Research Corner

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New Projects & Summer Grants

As this is being written, I have just returned from AESF Week in Florida. Besides an interesting and worthwhile technical program, the various Boards and Committees met, including the Research Board and the Research Sponsors Committee. It always amazes me how fortunate we are to have the talent and dedication in these groups. The AESF is well served by their efforts. And I know there's plenty of new talent out there—perhaps you, too, would like to join these dedicated folks.

This time around, I would like to review some recent results on two of the newer projects that we have undertaken this year. Also, there are a couple of rather interesting Summer Grant works on chromium plating that will be of interest to you.

Project R-96
Source Reduction Through Process Modification & Operational Improvement

Project Director: Prof. Yinlun Huang, Wayne State University, Detroit, MI

This project is particularly interesting in that it successfully applies the abstract to real life. Mathematical modeling is being applied to an industrial plating line, and it's being done the right way. What is involved here is the application of a waste minimization decision support system, based on real-life data on cleaning and rinsing. Another attractive part of this proposition involves consideration of the variety of processes in the line, including soak cleaning, electrocleaning and acid activation.

With the generous support and cooperation of Reilly Plating Co., a major shop in the Detroit area, Dr. Huang and his group have been given entrée to collect production cleaning line samples and data, including:

- Part dirtiness, found by the weight difference before and after cleaning,
- Cleaner usage, by daily monitoring of chemical inventory,
- Cleaner concentrations, by conductivity measurement at 5-minute intervals,
- Historical data on the cleaners and rinses, from the archives and
- Parts processed, including surface area, area and number of barrels processed.

With the actual process information on hand, cleaning and rinsing models were derived and used to simulate the process line on the computer, to predict sludge accumulation in a cleaning tank. At this stage in the project, only trends can be predicted, although the potential for process improvement and waste reduction is clear.

Future work calls for cleaner-specific models, *i.e.*, taking into account the different chemical mechanisms involved with the soak clean, electroclean and acid dip processes. Dr. Huang's plans also call for sludge characterization studies to be incorporated into this system. The end result will actually be a computer-controlled system programmed to optimize the process and minimize the waste. The bottom line is that it is derived from the real world.

Project R-97
An Effect of Leveling Maximum in Low Frequency Pulse Plating with Brighteners & Hydrodynamically Active Additives

Project Director: Dr. Mois Aroyo Technical University, Sofia, Bulgaria

For cost savings in metal distribution or for desired finish specifications, among other reasons, many plating applications call for optimum leveling. In this work, Dr. Aroyo is endeavoring to find the best conditions for leveling of electrodeposits by low-frequency pulse plating and mass transport (*i.e.*, solution agitation). He defines leveling power as "an ability to diminish the difference in heights between protrusion peaks and recesses in a surface microprofile." The greater this ability, the thinner the coating thickness required to achieve leveling. The current work has involved nickel deposits from Watts and sulfamate solutions.

Leveling power was determined by measuring the change in surface roughness resulting from plating, beginning with a known and controlled cathode roughness. All measurements were made with a contact profilometer. A rotating *and* vibrating disc electrode was used, along with a galvanostatic/potentiostatic power supply.

Both the Watts and sulfamate nickel formulations contained organic brighteners and "hydrodynamically-active" additives. Dr. Aroyo notes that, by using the latter, the brightener concentrations are three to four times lower than what is normally used in conventional DC plating. Plating was accomplished with the rotating disc at 250 rpm and no vibration, and at 50 rpm with 600 or 1200 cycles/min lateral vibration. The pulse frequency was varied from zero to 16 Hertz, with current and time adjusted to assure equal thickness. With the Watts bath, roughening, rather than leveling, was first observed as the pulse frequency was increased to seven Hertz. Beyond this point, leveling improved, up to a maximum of ten Hertz. Increasing the duration of the pulse tended to increase the range over which leveling improved. Similar results were observed in the sulfamate bath. Vibrating the rotating electrode did not change the leveling/ pulse frequency relationship, but it did tend to reduce the amount of change with frequency.

Electrochemical porosity measurements indicated a correlation between leveling and coating porosity. Dr. Aroyo also considered the effect of the additives in terms of adsorption and diffusion. His theoretical model was related to the relative amount of additive adsorbed on protrusions and recesses, and how this was altered by pulsing. Future work calls for similar experiments, to be performed on palladium and gold electrodeposits.

Summer Research Grant S-51 Characterization of Trivalent Chromium Deposits Structure after Hardening Thermal Treatment

Project Director: Dr. Patrick Benaben, École Nationale Supérieure des Mines de Saint-Étienne, Saint-Étienne, France

Environmental and health concerns about hexavalent chromium plating processes have spawned a wide-ranging search for alternatives in recent years. Probably one of the most viable ones is trivalent chromium plating chemistry. In use for a quarter century, it is seeing more use as time goes on. Trivalent chromium plating, however, has seen more success in the decorative field than in engineering applications, where thicker, hard chromium deposits are of concern.

At the École Nationale Supérieure des Mines, Dr. Benaben and his staff have been looking at hard trivalent chromium deposits. Specifically, they have been investigating the effects of thermal treatments on the physical properties of the deposits. For comparison, the behavior of hexavalent chromium deposits with like treatments was compared.

Thermal treatments were performed in an argon atmosphere, at five different temperatures, from 300 to 700 °C, for two, four and eight-hr duration. The samples were examined for microstructure, microcracking and hardness. The latter was measured on polished cross sections under a 100 g load.

Over the range of thermal treatments, the hardness of the hexavalent chromium deposits decreased from 1000 to 300 VHN_{100}. The deposit cracks tended to widen and, in some cases, coalesce. The X-ray diffraction peaks tended to narrow, indicative of some grain growth. The investigators report a rapid decline in hardness above 500 °C, in the range of the recrystallization temperature for chromium.

On the other hand, the trivalent chromium deposits became harder, at least up to 500 °C. The hardness increased from 1000 to 1800–1900 VHN_{100} over the same thermal range. At 300 °C, the precipitation of chromium carbides was noted. Beyond 500 °C, grain growth and declining hardness was observed. These results provide an intriguing approach to the use of trivalent chromium deposits in engineering applications.

Summer Research Grant S-55 Surface Etching Treatment for Promotion of Adhesion of Industrial Chromium Deposits to Steel

Project Director: Dr. Keith Sheppard, Stevens Institute of Technology, Hoboken, NJ

This study dealt with another aspect of engineering chromium deposits. Hard chromium is generally used under conditions of corrosion, abrasion and impact, so adhesion is critical. In many cases, anodic etching of the steel substrate is required to assure adequate adhesion, by the addition of a mechanical adhesion component, via roughening. On the other hand, the treatment cannot be too aggressive, or the final surface finish may be adversely effected. The primary goal in this work was to probe the chemical nature of the surface formed by anodic etching, using three different etchants.

Induction or flame-hardened steels were used as substrates. The etchants used were a 5 wt/o solution of sulfuric acid and two proprietary etchants. The proprietary materials were based on chromic/sulfuric acid chemistry, one having an organic additive and the other containing a fluoride additive. Cross sections were prepared to examine the interface between the etched and unetched steel. Chemical analysis was carried out by energy dispersive X-ray spectroscopy (EDX) and Auger electron spectroscopy (AES).

Only limited information was obtained, because of the very thin corrosion layer and the larger interaction volume associated with the EDX analysis. The sulfuric acid produced significant corrosion products over the entire steel surface. The proprietary chromic acid-based materials tended to form pits in non-hardened areas. In hardened areas, preferential attack was noted in areas containing pearlite structures. AES provided some chemical information from hardened and non-hardened regions. The only corrosion product was iron oxide, with little compositional variation as a function of thickness. Because of equipment difficulties, the investigators could not go much beyond that.

Although the adhesion mechanism was not apparent from the results, mechanical anchoring is seen to be part of it. When good adhesion is achieved, however, it is stronger than what could be attributed purely to mechanical anchoring. The best etching characteristics were obtained with the proprietary materials, which produced minimal oxides and selective etching. Dr. Sheppard and his group suggest that etching may influence the effects of carbides in the steel on the early stages of chromium deposition, when adhesion is established. Such a hypothesis could explain why obtaining adhesion to iron is easier than to steel and why different steel microstructures require different etch times. This story is not yet complete.

Looking Ahead

During AESF Week, the Research Board met to consider the program for the coming year. I am pleased to report that we funded one new full research project as well as continuing the ongoing work. In addition, we are able to continue our very productive Summer Research Grant program next year. I will describe the new research project for you in a later version of this treatise, after the contract papers have been signed, sealed and delivered. *P&SF*