Research Corner

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

AESF Research Program—Looking Ahead

In past columns, I have attempted to tell you what has been accomplished in the various research projects funded by the AESF Research program. This time, instead of telling you what we've done, I'm going to tell you what we're going to do. At SUR/FIN® '97 in Detroit, the Research Board met and, among other things, selected the Summer Research Grant projects for 1997. These are the short-term projects that we fund, which often lead the way to the full-scale research grants. By the time you read this, much of the work will have been done. Until the reports start coming in, let me whet your appetite by covering the goals and hopes of these short-term research projects.

AFM Study of Organic Additives in Copper Plating

Project Director: *Dr. Jacek Lipkowski, University of Guelph, Guelph, Ontario, Canada*

Organic additives are the mainstay of the plating industry. Without them, brightness, structure and metallurgical properties could not be as readily controlled. This is particularly true in the case of copper, where property control is paramount in areas ranging from printed circuitry to electroforming and electrowinning. While organics have been studied for decades, many tools are now available which were not even dreamed about in the early years.

Fourier transform infrared spectroscopy (FTIR) can be used to see how the organics are adsorbed on the surface and determine the copper structure. Atomic force microscopy (AFM) and scanning tunneling microscopy (STM) can be used to observe the surface on an atomic scale. Professor Lipkowski and M. Sc. student Tinghe Zhao will be using these advanced tools to see how various organic additives influence the rate of nucleation, the growth and the morphology of the copper deposit. This type of information can lead to a more effective approach in selecting additives. The emphasis here will be on electrorefining, but the information can be extended to other copper plating applications.

Kinetic and Hydrodynamic Factors on the Structure of Conversion Coatings

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

In conversion coat processes, such as chromating and phosphating, and in oxide forming processes such as anodizing, artificially induced and controlled corrosion is used to produce a metal surface layer, firmly bonded, which is actually an integral part of the original substrate. It can serve as a base for paints, oils and greases. Regardless of the process itself, there exists a common electrochemical mechanism involving linked anodic and cathodic reactions.

In this work, Dr. Aroyo intends to examine the influence of kinetic factors, as gleaned by pulsed signals, and hydrodynamic factors, via solution agitation, on such processes. He will consider anodization of aluminum, chromating of aluminum and phosphating of steel. His intent is to define the optimum conditions for forming conversion coatings and anodic films with homogenous and fine-grained structures.

Success here could lead to improved anti-corrosion protection by paints resulting from improved adhesion to steel, decreasing friction and improving anti-seizing properties of treated aluminum and improving the decorative appearance of aluminum through more uniform absorption of organic and inorganic dyes.

Anodic Treatments for Metal Finishing Effluent

Project Director: *Dr. David Gabe, Loughborough University, Loughborough, U.K.*

The rotating cylinder electrode reactor (RCER) has been extensively developed for electrowinning reactions at the Institute of Polymer Technology and Materials Engineering at Loughborough University under the able direction of Dr. Gabe. This project will investigate its extension to effluent treatment processes. Two particularly important anode reaction processes will be studied: 1) destruction of cyanide ions by anodic destruction and 2) regenerative anodic oxidation of trivalent chromium to the hexavalent state. Both of these subjects deal with chemistries that are not limited to electroplating. Cyanide metal strippers and cleaners as well as chromic acid-based passivation and anodizing processes enter in too.

The aim here is to study the two reactions while exploiting some advanced anode materials that promise to substantially increase the efficiency of these processes. Such anodes use a corrosion resistant base, such as titanium, niobium or tantalum, coated with a low polarization coating such as platinum, palladium or a precious metal oxide (RuO_2, IrO_2, etc.).

Beyond the anode material development, Dr. Gabe proposes to consider 1) the implications on stability of the metal ions, once the cyanide complex is destroyed and 2) the possibility of recycling the regenerated hexavalent chromium (either to plating or passivation solutions), which may require the use of cells divided by ion exchange membranes. The resulting package would contain: 1) cell design, 2) optimum anode materials for each reaction, 3) optimum operating conditions and 4) experience on usage on an industrial scale.

Electrolytic Recovery of Zinc from Pickling Baths

Project Director: *Dr. Thomas M. Harris, University of Tulsa, Tulsa, OK*

Sulfuric acid solution is commonly employed in pickling, the removal of the oxide film from steel prior to surface finishing (*i.e.*, galvanizing, etc.). The effectiveness of the pickling solution decreases as iron builds up. In time, the ferrous sulfate is crystallized out by chilling. This same solution can be used to strip zinc from galvanized steel sheet and parts that fail to meet quality standards. Here, the chilling operation would yield a mixture of zinc and iron sulfates. The amount of zinc is commercially significant, amounting to 20% of the total metal content. To address this, the work underway here is aimed at developing a process to recover the zinc in usable form.

The proposed process is electrolytic and is envisioned to operate either in a flow stream or by batch in a solution of the recovered mixed metal sulfate crystals. Taking advantage of anomalous codeposition conditions, a zinc-rich deposit can be obtained from an iron-rich bath. The approach here will determine the conditions of flow rate, pH and temperature under which anomalous codeposition is favorable.

Dr. Harris will be supervising Ms. Valerie Codner, an undergraduate student at the University of Tulsa. Ms. Codner has expressed an interest in pursuing a career as a chemist in the surface finishing industry. The importance of adding the talents of people like her to our industry is critically important these days, and this is an example of an added benefit of AESF Research.

The ultimate hope is to have a process for recovering the zinc from a waste stream in a hot-dip or electro-galvanizing plant. It is estimated that an average of $35,000 worth of zinc is lost annually from each hot-dip galvanizing plant. If this approach is feasible, a pilot scale study is envisioned.

Tribochemical Polishing of Electroless Nickel Deposits

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

This work considers the surface finishing of electroless nickel to an ultra-smooth state of polish by tribochemical techniques. Such highly polished finishes are essential in the highly planar integrated circuits grown on semi-conductor wafers required today and in the future. An important application for such surfaces lies in plated hard discs for magnetic data storage.

In chemical-mechanical polishing, an abrasive slurry is held in contact with the surface to be polished by a porous pad. Prior studies have suggested that the polishing is achieved by local removal of a protective film by the abrasive with a consequent enhancement of local dissolution. This differs from electropolishing, which is dependent of diffusion through a surface film, which can be perturbed by local flow anomalies or even gas bubbles. The technique proposed here, tribochemical polishing takes things one step further. No abrasives are used, but rather mechanical pressure is applied while the surface is immersed in a suitable chemical medium. Local dissolution is stimulated at surface asperities. Work at Stevens Institute to date has shown it possible to polish silicon carbide and silicon nitride to atomically smooth dimensions.

The work here will apply this technique to electroless nickel. Electrolytes used will be those in which electroless nickel-phosphorus forms a passive film. Positive results in this work could have a significant impact on the magnetic hard disc industry, which produces very large numbers of electroless nickel plated discs requiring an ultra-smooth finish. Increased performance requirements can be met by such advanced techniques.

Catalytic Activity Measurement for Fully Additive Printed Circuit Pattern Plating

Project Director: *Dr. E. Eric Kalu, FAMU-Florida State University, Tallahassee, FL*

The attractiveness for a low-cost and short-time manufacturing cycle in the printed circuit industry has led to a rapidly increasing interest in a technique for creating fully additive circuitry for the manufacture of flex circuits and printed wiring boards. In this process, a catalytic ink formulation of a palladium salt is used with a printing press or ordinary printer to print the circuit pattern on a dielectric substrate. The printed catalyst pattern is thermally or photochemically activated, and electroless plating is then deposited to the required thickness.

Unfortunately, there is no quantitative way of measuring the activity of the catalyst ink, nor is there a way of comparing the activities of one catalytic ink formulation with another. This work explores the feasibility of measuring catalytic activity by using electrochemical techniques, induction times and cyclic voltammetry. Such a technique will be beneficial to the industry in quantitative comparisons of catalysts. Further, it might evolve as a means of understanding how the catalysts work and how to best formulate them.

Preparation of Submicron Multilayers by Novel Electrodeposition Methods

Project Director: *Dr. Ken Nobe, University of California at Los Angeles, Los Angeles, CA*

Currently, there is considerable activity in the development of submicron multilayer structures. They consist of alternating magnetic and non-magnetic microlayers of two or more materials and are sought for their "giant magnetoresistance" (GMR) properties. Such properties are of particular interest in the area of sensors.

Most of these materials have been prepared by vacuum deposition processes, including evaporation, sputtering and chemical vapor deposition. Electrodeposition, however, is an attractive prospect for these materials in terms of simplicity and ease of scaling up to production volumes. Further, plating processes use lower temperatures and the operating conditions, in many cases, can be more precisely controlled.

This work is directed toward parametric studies for the fabrication of sub-micron-thick multilayer structures using a flow-through electrochemical cell, newly developed at UCLA. The cell may be adaptable to a single electrolyte approach, where the alternating deposits are derived from the same solution by varying deposition conditions. This avoids activation and cross-contamination problems associated with dual electrolyte techniques. Plans call for the cell and process to be optimized to achieve zero discharge of effluent. This work may lead to the development of methods for obtaining deposits with superior magnetoresistance properties for GMR applications.

Anodic Polarization Behavior of Zinc-Nickel Alloys

Project Director: *Dr. Howard Pickering, The Pennsylvania State University, University Park, PA*

This work is a continuation of Summer Research Grant work into the corrosion behavior of zinc- nickel alloy electrodeposits, used for fastener and body sheet metal applications in the automotive industry. Previous work showed that there was a critical corrosion potential above, which dealloying occurred. The potential was also associated with crack propagation. This transgranular cracking was also found to occur during potentiodynamic scanning studies when the critical value was exceeded.

This work is continuing, in order to determine the tendency for selective zinc dissolution during corrosion. In particular, this undesirable dealloying form of corrosion and the conditions leading to it will be more closely characterized. Such results should be invaluable in the design and development of improved zinc alloy coatings.

AESF Will Benefit from Up-&-coming Professionals

This summarizes the Summer Grant program for 1997. This aspect of the AESF Research program is particularly valuable. By investing our resources in these short-term projects, we have been able to evaluate a number of areas with funding equivalent to a full research grant. The results have shed light on the value of several areas, which can be considered for fuller study, if warranted. In future installments, I will be sharing the results of these works, as well as those of our full Research Grant projects with you.

As I said earlier, the industry receives the added benefit of talented, up-and-coming students being exposed to working in the interesting area of surface finishing. And we certainly need more people to come into this field, make their careers in it and advance it in coming decades. If this doesn't happen, we're all going to be sorry. **P&SF**