Research Corner

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Research Results Look Promising

With the calendar year 1995 now behind us, we can review the progress of AESF research and find much to be pleased about. This month, I would like to report on continuing progress on two of our newer full projects and three very interesting summer grants. All will benefit the commercial sector. We are now:

- Understanding how electroless deposits can plate on carbon steels and cast-irons.
- Working toward obtaining environmentally-sound replacements for cyanide copper strike solutions.
- Shedding light on what it takes to ensure adhesion of hard chromium.

In addition, we have:

- Studied the phenomena associated with deposition of the commercially-important nickel-iron alloys.
- Looked into new methods to more effectively handle the cyanide wastewaters that we still must contend with.

Project 90
Effect of Microstructure of the Steel Substrate and Bath Stabilizers on the Porosity of Electroless Nickel Coatings
Project Director: Dr. Der-Tau Chin
Clarkson University
Potsdam, NY, USA

Dr. Chin and his group continue to shed light on how the microstructure of steel and its alloying elements effect the porosity and corrosion resistance of electroless nickel deposits. Besides looking into how carbon and carbide inclusions influence how the deposit goes down, work has also been directed towards the electroless nickel deposit itself. You have to understand what you're depositing, as well as what you're depositing on.

To that end, transmission electron microscopy (TEM) and electron diffraction methods have been used to characterize the electroless nickel, which, in this work, contains 10 percent phosphorus. The TEM results showed no evidence that the deposit was crystalline. The electron diffraction pattern consisted of diffuse rings. These results indicate that the electroless deposit is amorphous. It has always puzzled me about where you draw the line between crystalline and amorphous structures, but this material was amorphous. If you're splitting hairs, it is "impossibly, infinitesimally fine-grained."

Last time, I noted that the group had developed a non-destructive electrochemical porosity measurement method. It tied the corrosion potential between an iron wire and the electroless deposit to the area fraction of the substrate surface exposed through pores in the electroless layer. Recently, a porosity curve was developed, based on commercial samples. With this data in hand, AISI 1010 carbon steel panels were coated from the same commercial bath. Our investigators found the electroless nickel porosity to decrease with increasing thickness (over the range of 0–30 μm). Above 30 μm, the porosity remained constant at an area fraction of 0.95 x 10^{-3}.

Work was continued on the effects of various stabilizers used in the bath. In the previous quarter, lead (Pb^{+2}) and iodate (IO_3^-) ions were studied. While work on iodate has continued, maleic acid has also been investigated. At different stabilizer concentrations, the deposition rate was measured as the nickel-phosphorus deposited on graphite that was galvanically connected to a steel coupon. Using scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS), the stabilizer's influence on the spreading of the deposit to carbon inclusions was observed. Less spreading could lead to more porosity. Indeed, the iodate ion decreased the deposition rate on carbon and increased the coating porosity. Maleic acid reduced the phosphorus content and also increased porosity.

Dr. Chin plans further studies of stabilizer effects, including mercaptobenzothiazole. Electrochemical polarization work will shed light on the effects of the four stabilizers on the kinetics of the electroless nickel process. Finally, the porosity of electroless nickel deposited on a eutectoid steel (AISI 1075) containing 0.8 wt% carbon will be studied.

Project 91
Copper Deposition from Cuprous Ligand Complexes: Contribution Toward The Replacement of Cyanide In Strike-Plating Baths
Project Director:
Professor Peter S. Fedkiw
North Carolina State University
Raleigh, NC, USA

On our newest project, Dr. Fedkiw is addressing the environmental concerns over cyanide copper. Historically, cyanide processes have been the mainstay of alkaline copper plating, but non-cyanide substitutes have been long sought. This group is attempting to replace the cyanide complex with cuprous ligand complexes.

In the last reporting period, a preliminary mathematical model was developed to describe the mass-transfer limited copper transport through the diffusion boundary layer at the cathode in a cuprous cyanide strike solution. In mathematical modelling, it is always prudent to start out with simple systems and increase the level of complexity. At this early stage, the model only allowed for the formation of the lowest order cyanide complex, $Cu(CN)_2^-$.

I last reported that the group had encountered numerical difficulties when the sodium cyanide concentration was less than the copper cyanide concentration. Although this is not the case in a typical strike bath, these mathematical inconsistencies could pose problems when possible cyanide replacements are considered. Two strategies for eliminating difficulties were explored. The terminology to describe these methods is taken from Dr. Fedkiw's reports, in quotes (no sense in me botching up the description).

First, "… problem was set up as a set of coupled, first-order differential equations of the boundary-value type and solved using the finite-difference method." Unfortunately, reliable solutions were still not obtained when the sodium cyanide concentration was less than that of copper cyanide. The reliability was determined by consistency checks to ensure solution accuracy. These checks were not always satisfied.

Second, "… quasi-potential transformation was applied to the problem to reduce the system description to a set of first-order, initial-value type differential equations that were integrated using step-size integrators." This method was able to solve the system of equations over the entire range of concentrations.

Once the solutions were established, it became apparent why the other methods were numerically faulty. The finite-differences method was very sensitive to a steep gradient in the potential curve where the sodium cyanide concentration was less than that of copper cyanide. The point that I would leave with you is that the mathematical discrepancies matched the curve. This attests to the reliable work to date.

Future work calls for expansion of the model to higher order cuprous cyanide complexes, including $Cu(CN)_3^{-2}$ and $Cu(CN)_4^{-3}$. The successful quasi-potential approach will be extended to these complexes. Solubility limits of sodium and copper cyanide will also be considered and will predict under what circumstances precipitation reactions will occur.

Summer Grant Project

Study of the Surface Etching Treatments Needed To Promote Adhesion Of Functional Chromium Deposits on Steel

Project Director:
Professor Keith Sheppard
Stevens Institute of Technology, Hoboken, NJ, USA

Hard chromium deposits are often used to withstand conditions where friction and wear are of primary importance. Chromium-plated shafts, stamping dies and other applications come to mind. In these areas, surface finish and adhesion are of paramount importance. In sheet-metal stamping, surface finish can reduce the friction between the die surface and the metal being drawn. Studies have shown that the surface finish of the chromium is influenced by the surface finish of the substrate. But, so is the adhesion.

With inadequate adhesion, the results can be catastrophic.

Plate adhesion can be augmented by etching of the substrate surface. In essence, a mechanical keying component is added to the equation. This summer project was undertaken to shed light on the effects of various etching process on chromium adhesion. Four electrolytic etching processes were studied: 5% sulfuric acid; chromic acid; propietary etch #1*; and proprietary etch #2**. A test matrix of process times from five to 120 seconds, and current densities (including zero current) from zero to four A/in^2 (58 A/dm^2), was studied.

Specimens consisted of induction-hardened injector pins from D4 steel. The mean substrate hardness was Rockwell "E" 55. The resulting etch morphologies were examined by scanning electron microscopy (SEM) at 6000X, augmented by image analysis software.

The results were very interesting and also shed light on further work that could be done along these lines. For all four etches, a general trend was observed over time. First, consider that etching produces microscopic cavities, or holes in the substrate. The image analysis showed that the area portion of cavities increases with increasing time. This may come as no surprise, but the other result, via cavity count, showed that the number of holes was unchanged after 30 seconds. Thus, after an initial interval, no new cavities are created by etching; rather the process acts to increase the size of those already formed. Etching might be characterized in terms of time and hole size, independent of chemical method.

With the exception of chromic acid, the three etchants applied without electrolytic current produced such a thick oxide layer that image analysis was impossible. The layer appeared to increase in thickness with time. Future research into the nature of this oxide was suggested. Such oxides could strongly interfere with plate adhesion. Under electrolytic conditions, the chromic and sulfuric acid solutions had a tendency to form oxides. Proprietary etch #1 provided rather consistent results. Proprietary etch #2 was very effective, according to the investigators. It has a limited operating range, however, and requires special procedures for storage and use.

Summer Grant Project

Anomalous Electrodeposition Of Alloys - Modelling Studies Of the Electrodeposition of The Binary Iron-Group Alloys

Project Director:
Professor Jan B. Talbot
University of California—San Diego, San Diego, CA, USA

Another important summer grant program dealt with a study into alloys of iron, nickel and cobalt. These alloys are commercially important because of their physical and magnetic properties. By controlling the alloy composition, you can literally "dial-up" the desired property over a wide range. Deposition of these alloys, however, is complicated by a phenomenon known as anomalous codeposition.

**HEEF 25, Atotech USA Inc., Somerset, NJ*

***HCR 840, Attotech USA Inc., Somerset, NJ*

In anomalous codeposition, the ease with which the metal deposits is opposite of what is expected. Because everything in nature ultimately seeks its lowest energy state (that is why it is hard to stay awake some days), the most noble of the three should be easiest to deposit. Considering the thermodynamics and kinetics of these systems, nickel should go down easier than cobalt, which should go down easier than iron. Although a gross simplification, a 50/50 mixture of nickel and iron should yield an alloy that contains more nickel, and so forth. Nevertheless, under certain conditions, the ease of deposition is reversed. This makes it difficult to predict the alloy composition.

Dr. Talbot and her coworker, Keith Sasaki, have addressed this phenomenon over the summer. An understanding could lead to prediction of alloy composition under a variety of conditions. In this work, three theoretical models were studied and compared with results obtained by galvanostatic electroplating from simple sulfate solutions for the nickel-iron system, onto a platinum rotating disk cathode. The predictive models were derived from works of Hessami and Tobias, Matlosz and Grande and Talbot.

The attempts to use the laboratory data in each of these models did not prove successful in reproducing the alloy compositions for any of the iron-group alloys. The general shape and magnitude of the resulting alloy compositions were not well simulated in any case. All was not lost, however. Analysis of the potential curves did shed light on one aspect of the deposition process. Within the potential range studied, the more noble metal (in this case nickel) was unchanged or inhibited in codeposition, while the less noble metal (iron) was promoted. This short summer project served to whet the appetite for more.

Summer Grant Project

Electrochemical Concentration And Treatment of Cyanide-Bearing Wastewaters

Project Director:
Professor James Fenton
University of Connecticut
Storrs, CT, USA

Project 91 seeks to find substitutes for cyanide in copper plating solutions. At the same time, there is plenty of cyanide plating still with us. With this goes the need to develop more effective ways of assuring that wastewater cyanides are effectively handled. In this summer project, a bench-scale, electrochemical ion exchange (EIX) reactor was set up to study the feasibility of handling copper cyanide-containing wastewaters. This study served to establish the “proof of the concept.”

The goal of EIX was two-fold: Concentrate the dilute copper cyanide solutions by electrodialysis; and oxidize, at the anode, the cyanide to innocuous nitrogen and carbon dioxide. Three anode materials were tried: Iridium oxide on a titanium substrate, the “dimensionally-stable anode (DSA) used in electrogalvanizing; graphite; and the venerable lead dioxide on a titanium substrate.

The lead dioxide anode was found to be most effective in cyanide destruction. At room temperature (25 °C), with an operating voltage of 7V, the original cyanide concentration of 500 ppm was reduced to less than 1 ppm during two-hours of electrolysis. Within the same time-frame, use of the graphite anode led to a concentration of 200 ppm. The iridium oxide did not promote cyanide destruction at all; cyanide content remained at 500 ppm. Using the lead dioxide electrode at an elevated temperature (70 °C) resulted at the same reduction to under 1 ppm in less than an hour.

In terms of concentration by electrodialysis, our investigators found that the reactor caused the migration of both cyanide and copper cyanide complexes across the anion-permeable membrane. These tests were run with the iridium oxide anode so that minimal cyanide was destroyed. In this way, migration results would not be perturbed by cyanide reduction effects. So the concentration aspect was feasible too. The results show EIX to be a safer and cheaper way to treat cyanide-bearing wastewaters from the plating industry.

Of course, the duration of this project led to as many questions as answers. Measurement of cyanide migration through the membrane with the effective lead dioxide anode is important. The effectiveness of the process, while the concentration and cyanide destruction reactions are going simultaneously, can thus be established. Further optimization of the system, including membrane materials, flow rates, pH and operating voltage is also envisioned.

This month, the Research Board will be meeting during AESF Week in Orlando (February 5–9) to plan the program for the 1996-97 year. Current work will be reviewed, the funding situation will be examined, and, it is hoped, new work can commence. These good works will help to improve the state of our industry, over time. But it can only be accomplished through your support and input. Keep up the good work. ***P&SF***

Federal Register Review

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- Department of Energy (DOE)
- Environmental Protection Agency (EPA)
- Fish and Wildlife Service (FWS) (under Department of the Interior)

These regulatory agendas are published twice each year and provide summaries of current and projected rulemakings, reviews of existing regulations, and designate actions completed since the publication of the previous agenda. (60 *Fed. Reg.* 59914, 59972, 59998, 60108, 60604; November 28, 1995.) ***P&SF***

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