Research Corner



Dr. Jim Lindsay Research Engineer General Motors Research & Development Center 30500 Mound Road Warren, MI 48090-9055

AESF Research Program Continues To Do Good Work

The New Year of 1997 has arrived and another year of valuable AESF Research is behind us. It is tempting to wax poetic and suggest, in living color, that we are embarking on new scientific frontiers, building a bridge to the 21st century (but I think that one's been taken) and making breakthroughs into uncharted realms of scientific endeavor. However, because we seem to be constantly plagued with inane buzzwords these days, let me just say that the AESF Research Program continues to do its usual good works.

This time, I would like to summarize the final results for our project at Clarkson University and report on continuing progress at North Carolina State. Finally, the results from one of our Summer Grants for 1996 may be of interest to you.

Project R-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

Project #90 has concluded and all of the results are in. This work has been particularly interesting, because its outcome has shed light on the coating of mixed-phase substrates. Dr. Chin and his group have made a very important contribution in this regard.

Electroless nickel coatings are widely used to provide wear and corrosion protection of ferrous alloys. Because the nickel deposit is more noble than the substrate, the corrosion performance is strongly dependent on the coating porosity. The porosity is, in turn, influenced by such factors as the substrate microstructure and process solution additives. Ferrous alloys—and cast irons in particular—contain carbon and iron carbides in their microstructures. Such entities may not promote electroless nickel deposition. The local sites where carbon and iron carbide are present on the substrate may become potential sites for pore formation in the deposit. Further, bath stabilizers, which are added to the solution to extend its useful life, or their reaction products, are often codeposited with the electroless nickel. Porosity can arise this way, too.

Project #90 endeavored to address these concerns. The effect of carbon and iron carbide inclusions in ferrous substrates on pore formation was investigated. The effect of four bath stabilizers—lead ions, iodate ions, maleic acid and mercaptobenzothiazole—on deposition rate and porosity was also studied.

Specially-configured half-iron/halfgraphite substrates were used to examine the spreading of electroless nickel from the iron to the graphite areas. Deposition on gray cast iron, which contains large amounts of graphite flakes in its microstructure, was the next step. Porosity was examined by scanning electron microscopy (SEM) and energydispersive spectroscopy (EDS). In addition, a non-destructive electrochemical porosity measurement technique was used to measure porosity. Finally, electrochemical polarization measurements were used to examine the effect of the substrate and bath stabilizers on the anodic and cathodic half-reactions of the electroless nickel deposition process.

The results indicated that spontaneous electroless deposition occurred on iron carbide, but not on carbon. It was found, however, that deposition could be induced on carbon by galvanic activation. Using stabilizers decreased the deposition rate on both steel and carbon substrates. Lead and sulfur codeposited when lead ions and mercaptobenzothiazole, respectively, were used as stabilizers. Maleic acid reduced the phosphorus content of the deposits. As for the porosity, it increased as the substrate carbon content increased, and when bath stabilizers were used.

Several techniques were considered to reduce porosity. Classic palladium activation increased the plating rate, but did not reduce porosity. Mechanical or electrochemical polishing of the substrate to a surface roughness, R_A , of one micron, reduced porosity and the tendency to form nodules. Using an electrolytic nickel strike prior to the electroless step also decreased porosity. Here, the exposed carbon and other non-catalytic substances on the surface were covered with a catalytic nickel layer.

In all, this was a very worthwhile project that answered a number of questions. Anyone considering electroless deposition on mixed-phase substrates would do well to examine the results of this work. A comprehensive 180-page final report on Project #90 is available by contacting AESF Headquarters.

Project R-91

- Copper Deposition from Cuprous Ligand Complexes: A Contribution Toward the Replacement of Cyanide in Strike-Plating Baths
- **Project Director:** Professor Peter S. Fedkiw, North Carolina State University, Raleigh, NC

In this work, Dr. Fedkiw is taking a modeling approach toward the use of cuprous ligand complexes as replacements for the venerable cyanide ligand in alkaline copper plating. During the year, considerable progress has been made in developing that model and undertaking experimental work to confirm its validity.

Developing the model has been a laborious task. Preliminary models for alkaline cyanide copper plating were very simple, dealing with the lowestorder cyanide complexes. Currently, the model describes the discharge of copper from a cyanide electrolyte on a planar cathode. It describes mass transport by diffusion and migration of all complexes formed from cuprous and cyanide species: $CuCN_{aq}$, $Cu(CN)_{2}^{-1}$, $Cu(CN)_{3}^{-2}$ and $Cu(CN)_{4}^{-3}$. It accounts for the effects of solution composition, in terms of pH, copper cyanides, sodium cyanides and carbonates, on the mass transportlimited current density, electrode potential and species concentrations at the electrode surface.

In order for the model to do a reasonable job of predicting behavior, one must have accurate physical and chemical constants on which to base the predictions. Here, the diffusion coefficients for the copper-containing species that carry most of the current [*i.e.*, the three complexes, $Cu(CN)_2^{-1}$, $Cu(CN)_3^{-2}$ and $Cu(CN)_4^{-3}$] were unknown and needed. Rotating disk voltammetry (RDV) was used for this.

Under all conditions studied, the diffusion-limiting currents for copper deposition were masked by the current attributed to hydrogen reduction. In order to eliminate this "background noise," hydrodynamically modulated rotating disk voltammetry (HMRDV) was employed. In RDV work, the potential is varied while the electrode rotation speed is kept constant. In HMRDV, the potential is held constant while the rotation speed is varied. The net result is to split-out current components that are independent of rotation rate, such as hydrogen evolution.

In the end, Dr. Fedkiw and his colleagues still found difficulty in determining diffusion coefficients by HMRDV. They hoped that the method would be more sensitive to mass transport than kinetics. Unfortunately, both were significant. They haven't given up on this technique, however. They plan on trying multivariate regression techniques to extract diffusion coefficients from the HMRDV data. Further modeling refinements will also continue.

Summer Research Grant S-52 Magnetic Thin Film Alloy Electrodeposits

Project Director: Keith B. Chin, Graduate Student, Department of Chemical Engineering, UCLA, Los Angeles, CA

The need for higher performance recording heads in computer applications has prompted the search for new alloy thin films with superior magnetic properties. To this end, a rather ambitious program was undertaken to electrodeposit cobalt-iron, cobaltiron-vanadium, cobalt-nickel, cobaltnickel-vanadium, nickel-iron and nickel-iron-vanadium alloy thin films and determine their magnetization and corrosion-resistance properties. In general, the solutions were based on mixed sulfate-chloride systems. Magnetization was determined by measuring forces induced by a permanent magnet, using an analytical balance. Corrosion was measured by AC impedance methods. The results are briefly summarized below.

Cobalt-iron

The alloy composition was 90 percent cobalt and 10 percent iron. The films deposited at low pH (5.6), had better magnetization and corrosion properties than those obtained at pH values between 6.0 and 7.5. The low-pH deposits also exhibited a bright metallic appearance. Those from higher pH solutions did not.

Cobalt-iron-vanadium Increasing pH decreased the iron content and increased the vanadium content. At pH 5.5, the deposit contained 93.0 percent-6.5 percent-0.5 percent (Co-Fe-V), while at pH 7.2, the corresponding composition was 93.7 percent-4.2 percent-2.1 percent. Magnetization and corrosion properties increased with current density and with the introduction of pulse plating. Increasing the vanadium content decreased these properties.

Cobalt-nickel

& cobalt-nickel-vanadium Magnetization was strongly influenced by the presence of vanadium. The magnetization was increased fivefold with a 93.2 percent-4.5 percent-2.3 percent (Co-Ni-V) vs. 87.6 percent-12.4 percent (Co-Ni). Magnetization was also increased by pulse plating.

Nickel-iron

& nickel-iron-vanadium Alloys with high nickel contents (above 90-percent nickel) showed high corrosion resistance, but low magnetization. Pulse plating increased the corrosion resistance of nickeliron, but decreased that of nickel-ironvanadium.

Proposed Research for 1997 This month, during AESF Week '97, the Research Board will be deliberating on the program for Fiscal 1997. Several proposals for high-quality research will be reviewed, both for full research projects and for the Summer Grant program.

I look forward to telling you about the outcome of these deliberations in the next installment. **PASF**

Free Details: Circle 118 on postpaid reader service card.