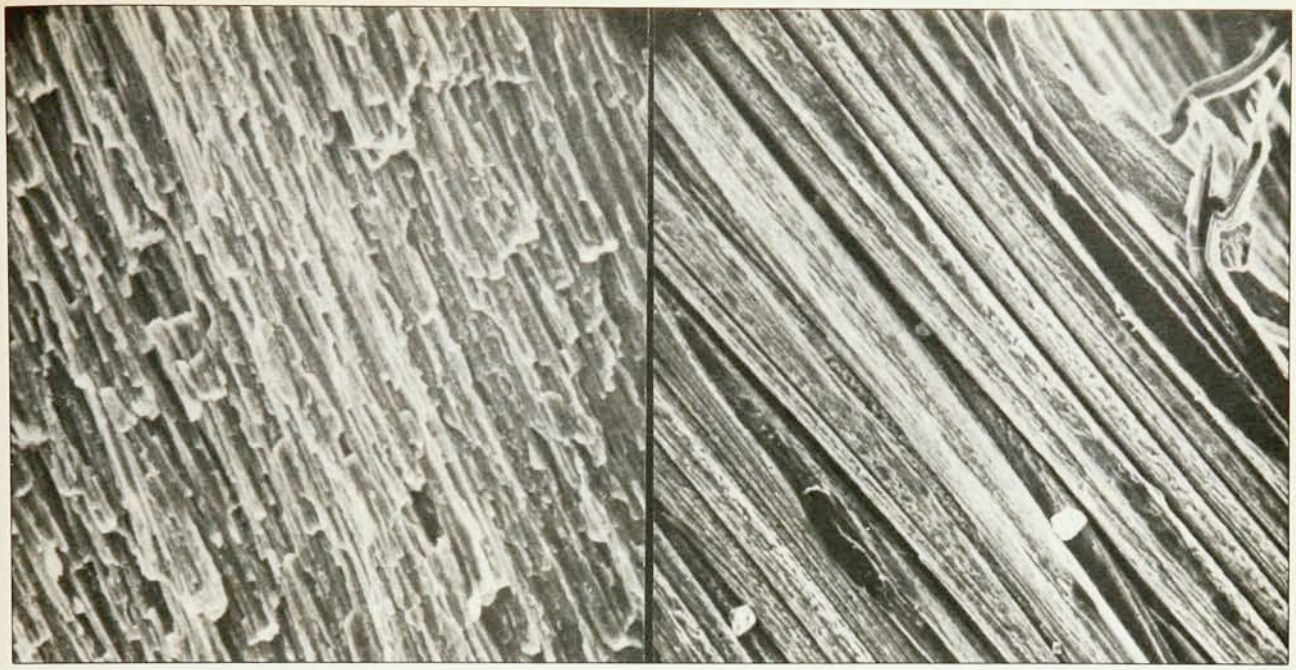
In addition, the unique microstructure of the deposited material may lead to such effects as anomalously low annealing and recrystallization temperatures where the internal stresses and high defect concentration aid in atomic rearrangement. Figure 5 shows the effect of heat treatment of a chemically vapor deposited TiB_2 film deposited at 930 °C on graphite as determined by the deflection of a coated beam.[3] Note that significant stress relaxation can be seen at 700 °C, although the melting point of TiB_2 is 3225 °C.

The high value of grain-boundary area to volume ratio found in fine-grained deposited material means that diffusion processes may be dominated by grain boundary rather than bulk diffusion. The fine-grained nature of the materials also affects the deformation mechanisms such as slip and twinning. For thin films, the ratio of free-surface to volume is high, and the pinning of dislocation by the free surface leads to the high tensile strengths often measured in thin films of materials.

In vapor deposition processes, impurity incorporation during deposition can give high intrinsic stresses or impurity stabilized phases, which are not seen in the bulk forms of the materials. Reactive gas or vapor species allow the deposition of compounds such as nitrides, carbides, borides and oxides; these deposits may be graded by composition.

Vapor deposition processes are able to produce unique and/or nonequilibrium microstructures. One example is the fine dispersion of oxides in metals when the oxide particle size and spacing are very small (100–500 Å). Metals and alloys deposited under Zone 3 conditions have properties similar to those of conventionally fabricated (cast, worked and heat-treated) metals and alloys. Figure 6 shows that the relation of yield strength to grain size for wrought and vacuum deposited Ni-20 Cr alloys are very similar.[5]

Multilayer deposits may be formed by alternating deposits of different materials. Figure 7 shows a fracture section through alternating layers of metal (Ni-50 Cr) and ceramic ($ZrO_2 + Y$) material deposited by sputter deposi-



Fracture surfaces of thick vacuum deposits of stainless steel (left photograph, about 90 microns wide) and aluminum (right photograph, about 900 microns wide). The aluminum shows Zone 1 structure, the stainless steel, Zone 2. Figure 4

tion.[7] The columnar ceramic material has failed between columns, and the metal layer has failed in a ductile mode. Figure 8 shows a multilayer deposit consisting of alternating layers of nickel and copper of a 50 Cu–50 Ni alloy fabricated by dual-source evaporation.[8] The same alloy in wrought form would be a single-phase material. Both examples illustrate the power of deposition technology for the generation of unique phase compositions and microstructures.

Applications

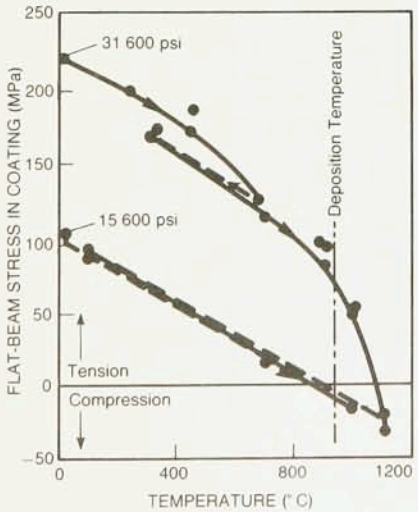
The applications of coatings in current metallurgical technology may be subdivided into the following generic areas:

- Decorative: Aesthetically pleasing coatings on all kinds of consumer products.
- Optically functional: Laser optics (reflective and transmitting), architectural glazing, home mirrors, automotive rear view mirrors, reflective and antireflective coatings, optically absorbing coatings, selective solar absorbers.
- Electrically functional: Electrical conductors, electrical contacts, active solid-state devices, electrical insulators, solar cells.
- Mechanically functional: Lubrication films, wear and erosion resistant coatings, diffusion barriers, hard coatings for cutting tools.
- Chemically functional: Corrosion resistant coatings, catalytic coatings, engine blades and vanes, battery strips, marine use equipment.

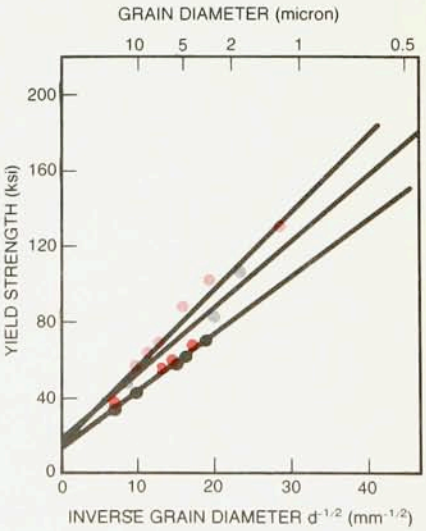
Let us look at a few illustrative examples of these applications.

Decorative/functional coating in the automobile industry. Weight reduction is a high-priority item to increase gas mileage. Therefore, heavy metallic items such as grilles are being replaced with light-weight plastic overcoated with chromium by sputtering to give the accustomed and acceptable appearance.

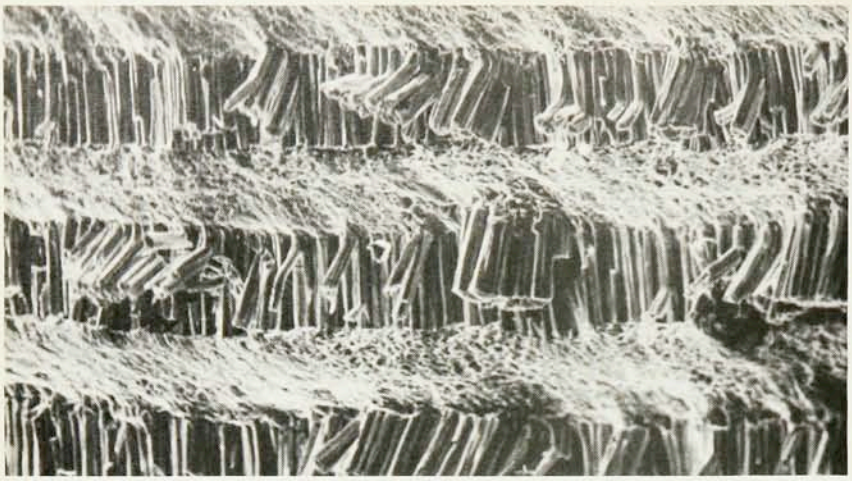
High-temperature corrosion. Blades and vanes used in the turbine-end of a gas-turbine engine are subject to high stresses in a highly corrosive environment of gases containing oxygen, sulphur and chlorine. A single (or "monolithic") material, such as a high-temperature alloy, is incapable of providing both functions. The solution is to design the bulk alloy for its mechanical properties and to provide the corrosion resistance by means of an overlay coating of an *M*-Cr-Al-Y alloy where *M* stands for Ni, Co, Fe or Ni + Co. The coating is deposited in production by



Effect of heat treatment on a chemical-vapor-deposited coating of TiB_2. The intrinsic stress level changes as the material anneals at temperatures less than 700 °C, far below the 3225 °C melting point. Figure 5



Yield strength versus grain size of wrought and vacuum deposited Ni—20 Cr alloy at 25 °C. Data points: light color, wrought; gray, vacuum deposited; black, reference 5; dark color, reference 6. Figure 6



Multilayer sputter deposit of a metal (Ni—50 Cr) and a ceramic (ZrO_2). This photograph of a fracture surface shows a section about 0.2 mm wide. Figure 7

electron-beam evaporation and in the laboratory by sputtering or plasma spraying.

With the potential future use of synthetic fuels, considerable research will have to be undertaken to modify such coating compositions for the different corrosive environments as well as against erosion from the particulate matter in those fuels.

Environmental corrosion. Thick ion-plated aluminum coatings are used in various irregular-shaped parts of aircraft and spacecraft as well as on fasteners. They can replace electroplated cadmium coatings (which sensitize the high-strength parts to hydrogen embrittlement), they can provide protection against galvanic corrosion (which would occur when steel parts contact titanium) and they provide good brazeability.

Friction and wear. Dry-film lubricant coatings of materials such as gold, MoS_2, WSe_2 and other laminar materials are deposited on bearings and other sliding parts by sputtering or ion plating to reduce wear. Such dry-film lubricants are especially important for critical parts used in long-lifetime applications, since conventional organic fluid lubricants are highly susceptible to irreversible degradation and creep over a long time.

Materials conservation. Aluminum is continuously coated on steel strip 2 feet wide and 0.006 inch thick to a 250 micro-inch thickness in an air-to-air electron-beam evaporator at the rate of 200 ft/minute. The aluminum replaces tin, which is becoming increasingly scarce and costly. The strip then goes to the lacquer line and is used for steel can production.

Cutting tools are made of high-speed steel or cemented carbides. They are subject to degradation by abrasive wear as well as by adhesive wear. In the latter mode, the high temperatures and forces at the tool tip promote microwelding between the steel chip from the workpiece and the steel in the high-speed steel tool or the cobalt binder phase in the cemented carbide. The subsequent chip breaks the microweld and causes tool surface cratering and wear. A thin layer of a refractory compound such as TiC, TiN, Al_2O_3 prevents the microwelding by introducing a diffusion barrier. Improvements in tool life by factors of 300 to 800% are possible as well as reductions in cutting forces. The coatings are deposited by chemical vapor deposition or physical vapor deposition.

Nuclear fuels. Pyrolytic carbon is deposited on nuclear fuel particles used in gas-cooled reactors by chemical vapor deposition in fluidized beds. The coating retains the fission products and protects the fuel from corrosion.

Biomedical uses. Parts for implants

Methods of fabricating coatings

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
- D-gun
- Flame spraying

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 (oxide)
- Fused salts

Chemical—liquid

Chemical—vapor
- Thermal
- Plasma

Leaching

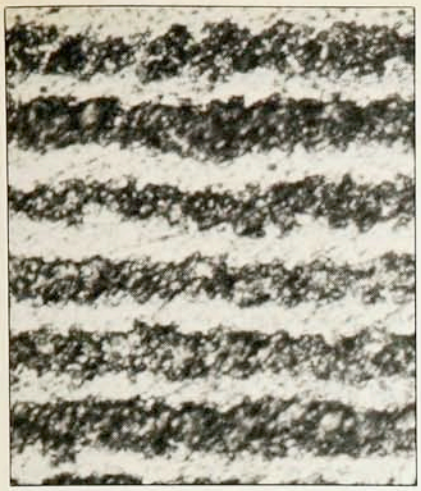
Mechanical
- Shot peening

Thermal

Surface enrichment
- Diffusion from bulk

Sputtering

Ion implantation



Polished and etched surface of a multilayer vacuum deposit of alternating layers of copper (50%) and nickel (50%) fabricated by dual-source evaporation. Figure 8

such as heart valves are made of pyrolytic carbon by chemical vapor deposition techniques. Metal parts are coated with carbon by ion plating to obtain biological compatability.

We have seen in all the techniques and applications discussed in this article that coating technology allows the properties of the surface materials to be separated from those of the bulk material. Materials formed by deposition processes often have structures, properties and stress-response behaviors uniquely different from bulk materials formed by traditional metallurgical procedures. These materials provide a challenge to those interested in understanding the fundamental properties of materials and how they relate to the composition, structure and microstructure of materials and surfaces.

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