Advanced Techniques for Replacing Chromium: Third Information Exchange

As reported by Dr. Jim Lindsay, Contributing Technical Editor

Because this issue of *Plating and Surface Finishing* follows on the heels of the environmental and resource-oriented programs of AESF Week 1997, it is a good time to note another program that took place last November 4–6, 1996, at the venerable, but at the time snowless, Seven Springs Ski Resort, in the Laurel Highlands of Pennsylvania. The third annual information exchange on *Advanced Techniques for Replacing Chromium* dealt with the issue of substitutes for chromium-based coatings derived from hexavalent processes.

The *Advanced Techniques for Replacing Chromium* conference was sponsored by the National Defense Center for Environmental Excellence (NDCEE), which is operated for the government by Concurrent Technologies Corp., Johnstown, PA. The NDCEE sponsored the conference for the Environmental Security Technology Certification Program (ESTCP). Among the many participating agencies and organizations of this event was the AESF.

The purpose was to discuss activities aimed at reducing or eliminating hexavalent chromium processes. The bulk of the three days dealt with technical presentations, but time was also taken to tour the Concurrent Technologies facilities. The highlights of the technical presentations are covered here. In reading through them, keep in mind that many of these processes offer superior properties in many cases. Cost and the lack of a manufacturing base of sufficient volume, however, may preclude their overnight application.

As a keynote to the meeting, Dr. Robert Elves of Concurrent Technologies presented an overview of chromium toxicology. It is the hexavalent chromium ion, present in chromium plating solutions, chromate conversion coatings, etc., which is the recognized human carcinogen. Chromium metal and chromium compounds based on chemistries other than hexavalent are not the concern here.

Plating

Among the alternative plating processes with a manufacturing base of commercial volume, is trivalent chromium plating. In addition, there is a 25-year history behind the technology. More than 200 decorative installations currently exist. While primary success has been found in the thin, decorative overlayers for nickel-chromium plating, time has not stood still in development for thicker, functional coatings. The use of pulse reverse current (PRC) with a trivalent chromium bath has been applied to production-line shock absorber rods. At equal coating thicknesses, the deposits exhibit hardnesses equivalent to those from hexavalent baths. Further, they can be produced at slightly higher plating rates, with higher current efficiencies.

Alloy substitutes for chromium deposits are numerous, particularly where functional applications—such as wear—are needed. Nickel-tungsten-boron coatings are under study at the University of California—Davis. Nickel-silicon carbide composite coatings were reported to be successfully used in engine cylinder bores, where chromium platings had been used. Silicon carbide, ranging in size from submicrons to 20 microns, was codeposited with nickel to provide coatings with hardness values of VHN_{100} 600-650.

Electroless nickel has been considered as an alternative to chromium for some time. One of the drawbacks has been the finite life of the solution. This concern has been addressed through the use of an electrodialysis treatment. In this way, the process life can be considerably extended, mainly through removing impurities that have built up as byproducts in the solution.

Vacuum Coatings

Diamond-like carbon deposits are an alternative to hard chromium. The coatings are produced via RF plasma techniques with simple hydrocarbons as raw materials. These coatings have found use in such widely ranging applications as air-bearing and roller-bearing surfaces, microtools, magnetic media heads, barcode scanner windows and eyeglass lenses. Coatings of one to five microns in thicknesses were reported to have hardnesses of 2000–5000 on the Vickers scale (test load not reported), vs. 900 for hard chromium. Surface friction behavior was similar to that of hard chromium.

Among the PVD coatings that have shown promise is a layered chromium nitride. In evaluation tests for piston rings, scuffing tests have shown this coating to be superior to hard chromium. PVD coatings were also reported as chromate substitutes, which will be discussed later.

A novel combustion-chemical vapor deposition process was introduced at this meeting. Although not actually a vacuum process, it bears discussion here. It is a flame-assisted, open-atmosphere, thin film deposition process. To date, more than 50 materials have been deposited in an open atmosphere, including alumina, silica, titania and chromia. Most interesting was the demonstration of 22 alternating, 40-nm-thick layers of YSZ and alumina.

Thermal Spray

Spray casting is a thermal spray technique to fabricate near net shapes from difficult-to-machine refractory metals and alloys. The deposition of nickel alloys by this method is under study at Concurrent Technologies. Demonstration and commercialization efforts were described as applied to corrosion and wear-resistant applications.

Among the techniques showing promise in the metal spray arena, is the high velocity oxy-fuel (HVOF) method. Several metals and alloys were cited. Tungsten carbide-cobalt coatings have been applied to aircraft hydraulic components. In addition to the usual corrosion and wear properties, sealing capability (*i.e.*, leakage) must also be evaluated.

Work on plasma spray methods was reported by several speakers. The process has been successfully applied to steel, aluminum and magnesium components. Reported metals and alloys are numerous and the compositions are widely varied. It is futile to be more specific than that—suffice to say that this field does show promise.

Although not purely a thermal spray process, a method called electrospark deposition was described for producing chromium-like coatings in advanced nuclear reactors, for wear and corrosion resistance. It was described as a micro-welding process, which allows the substrate to remain nearly at ambient temperature. This eliminates thermal and metallurgical distortions. Nearly any metal, alloy or cermet can be deposited. Rapid solidification yields nano-structured coatings (not quite amorphous) that adhere with true metallurgical bonds.

Conversion Coatings

Besides chromium plating, the area of chromate conversion coatings has also been given scrutiny. Because of the aerospace and military representation at this meeting, processes on aluminum substrates were emphasized. Different chemistries, such as silane-based systems, are under development. Different technologies, including plasma methods, are also being studied.

Reports on silane-based rinses claimed effective replacement for phosphate, as well as chromate treatments. Such coatings are usually applied on coated sheet steels to promote paint adhesion. The silane processes have been applied with good results to plain, cold-rolled steel, hot-dip galvanized and electrogalvanized steels, and aluminum alloys.

Paint adhesion was the goal of other work involving vacuum deposition. Electron beam evaporation and magnetron sputtering were used to produce nanometer-thick layers of various metal oxides (titanium, chromium, aluminum, silicon and iron). They were applied to several sheet metals (steel, magnesium, copper and aluminum) and coated sheets (tin- and zinc-plated steel) for lacquer adhesion purposes, where chromates would be otherwise used. Silicon oxide, in particular, showed promise.

Several proprietary non-chromate chemical conversion coatings were evaluated at Hughes Aircraft as possible alternatives. Specifically, they have been screened on 2024, 6061 and 7075 aluminum alloys. Using MIL-C-5541 and MIL-C-81706 specifications, none had met the 336-hr salt fog requirements met by chromates, and all were more expensive than chromates.

Polymer coatings of various types were discussed. Included was an inorganic polymer that showed improved corrosion properties, as measured by electrical impedance methods. A conductive polyaniline-based polymer coating was also described, which offered good chemical stability and corrosion properties. Here, the coating was not a barrier, but rather offered a path for passivation of the aluminum substrate.

One plasma technique reported used a plasma etching process to prepare the aluminum surface prior to plasma polymerization. The resultant layer offered protection superior to that offered by the darker chromates.

A commercial chemical vapor deposition substitute was described, based on polysiloxane precursors. Applied as a clear coat for automotive aluminum wheels, it was reported to exhibit high hardness, transparency and corrosion protection. It survived thousands of hours of salt spray exposure.

Chromate conversion coatings do provide excellent corrosion-resistant properties, and many users remain unsatisfied with current substitutes. Not all property requirements are met. Because of this, efforts are also under way to safely operate hexavalent chromate conversion processes under closed-loop conditions. Successful closed-loop operations were reported in processes for aerospace applications. Advanced reverse osmosis was used on process rinsewaters. Membrane electrolysis methods have been used effectively in regenerating chromate solutions. Besides closing the loop, more effective process control has resulted from instituting these practices.

Other Areas

The concerns of this conference were not limited to plating and conversion coatings. People are examining all chemical processes that rely on hexavalent chromium chemistry. These include cleaners, deoxidizers, inspection etchants and anodizing sealers. Sealants involving long-chain carboxylic acids were found to be effective on sulfuric acid anodized aluminum.

In all, this third information exchange on *Advanced Techniques for Replacing Chromium* offered much new material toward the elimination or replacement of coatings derived from hexavalent chromium chemistry. This forum has proven to be valuable over the years, as has its companion program on alternatives to cadmium coatings. Anyone desiring more details should contact Concurrent Technologies Corp., 1450 Scalp Avenue, Johnstown, PA 15904. Information is also available on the World Wide Web at www.ndcee.ctc.com. *P&SF*