Special Conference Comes to Grips With Hexavalent Chromium

By James H. Lindsay, Contributing Technical Editor

As AESF COMPLIANCE WEEK approaches the 13th of this month, it is appropriate to note a rather important event that took place a couple of months ago in the hills of South Central Pennsylvania. On October 12–13, 1994, a workshop-style conference—Advanced Techniques for Replacing Chromium: An Information Exchange—was organized and conducted by the National Defense Center for Environmental Excellence (NDCEE), which is operated for the Department of Defense by Concurrent Technologies Corporation (CTC), in Johnstown, PA. The event was co-sponsored by the American Electroplaters and Surface Finishers Society (AESF), the U.S. Environmental Protection Agency (EPA), the National Center for Manufacturing Sciences (NCMS) and the Society of Vacuum Coaters (SVC).

The primary goal of NDCEE is to lead and support the military and the commercial industrial base in the transition to environmentally acceptable manufacturing technologies. The Johnstown center provides a means of testing, evaluating and applying new environmentally safe technologies in a low-risk setting. As operated by CTC, the facility provides a unique capability for full-scale process testing. A manufacturer interested in a given technology can literally try it out, full-scale.

In the area of surface finishing, expertise is available to demonstrate technology in the areas of:

- Metal plating waste reduction
- Chlorinated solvent cleaning alternatives
- Environmentally acceptable painting systems
- Clean corrosion- and wear-resistant coating systems
- Clean maintenance and refurbishment systems.

Another goal of the NDCEE is to serve as a national resource for environmental technological information. Recognizing the widespread usage of hexavalent chromium chemistry in commercial practice, the NDCEE, with the leadership of Brian Manty of CTC (who also serves as AESF first vice-president), set up this workshop to address the environmental and toxicological effects through minimization or outright elimination of hexavalent chromium. Originally it was envisioned that about 30 industrial experts would be interested in participating. It soon became pleasantly apparent that the NDCEE had struck a chord, for the eventual attendance totaled more than 125 individuals. To accommodate this larger audience, the meeting venue had to be moved to a larger facility at the Conference Center of the University of Pittsburgh— Johnstown Campus.

The purpose of the information exchange was to discuss activities aimed at reducing or eliminating hexavalent chromium plating. The two-day event consisted of one day of presentations, the contents of which make up the bulk of this article. The second day was devoted to round-table discussions. The morning discussions were divided by process interest: Electroplating, thermal spray and vacuum deposition processes, plus one devoted to processes from the governmental perspective of the General Services Administration (GSA). The afternoon discussions were divided by application interest: Decorative, functional and, again, the GSA application perspective.

Toxic Effects Of Hexavalent Chromium

Robert Elves of NDCEE /CTC reviewed what industry is up against with these chromium issues. The chief uses of chromium and chromium compounds are in stainless and alloy steels, refractory products, tanning agents, pigments, electroplating, catalysts and in corrosion-resistant products. The chromium compounds vary in their toxic and carcinogenic effects. For this reason, it is necessary to divide chromium and its inorganic compounds into a number of groupings, each with recommendations based on available toxicological and epidemiological evidence, namely: Metallic, bivalent, trivalent and hexavalent chromium.

The key to the action is that hexavalent chromium will cross cell membranes, while trivalent chromium will not. Once inside the cell, hexavalent chromium is reduced to trivalent chromium, which in turn binds the nucleic acid within the cells, leading to tumor growth. It is ironic that it is the trivalent ion, benign outside the cell, which is formed from the hexavalent ion to do the dirty work.

Hexavalent chromium compounds have a TLV-TWA of 0.05 mg/m^3. This had been considered adequate to reduce the potential for irritation of the respiratory tract and possible kidney and liver damage. Certain water-soluble hexavalent chromium compounds have a TLV-TWA of 0.05 mg/m^3 and have a designation as an A-1 confirmed human carcinogen. It was reported that there has been an increase in lung cancer of 15 percent in workers in the chromium plating industry.

Regulatory Outlook

Carolyn Freeman, project officer from the Occupational Safety and Health Administration (OSHA), outlined how new regulations will be put into effect. In May of 1995, the proposed new regulations will be published in the *Federal Register*. Hearings will be held three months later for comment on the proposed new regulations. The final regulations will be completed three to four months thereafter. OSHA desires as much information as possible with which to develop these regulations. It was expected that there will be a major change in exposure limits written into these new regulations.

Programs for Chromium Alternatives

There are several governmental programs charged with evaluating various technology alternatives to hexavalent chromium. Teresa Harten, of the U.S. Environmental Protection Agency, reviewed the programs under the Environmental Technology Initiative. Among them are:

- Use of a nickel-tungsten-boron alloy to replace chromium.
- Replacement with physical vapor deposits (PVD) (chromium-, titanium- and titanium-aluminum-nitrides).
- Alloy deposition of hard coatings (nickel-tungsten-silicon carbide and electroless nickel-tungsten).
- Deposition of powdered chromium with an inductively coupled radio-frequency plasma torch.
- Hard chromium via sputter deposition
- Chromium-free conversion coatings as a pretreatment for powder coatings.
- Plasma process for pretreatment of aluminum (a chromate alternative).
- Silane-based pretreatment to replace chromates.

For the industrial sector, Dennis Dull described Boeing's initiatives in replacing hexavalent chromium as part of its comprehensive chemical reduction program. Boeing's coatings personnel have looked at all of their processes and found hexavalent chromium present in the following:

- Hard chromium plating. (Non-plated coating alternatives include high-velocity oxyfuel spraying (HVOF), detonation gun deposition, plasma-source ion implantation (PSII) and diamond-like carbon deposits.)
- Chromated organic primers. (Alternative includes non-chromated low-VOC primer.)
- Conversion coatings for aluminum. (No commercial alternative available at present.)
- Anodizing of aluminum. (Boric/sulfuric acid anodizing reduces amount of chromic acid required.)
- Anodizing of titanium. (Alternatives include boric/sulfuric acid anodizing, sodium hydroxide anodizing and titanium dioxide sputtering.)
- Anodizing of magnesium. (Considering changing casting alloy grade.)
- Epoxy smear removal in printed wiring boards. (Alternative method uses permanganate.)
- Chromating of zinc plating. (Exploring anodizing of zinc or other conversion coats.)
- Passivating stainless steel. (No commercial alternative available at present.)

Chromate Substitutes

The National Center for Manufacturing Sciences (NCMS), Ann Arbor, MI, is sponsoring a cooperative research project, "Alternatives of Chromium for Metal Finishing," with the goal of evaluating the capabilities of chromium-free conversion coatings for aluminum alloys. This work is being sponsored by a variety of industries and universities. Nearly 30 distinct coating types are to be evaluated from 15 different suppliers.

Aluminum alloy substrates will be: 2024-T3, 3003, 6061-T6, 7075-T6 and 356 casting alloy. The project will address the environmental impact of the alternatives; after all, they could pose worse problems than the original hexavalent process.

Electroplating Alternatives

Considerable discussion was given over to trivalent chromium processes. Where keeping chromium is desirable, trivalent chromium processes offer an easy, environmentally acceptable alternative to hexavalent processes. The deposits offer comparable physical properties and the baths operate more easily and efficiently. Further, there is an established supplier base. The processes offer faster plating rates, increased covering/throwing power and reduced tendency toward burning. When the reduced waste treatment effort is taken into account, the costs of these processes are comparable with the old hexavalent solutions. Dr. Donald Snyder, of Atotech USA, Cleveland, OH, emphasized the 20 years of commercial experience at about 200 installations with these processes. Developments over that time have successfully proven out trivalent processes for both decorative and functional applications. Requirements for corrosion, adhesion, hardness, wear and appearance have been met.

Tamara Davidson, of Enthone-OMI described cobalt-based alloy alternatives to decorative chromium plating. A number of processes are available that act as both chromium and nickel/chromium multilayer replacements. Available in rack or barrel mode, the resulting deposits provide corrosion resistance superior to the traditional hexavalent deposits.

Another chromium replacement noted was a nickel-tungsten-boron alloy, as described by Peter Vignati, of Fidelity Chemical Products Corporation, Newark, NJ. The deposit is unique in that it is, in Vignati's words, an "amorphous/nanocrystalline" composite containing a nominal 35-percent tungsten. If it's not purely amorphous, it is certainly infinitesimally fine-grained. As-deposited hardness is 600VHN, with heat treatment increasing the numbers to 950–1050VHN (load not given). Corrosion resistance to acids is excellent and a barrier type of protection is evident. There are currently seven pilot installations using this process. There is an active program with the California EPA and U.S. EPA in which this coating is being evaluated as a chromium alternative.

Electroless nickel-phosphorus coatings from conventional hypophosphite solutions were reviewed by Richard Dorset, of Enthone-OMI, West Haven, CT. The corrosion and wear properties are dependent on the phosphorus content, which can be varied from 1.0 to 12.0 percent. New forms of the process can codeposit particulate Teflon® or silicon carbide.

Electroless nickel deposits, from borohydride chemistry rather than hypophosphite chemistry, were covered by Charles McComas, of National Chemical Co., Stuart, FL. When compared to hard chromium, the deposits were said to exhibit better wear, lower friction and improved hardness. In terms of stress on the environment, the nickel-boron process was favorable when compared to hard chromium. This coating has been successfully applied in jet engines, glass manufacturing, foundry molds, gears and cams.

Metal Spray Alternatives

High velocity oxygen fuel (HVOF) thermal spray coatings were emphasized in several presentations in the metal spray arena. According to Michael Poe, of METCO, Lake Ridge, VA, these processes are cost-effective and produce a wide range of coatings in an environmentally safe manner. Among materials produced are iron-chromium-molybdenum and iron-nickel-chromium-molybdenum alloy, for sliding wear, and nickel-chromium-tungsten-molybdenum alloy, for corrosion resistance. In contrast to typical thermal spray coatings, the HVOF process produces coating densities greater than that of hard chromium.

A new pressure-controlled atomization process, or spray casting, was described by Ronald Glovan, of MSE, Inc., Butte, MT. Here, a liquid metal is atomized in a supersonic nozzle, which in turn directs the spray to the substrate. Nickel alloys, Versaloy 50 (containing carbon, silicon and boron with 11-percent chromium) and Versaloy 25 (without the chromium), have been deposited with improved fatigue properties. Microhardness was improved with heat treatment.

William Gooden discussed work on this spray casting process at the Armstrong Laboratory (U.S. Air Force). Again the driving force is the reduction of hazardous waste and of maintenance and material costs through the elimination of hexavalent chromium. The Air Force plans on working with the NDCEE.

Vacuum Deposition Alternatives

Vacuum-based technologies have always had the potential of replacing electrodeposited coatings in certain applications. As the various participants to this workshop indicated, such technologies have potential in replacing hexavalent chromium plating. Prominently mentioned at the meeting were ion implantation, ion-beam-assisted deposition, plasma-assisted ion implantation, cathodic arc deposition and ion nitriding.

Among the more prevalent replacement candidates were those utilizing ion beam processes to enhance deposition rates (among other features). Melissa Weis, of CTC, described the ongoing evaluation of ion beam processes at the NDCEE. Recognizing the potential of ion beam methods as a viable substitute for chromium, 250 candidate parts were evaluated and reduced to 12, for demonstration and evaluation. These parts will be evaluated, using one or more of the following four coating strategies:

- Thick chromium on aluminum substrate: Ion implantation or ion beam deposition to be used prior to chromium plating—objective to augment adhesion only.
- Thick chromium on steel substrate: (1) Nitrogen implantation onto chromium deposit, enhancing wear properties—objective to reduce required chromium thickness.
- Thick chromium on steel substrate: (2) Ion-beam-assisted deposition coatings on chromium plate—objective to reduce required chromium thickness.
- Thin chromium on steel substrate: Ion-beam-assisted deposition coatings directly on substrate—objective to replace chromium.

An ion beam equipment design facility is to be established at NDCEE by CTC to document the operation, costs and process/material specifications.

High energy metal ions, used either for ion implantation or to assist (or enhance) physical vapor deposition (PVD), were discussed by Anthony Perry, of ISM Technologies, San Diego, CA. When used to enhance PVD, high energy ions have been shown to reduce the required deposition temperature. This had been an obstacle to replacing chromium with PVD coatings. By applying a pulsed, high-voltage bias to the substrate, the deposition temperature has been reduced to 150 °C, which is low enough to coat aluminum and carbon without degrading the mechanical properties of these materials.

Ion beam technologies offer viable replacements for hexavalent chromium plating, according to Larry Stelmack, of Implant Sciences Corporation, Wakefield, MA. Hard chromium coatings can be produced with improved wear performance, which is further enhanced by implantation with nitrogen ions. The process is controllable and reproducible. By manipulating the operating parameters, a graded interface is produced that leads to major assurance of adhesion. In addition to the chromium coatings, non-chromium substitutes are under development at Implant Sciences. These include diamond-like, carbon nitride and silicon carbide layers.

Cathode arc deposition technology is also under development at Implant Sciences. The process utilizes a high-energy, fully ionized metal plasma beam. The deposition rates are the highest of any physical vapor deposition process to date. The process is energy efficient and scalable and costs are competitive. Stelmack noted that the technology is medium-term, with two to three years foreseen to commercial development.

Ion-beam-assisted deposition was also discussed by Ray Bricault, of Spire Corporation, Bedford, MA. This technique combines evaporation with concurrent ion beam bombardment to impart (1) excellent adhesion, (2) highly ductile films, (3) wear and abrasion-resistant films, and (4) control over film stress. It is possible to deposit binary and ternary alloy coatings with precise control of composition. Zinc, chromium, nickel and aluminum have been deposited. Examples of alloy deposits produced to date are: Zinc-chromium, zinc-iron, zinc-nickel, zinc-aluminum, zinc-tin, zinc-chromium-titanium and zinc-chromium-nickel.

Jesse Matossian, of GM Hughes Research, described work in the commercialization of plasma-based ion implantation (PII). PII has been successful in surface hardening chromium platings with implanted nitrogen ions. As such, reduced thicknesses of chromium for a given wear life are possible. Taking things one step further, Hughes is also working on plasma-enhanced magnetron sputter deposition (PMD). Here, titanium nitride coatings are formed and simultaneously bombarded with argon on the workpiece. The result is an exceedingly high deposition rate on the order of 6 µm or greater. A 30 µm thickness is possible. This process, coupled with ion bombardment, will eliminate—rather than reduce chromium.

Workshop Discussions

The workshop discussions were often lively and served to emphasize the concerns of the audience after having heard all of the technical presentations. It was deliberately planned that any comment on the technical talks be reserved until the workshops. This allowed the audience to hear the technical talks without interruption and gave them time to more carefully consider their questions. What follows emphasizes the process workshops.

Plating. The discussion on plating processes were wide-ranging. While many of the issues raised were not settled in this sitting (nor could they be), these issues served to indicate what concerns most people. While hexavalent chromium was considered to be the problem, there was concern over whether a given replacement would be any safer. One could be going "out of the frying pan and into the fire" if one is not careful. If, in a given application, there was no alternative to hexavalent chromium, were efforts underway to make the current process safer? As to the potential for regulation of trivalent chromium, it was noted there are no current plans for doing so.

One participant pointed out that there are questions of liability for a plated article, whether it lies with the applicator or the user. Another, following up, pointed out that improved communication between supplier and end user could solve many problems, including data requirements.

The issue of specifications was raised. It was noted that changing specifications is far more difficult in North America than in Europe or Asia. It is this sort of thing, coupled with technological inertia, noted one speaker, that is an impediment to replacing chromium.

Thermal Spray. The discussion here was strongly focused on military applications, as opposed to regular commerce. From the military perspective, one has to factor in differences between the various military services and even between bases. The production volumes are lower than what is encountered in regular industry. Process controls, including training and certification of the process and operators, are important considerations in any alternative process.

In technical terms, the HVOF processes were felt to be the up-and-coming thing with improved properties in comparison with plasma spray processes. Overall, within the military, there was a perception of low robustness with general thermal spray coatings that had to be overcome, and which the HVOF coatings were felt to provide. The need for thinner coatings by these processes was noted; they can't be made thin enough and coatings on a nanometer scale would even be desirable. A need for effective stripping processes for these coatings was also noted.

Vacuum. Considerable time was spent discussing the thickness ranges for which PVD processes were most appropriate. In terms of heavy build-up, such as on large shafts, no PVD replacement was seen as viable to date. However, cathodic arc processes, with their high deposition rates, seemed likely candidates in time. PVD coatings seemed to be best for thin coats. Hybrid multi-layers of electrodeposits, topped by the special properties afforded by PVD coatings seemed to be one answer to thicker deposit applications.

Several new approaches are being taken to replace or minimize hexavalent chromium. Vacuum techniques involving ion-beam-based processes seem to be getting the most attention. Many companies have joined forces with government agencies, including funding in these areas, and progress is being made. It is realistic to see several plasma-based processes becoming commercially available within the year. Most important, the response to this meeting, as indicated by the overwhelming attendance, shows that the search for hexavalent chromium alternatives is a timely and vital issue, and that the pace of progress is accelerating. One can hope that this won't be the last such meeting. o