Research Corner



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Valuable Work at Stevens Institute & University of South Carolina

s I noted in my last column, A several projects were completed during the AESF fiscal year ending March 31, 1996. At that time, the researchers compile a final report on the entire project, which covers the work in its entirety. Some of these reports represent three years of research efforts. Others represent work for a project year. Still others, as in the case of the Summer Grants, represent a number of months of diligent work, which often point to further research. What follows is a summary of two of the larger works from this fiscal year.

This month, I will be covering the valuable work done at Stevens Institute on substitutes for fluoborates in lead-tin solder plating, and the attempts to eliminate lead in solder plates by substituting bismuth. I will also summarize the work done at the University of South Carolina on zincnickel and zinc-nickel-silicon dioxide processes. These have major potential in answering the call for cadmium substitutes, improved corrosion resistance and improved hydrogen embrittlement characteristics.

Project 88

Pulsed Electrodeposition of Lead-Tin and Lead-Free Solder Alloys from a Sulfonate Bath Project Director: Professor

Keith Sheppard Stevens Institute of Technology,

Hoboken, NJ The primary objective of this project, undertaken by Professor Keith Sheppard and his group at Stevens Institute, was to provide a less aggressive electrolyte for solder, *i.e.*, lead-tin alloy, plating. Plated lead-tin alloys had been widely used in the electronics industry for packaging applications such as circuit boards. Indeed, they have recently been employed for solder bump interconnects. Because of their stability and inherent high plating rates, fluoborate solutions have been the mainstay in solder plating technology.

Unfortunately, fluoborates also carry a few burdens. The electrolyte is very corrosive; environmental and workplace safety concerns are present. Without the use of organic surfactants, fluoborate processes foster easy dendritic growth during plating. The breakdown products of these additives could be incorporated into the deposit and negatively alter certain critical properties in given applications. It was desirable, therefore, to develop a less aggressive, environmentally friendly solution, which also might be less amenable to promoting dendrites. It was hoped that significantly reduced surfactant consumption could be realized.

In recent years, proprietary systems have been developed, based on sulfonate electrolytes. Dr. Sheppard undertook work on the methane sulfonate system. The bath was less corrosive and amenable to safe disposal. The process still required the use of a surfactant to suppress dendritic growth, but other approaches were tried, specifically the use of pulse plating.

Pulse plating, because it provides a measure of control over mass transport and deposit crystallization, offered the possibility of influencing both composition and morphology (*i.e.*, suppressing dendrites). The potential for eliminating or reducing the use of additives was there. Even with the use of additives, pulse plating could reduce the tendency toward codeposition. This had been shown to be the case with pulseplated gold, where desorption from the surface occurred during the offtime portion of the cycle.

The effects of different amounts of a surfactant and a brightener (2,4,dimethoxybenzaldehyde) were investigated in a methane sulfonate solution via rotating disc electrode studies. The results showed that pulse plating in this system allowed a reduction of surfactant concentration of one order of magnitude when compared to direct-current (DC) plating. With DC current, 5.0 mL/L of surfactant were required to suppress dendrites. The same effect was achieved with 0.3 mL/L of surfactant with pulse plating.

Dendritic growths were suppressed while maintaining good control over deposit morphology and composition over a wide range of lead-tin alloys. Indeed, pulse plating appeared to offer control over a large current density range.

Pulse plating tended to promote the deposition of lead, when compared to DC plating at the same average current density. The tin content, therefore, was reduced from a wide range of solution compositions.

Variations in pulse frequency and duty cycle were done to determine the optimum pulse plating conditions. A duty cycle of about 10 percent and a frequency on the order of 100 Hz were the optimum parameters to obtain the desired morphology.

Tensile studies were done using the mini-tensile test method developed at Stevens under previous AESF Research grants. The as-plated alloys of 60 percent tin/40 percent lead and 10 percent tin/90 percent lead showed resistance to necking during the tensile tests. This indicated elongation levels in the superplastic range. After reflowing these deposits, such behavior was no longer observed.

With concerns about lead and its toxicity, studies were extended to "get the lead out" of solder, as well as to provide a fluoborate substitute. To this end, a study into producing tinbismuth alloys from sulfonate-based electrolytes was undertaken. Only limited success was achieved. The metals could only be codeposited by pulse plating. The complexants that were tried were not effective in shifting the bismuth deposition potential to a more negative value. This would have allowed it to be codeposited in significant alloy fractions. Further, the morphology of the deposits that were obtained were far from satisfactory.

Project 93

Electroplating of Thin Films of Zinc-Nickel Composites onto Steel to Prevent Corrosion and Hydrogen Embrittlement Project Director: B. N. Popov &

R.E.White University of South Carolina,

Columbia, SC

With increasing interest in zinc-alloy platings in recent years, this work has served to provide an understanding into the workings of the coatings and, consequently, new insights into their improvement. Zinc-nickel alloys, in particular, have been shown to impart improved corrosion resistance and resistance to hydrogen embrittlement. They have found application in several areas, from barrel-plated fasteners and small parts, to continuously plated sheet metal for automobile body stampings. Recent concerns over the toxicity of cadmium metal has led to substitution of zinc-nickel for cadmium in many civilian and military applications.

Allied with this work has been a study into nickel-zinc-composite coatings, specifically, the co-deposition of silicon dioxide (SiO₂) particles in a zinc-nickel matrix. This system has the potential to blunt hydrogen penetration to the substrate. This leads to great positive advantages when it comes to hydrogen embrittlement concerns.

With these potential advantages in mind, Drs. Popov and White have undertaken to study these coatings in detail. They began with the kinetics and growth mechanism of microcrystalline Zn- Ni alloys on steel, without silicon dioxide. They have advanced to the Zn-Ni-SiO₂ codeposition process. Here, the Zn-Ni bath contains colloidal SiO₂ and organic additives.

Experimentally, the deposition of zinc-nickel alloys was investigated for different agitation conditions by using galvanostatic pulse and pulse reverse plating, on a rotating disc electrode, from sulfate solutions with and without the organic additive, nonvl phenyl polyethylene oxide. The bath contained the following molar concentrations: 0.5M nickel sulfate, 0.2M zinc sulfate and 0.5M sodium sulfate (conducting salt). At low current densities, the zinc deposition is under kinetic control and increasing the polarization increases the zinc content. Here also, the zinc content decreases as the speed of the rotating disk increases. Mass transfer limitations become more important at higher average current densities. Here, the zinc content increases as the disk speed increases. The additive effects were explained by the effect of surface coverage.

A mathematical model was also developed that estimated the concentration profiles and their potential responses for both pulse and pulse reverse plating of these alloys. It accounted for the effects of average current density, rotation speed of the disk electrode and the presence of nonyl phenyl polyethylene oxide.

The zinc-nickel solution equilibrium concentrations at various pH levels was determined by studying the solution chemistry. The results indicated that, up to pH 7.0, the metal ions were predominantly in their bivalent (+2) state. The concentration of metal monohydroxide ions increases with increasing pH and reaches a maximum just before the onset of hydroxide precipitation. From these results, an equilibrium diagram was generated that allowed estimation of the interface concentrations of the metals in pulse and reverse pulse plating modes.

Linear sweep voltammetry was used as an *in situ* technique to characterize the thin layers of zincnickel and to assess the electrochemical behavior (*i.e.*, corrosion behavior) of the alloys. The zinc dissolution potentials were found to be more noble than those for pure metal ions. This was because of the formation of two alloy intermediate phases, γ (gamma) and δ (delta).

Finally, an attempt was also made to determine the hydrogen permeation characteristics of the deposits. The Devanathan-Stachurski permeation technique was used to investigate the rate of hydrogen permeation through an iron membrane with consecutively plated zinc layers. Hydrogen evolution and permeation rates were followed as functions of time at different applied potentials. Both evolution and permeation decreased with each successive zinc layer until finally reaching an average decrease of 93 percent and 96 percent, respectively, as compared with bare iron. The decrease in the hydrogen permeation rate through the iron membrane was because of: (1) The decrease of the hydrogen discharge rate on the zinc, and (2) the suppression of hydrogen ab- and adsorption on the zinc layers.

Translating this to the alloy and alloy composites, the Zn-Ni and Zn-Ni-SiO₂ composites were the most effective in reducing the hydrogen permeation entry efficiency. It was reduced to 2.0 percent and 1.2 percent in the presence of the deposited alloy and alloy composite, respectively.

The results reported here range from the practical to the theoretical. The important thing is that all of these results ultimately will find their way to practical usage. That is the astounding thing about scientific investigations. The most theoretical kernel will find its way to improvements in or developments of new technology, which will ultimately benefit our industry. The foresight of the founding members of AESF in spawning the AESF Research Program decades ago still bears fruit today.

In the next "Research Corner," I will summarize the results of the Clarkson University work on electroless nickel plating on cast-iron substrates, which has unveiled several insights on just how deposition proceeds on such mixed-phase substrates. I will also review the work at North Carolina State University in the quest for substitute ligands to replace cyanides while retaining the advantages of cyanides in solution chemistry. **Pasf**