PVD Chromium As a Replacement For Hexavalent Chromium

By Dr. Brent Lee

An operator inspects the coated parts inside the coating chamber immediately following completion of the PVD process.

The coating room, equipped with coating chamber and control panel.

Vacuum-based technologies have always had the potential of replacing electrodeposited coatings for certain applications. Unfortunately, these processes offer only thin coatings, and therefore can only replace thin chromium coatings (unless used in conjunction with another process that can build thick coatings). A cathodic arc plasma deposition system has been developed that can achieve decorative as well as functional (corrosion resistance and wear/abrasion resistance) coatings. This commercially available, computer-commanded and PLC-controlled system provides a high degree of versatility and capability, and can coat a quantity of large-area, three-dimensional objects. Vacuum Plating Technology, San Jose, CA, used a proprietary coating process whereby one coat of chromium film was deposited on brass, steel, and aluminum substrates, respectively. (As an option, ZrN or TiN multilayer films can provide decorative color and shine.) All the coating processes were accomplished in one batch chamber with multiple cathode assemblies. Advantages and disadvantages—as well as the fundamentals—of this PVD process are reported here.

Decorative chromium has been in demand for a variety of applications because of its unique color, high reflectivity, excellent tarnish resistance, and good scratch-, wear-, and corrosion-resistant properties. Conventionally, electrodeposition (*i.e.*, electroplating) is an economical means to apply a chromium finish to parts used in many diverse industries. Because of recent health and environmental concerns with hexavalent chromium, however, there are several governmental programs charged with evaluating various technology alternatives to hexavalent chromium.

As reported in numerous articles,[1] vacuum-based technologies have always had the potential of replacing electrodeposited coatings for certain applications. Among the more prevalent replacement candidates was cathodic arc plasma physical vapor deposition (PVD).

Cathodic arc deposition is a unique technology. A great deal of vacuum arc ion source development has been carried out by a number of research groups around the world, and some novel and striking advances have been reported. Researchers at Vacuum Plating Technology Corp. have developed commercial applications primarily for decorative coatings. Advances in vacuum arc technology have been accompanied by a deeper understanding of its unique characteristics and features.

The following is a short overview of some fundamentals as compared to conventional electrodeposition processes, with emphasis on some of the recent developments in vacuum arc applications for decorative coatings.

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General Principles

When electrodeposition is considered, a simplified plating cell (shown in Fig. 1[2]) may be a familiar concept to readers. For comparison, a simplified diagram of a cathodic arc plasma process with the basic components is shown in Fig. 2. These components include a vacuum chamber with pumping equipment, a cathode and its power supply, a means of arc ignition, an anode, a substrate and a substrate bias power supply.

At the core of the cathodic arc process are the arc spots that, when ignited by a mechanical striker, erode the consumable cathode. Metal ions, electrons, microdroplets and neutral particles are emitted from solid cathodes by small and intense arc spots that rapidly traverse the surface, either randomly or under the influence of magnetic fields. A high percentage of particles eroded from the cathode consists of ions. The average kinetic energies of the ions are in the 10–100 eV range. The phenomenon of vacuum arc ion source has been studied by many investigators and has formed the basis for some well-established technology.[3] Similarities to electroplating include:

- A cloud of plasma is formed through evaporation of the arc

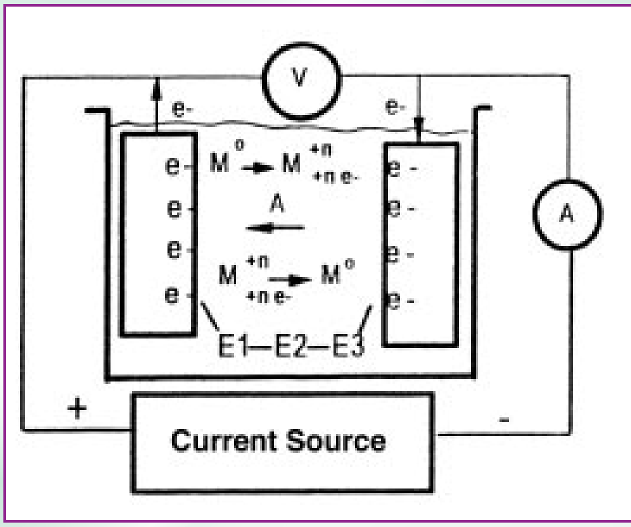

Fig. 1—Plating cell.

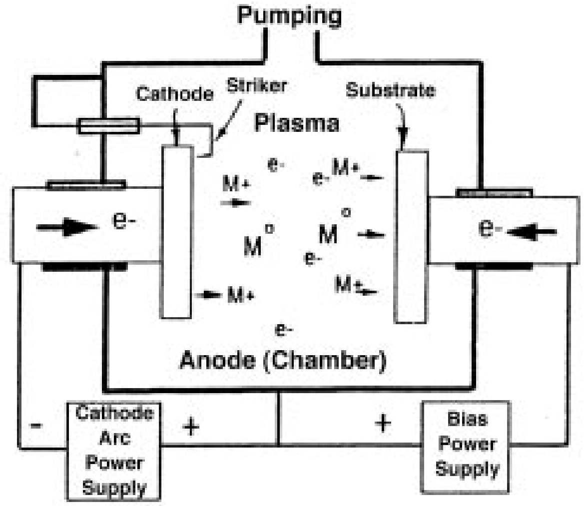

Fig. 2—Cathode arc plasma PVD principle.

spots when the substrate in the chamber, which is immersed in the plasma, is similar to the substrate immersed in the chemical solution.

- Cathode power supply, usually in DC mode, is characterized by low voltage (about 20 V) and high current (typically 35–500 A).
- An anode is a conductive device around the cathode, or the chamber wall acting as an anode. The typical range of substrate bias potential is 0–300 volts referenced to the anode potential.

Vacuum deposition processes have generally been considered competitive processes to conventional electroplating. The advantages of vacuum deposition in the past included a wide choice of both substrates and coatings. The disadvantages, however, far outweighed the advantages of aqueous deposition, which were: Lower costs, thicker coatings, coating complex shapes, control and modification of deposit properties, and control of residual stress.[2]

In the case of cathodic arc plasma, however, its unique characteristics enable PVD processes to provide even more applications than before. The disadvantages associated with PVD therefore become advantages with cathodic arc plasma, as follows.

Control of Residual Stress

A wide range of surface modification techniques employs vacuum arc plasma to achieve desirable characteristics of the material surface and to "tailor" the structure of surfaces and interfaces. Surface films of a variety of elements, compounds and alloys can be deposited.

Multilayer structure is receiving increasing attention. With multiple cathodic arc sources, some with different metal species, variation of pulse length of the metal plasma pulse, and phasing of the high-voltage bias pulse with respect to the plasma pulse—all of these parameters can be tailored throughout the duration of the surface processing operation to fabricate a wide range of surface structures. By adding a reactive gas flow to the deposition and implantation processes, the variety of films that can form is greatly expanded. In addition to metallic films, for example, films of compounds, such as ceramic oxides and carbides can be formed.

Cathodic arc plasma technology is, therefore, very versatile. The bonding transition zone between a substrate and film can be tailored to provide a good match with mechanical properties with strong adhesion and low residual stress.

Control & Modification Of Deposit Properties

The ionization efficiency for vacuum arc plasma (~70 percent) is significantly higher than other PVD processes, such as sputtering and evaporation (2–8 percent). High ionization efficiency and high ion energies involved result in coatings with enhanced adhesion and density. In addition, these characteristics allow deposition of quality films over a broad range of substrate temperature, substrate bias voltage, gas pressure and coating rate. Vacuum arc characteristics are fairly constant for external currents ranging from 50 to 100+ amps. These features contribute to control panel design simplicity as an industrial tool. As a result, a computer-commanded and PLC-controlled unit was integrated into the cathodic arc system.

The benefits of ion bombardment of growing films are well established. They include increased surface mobility of adatoms, formation of dense film structures, good adhesion, desorption of weakly bound species, etc. The energy delivered by ion bombardment allows good films to be grown at low substrate temperatures. The effect of ion bombardment is similar to that of elevated substrate temperature in CVD, and evaporation or sputter deposition is required in order to achieve adhesion.

Deposition from solutions in which the metallic ions are combined with other ions or ligands as complex ions involves more complicated mechanisms. In the plating process, the chemistry of the electrolyte is a time- and space-dependent, complex function. The current potential changes in relation to the resistance that builds up over the cathodic surface. Advanced integrated sensors map the conductivity of the plating solution, and computerized intelligent inference techniques study the chemistry of the plating solution. Other factors, such as electrical contact, volume, temperature, shape and tank size are collected as system influences.

With all the above data collected, the resistance or conductivity and

The back side of the coating chamber, vacuum pump system and power supply system.

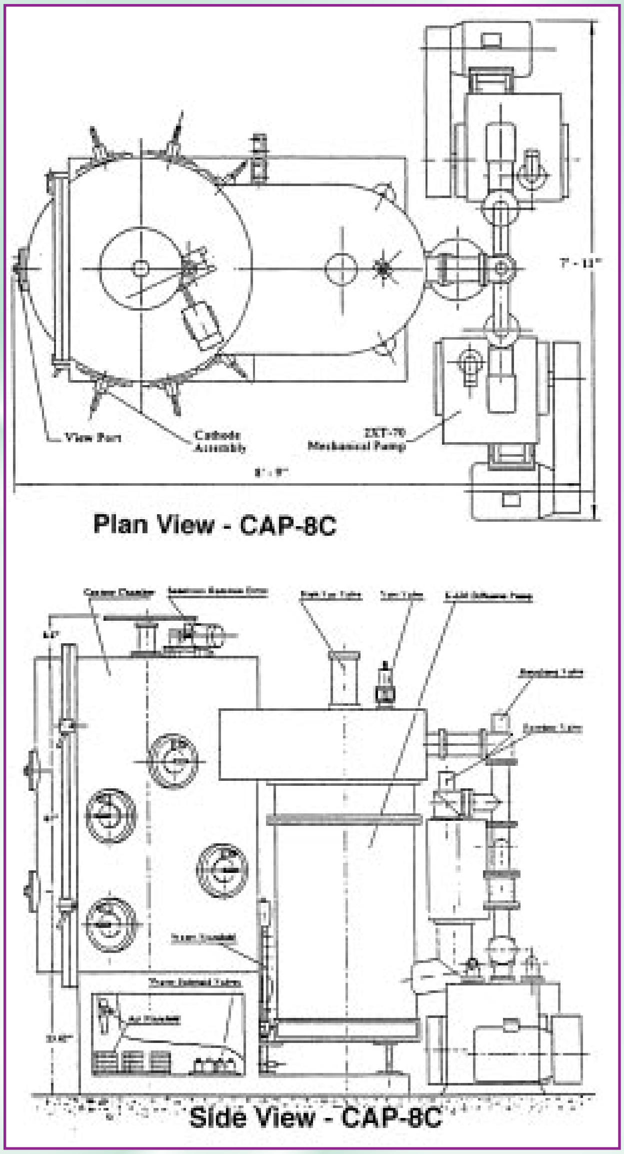

Fig. 3—A commercial-sized cathodic arc plasma (CAP) system.

linear behavior of the system can be determined. Staff chemists are required to continually monitor the system behavior, and/or a commercially available computerized plating controller can sense the plating system's reaction to the influx current, responding with a pre-programmed complex form of voltage and current to eliminate the effects of the shielding layer.[4]

Coating Complex Shapes

In sharp contrast to conventional ion beam processing methods, this PVD technology is *not* strictly a line-of-sight method. In conventional vacuum evaporation or sputtering techniques, for example, the straight, rigid trajectory of the particles necessitates that a complex target be scanned and/or rotated/manipulated in order to process the entire surface. This is usually a difficult and expensive part of the overall job, and is a feature that has hindered the widespread use of PVD as a non-semiconductor surface-modification tool.

Important factors that play a role in establishing uniformity of the coatings are: Scattering from gas in the chamber and Coulomb scattering in the plasma. Because of the high degree of ionization rate with cathodic arc plasma, Coulomb scattering is an important feature. The object to be processed is totally or partially immersed within the relatively low-energy plasma so that the line-of-sight feature is greatly diminished, if not completely removed. In the current system, a planetary rotation fixturing system is sufficient to achieve the desired uniformity.

For fixed-arc current and deposition chamber pressure, the front-side/back-side thickness ratio depends on the distance between the cathode and the substrate. As reported,[5] at a deposition chamber pressure of 10^{-2} Pa, the thickness of TiN coatings on surfaces facing away from a cathode (back side) is normally 10 percent of that registered on surfaces facing the cathode (front side). For a deposition chamber pressure of 6 Pa, the ratio of front-side to back-side coating thicknesses approaches unity.

Thicker Coatings

Deposition rates for cathodic arc deposition technology vary widely—from nanometers per minute to tens-of-micrometers per minute. The deposition rate required will depend on such factors as the desired film morphology, the substrate temperature limitations, and whether the material being deposited is a metal or a compound.

Multiple cathodic sources could multiply the deposition rates and add to the uniformity of the coatings. Typical deposition rates observed for chromium—as high as a μm/min with good adhesion—are achievable under industrial production conditions.

The deposition rate for vacuum arc plasma is directly related to the arc current supply. The inherent feature of macroparticles—small droplets of micrometer size—becomes volatile, however, when the arc current increases. Macroparticles are produced at the cathode spots along with the plasma, and the contamination of the films by macroparticles of sizes up to a few μm represents a major obstacle to the broad application of vacuum arc plasma deposition. Many attempts have been made to separate the plasma and macroparticles, among which filtering of the plasma by magnetic fields is the most common.[6]

The underlying idea of filtering is to guide the vacuum arc plasma from the cathode spots to the substrate by a magnetic field. The macroparticles cannot reach the substrate because they move along nearly straight trajectories, and their inertia is lost to the duct walls. This magnetic duct design will add to the complexity of the system, as well as aid in reducing the deposition rate.

The degree of contamination by macroparticles allowed depends on the application. For decorative coatings, a certain percentage of contamination does not seem to concern consumers. In deposition of metals, the macroparticles are normally integrated into the coating in such a manner that it is difficult to distinguish them from coating material that arrived as ions, because the ions arrive at the substrate with high energy and dense packing.

The team at Vacuum Plating Technology Corp. uses a proprietary metal shield device to simply block the macroparticles. The deposition rate, therefore, is also reduced. In summary, this problem can be solved through a compromise between deposition rate, degree of macroparticle contamination allowed, and complexity of the system design.

Lower Costs

The future of PVD chromium as a replacement for hexavalent chromium depends in large part on the difference between the cost of cathodic arc plasma vs. electrodeposition. Vacuum arc is an efficient means of generating metal plasma. Cathodic arc PVD systems involve large pieces of equipment and are designed to apply metallic coatings to large substrate areas. Usually it is a batch process with a cycle time as short as 30 min. A diagram of the equipment is shown in Fig. 3.

The start-up cost, unfortunately, is high because of the cost of the vacuum equipment. Based on our analysis, however, the operating cost is no more than that of electrodeposition. Because cathodic arc plasma is still in its infancy, the cost will decrease with time as advances in equipment design are achieved. In contrast, because of added expenses and problems associated with plant effluent (pollution) control and waste treatment, the cost of electrodeposition has increased significantly, and could continue to increase with the probability of tighter EPA regulations.

Conclusion

The most important feature of cathodic arc plasma technology—its versatility—adds greatly to its value and to the stimulus to move it into industry applications. Vacuum arc plasma deposition is a promising technique for the production of thin metal films. Uniform, smooth, pinhole-free, and broad-area films of high quality can be commercially produced.

In conclusion, the cathodic arc plasma deposition process offers great potential as a means of modifying the surfaces of components facilitating the deposition of decorative and functional coating with unique properties. ***P&SF***

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About the Author

Dr. Brent Lee is the founder of Vacuum Plating Technology Corp., 254 Kinney Dr., San Jose, CA 95112, where he directs an R&D team for surface finishing on metal and plastic substrates using PVD technology. He received his PhD in nuclear engineering from the Pennsylvania State University, and previously worked for General Electric’s Nuclear Energy Division. He has published various technical papers, and hold patents in several technical fields.