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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Research had demonstrated several significant effects caused by the application of magnetic fields during electrolytic thinning and electrodeposition of metals. The purpose of the research supported by this contract was to continue studies of these effects. Research sought to determine what applied magnetic field strength and other parameters of electrolysis would maximize the following effects:

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20. ABSTRACT CONTINUED:

(a) Improvement in the uniformity of both anode and cathode processes. There is a natural tendency for much higher electric fields, and therefore, higher rates of electrolytic reactions at edges and asperities than at other points on the electrodes. Because the Hall effect is greatest where the electric field is greatest, a magnetic field improves uniformity of electrode processes.

(b) Increase in the speed of electrodeposition. Depletion of metal ions in the layer of electrolyte adjacent to the cathode normally limits the rate of electrodeposition of metals. The Lorentz force causes intense stirring in this layer, thus permitting replenishment of the metal ions and increase in the speed of deposition.

(c) Inhibition of hydrogen gas formation during electrodeposition. Because of their higher mobility, the Hall effect on hydrogen ions is expected to be greater than on metal ions. This is expected to decrease the supply of hydrogen ions at the cathode and thus suppress hydrogen gas formation.

An additional goal of this research was to determine effects of magnetic fields on the properties of metallic deposits.

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Electrodeposition of Chromium and Copper in Magnetic Fields

Final Report

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2-28-85

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A. Statement of the problem studied.

Our previous research had demonstrated several significant effects caused by the application of magnetic fields during electrolytic thinning and electrodeposition of metals. The purpose of the research supported by this contract was to continue studies of these effects. We sought to determine what applied magnetic field strength and other parameters of electrolysis would maximize the following effects:

(a) Improvement in the uniformity of both anode and cathode processes. There is a natural tendency for much higher electric fields, and therefore, higher rates of electrolytic reactions at edges and asperities than at other points on the electrodes. Because the Hall effect is greatest where the electric field is greatest, a magnetic field improves uniformity of electrode processes.

(b) Increase in the speed of electrodeposition. Depletion of metal ions in the layer of electrolyte adjacent to the cathode normally limits the rate of electrodeposition of metals. The Lorentz force causes intense stirring in this layer, thus permitting replenishment of the metal ions and increase in the speed of deposition.

(c) Inhibition of hydrogen gas formation during electrodeposition. Because of their higher mobility, the Hall effect on hydrogen ions is expected to be greater than on metal ions. This is expected to decrease the supply of hydrogen ions at the cathode and thus suppress hydrogen gas formation.

An additional goal of this research was to determine effects of magnetic fields on the properties of metallic deposits.

B. Summary of the most important results

(a) To determine effects on uniformity and speed of deposition and on properties of the deposits, copper electrodeposition from copper sulphate solutions in magnetic fields was studied. It was found that compact copper deposits can be made at a current density of 0.32 A/cm^2 in a magnetic field of 7 kG. The literature indicates that this current density is comparable with that which can produce compact deposits by employing high speed solution flow together with a spinning cathode. Very large or very small crystalline deposits can be produced, depending on the current density and the applied magnetic field. For example, with current density of 0.08 A/cm^2 and 10 kG, the substrate crystals grow epitaxially into the deposit, and the deposit hardness is the same as the substrate hardness. By increasing current density to 0.16 A/cm^2 with the same magnetic field strength, the deposit is smoother, crystal size of the deposit is too small to be detected with the light microscope, and deposit hardness is about twice that of the substrate. Periodic effects seem to occur. For example, at fixed current density, increasing the magnetic field strength produces deposits with smaller and smaller crystals, until a certain minimum size (not yet measured) is produced. Further increases in magnetic field strength cause increase in grain size of the deposits. These results suggest the possibility of producing deposit microstructures ranging from single crystal to amorphous.

Recently, Al_2O_3 particles have been co-deposited with copper from a $CuSO_4$ solution. The Al_2O_3 particles placed in the $CuSO_4$ solution settle to the bottom of the container. These particles remain undisturbed at the bottom of the container with a DC current applied. However, the particles disperse throughout the solution and co-deposit with copper when the magnetic field is turned on. Results of preliminary experiments are promising. For example, it is possible to co-deposit either alpha or gamma Al_2O_3 with copper in an applied magnetic field. The literature states that only alpha Al_2O_3 can be co-deposited with copper when mechanical stirring is employed to suspend the Al_2O_3 particles in the electrolyte.

(b) To determine effects on hydrogen gas formation, chromium electrodeposition from chromic acid solutions was studied. The maximum suppression of hydrogen gas formation by an applied magnetic field was found to be about 10%. This suppression was attributed to lowering of the cathode temperature due to intense stirring at the interface. The greater Hall effect on hydrogen ions does not seem to be a factor in hydrogen gas suppression.

During the course of these experiments, it was accidentally discovered that a small amount of methanol added to the chromic acid electrolyte causes an increase of about 20% in the current efficiency of chromium deposition. With further research it was determined that large concentrations of Cr^{3+} and Fe^{3+} in the chromic acid solution at pH of about 1.6 results in deposition of chromium-iron alloys at current efficiencies of about 60% compared with about 20% for the conventional process. Deposits made at 60% current efficiency contain about one-half as much hydrogen as those made by the conventional process.

A presentation on this research was made at the ARO-sponsored Protective Coatings Workshop (Charleston, South Carolina, Dec. 13-16, 1982). The questioning afterward indicated that at least several scientists present did not believe that magnetic fields could significantly affect electrolysis. Subsequently, we produced a motion picture film to show the effects of magnetic fields on the bulk electrolyte and on gases formed at the electrodes. This film has been well-received at scientific meetings, and our results are no longer met with skepticism (at least not the vocal type).

C. List of publications.

1. "Effect of Magnetic Fields on the Structure of Electro-deposited Copper", Proc. 38th Annual Meeting of EMSA, San Francisco, 1980 (Baton Rouge, Claitor's Publishing Div.) p. 144, with K. Housen.

2. "Use of AS1 for Increasing the Current Efficiency of Chromium Plating", Invention Report, PSU 1980, with A. Kasaaian.

3. "Radiation Emitted from a TEM due to an Air Leak", Bulletin EMSA 11, No. 2, 66 (1981), with B. McLaughlin.

4. "Improving Efficiency of Cr Plating with Higher Sulfate and Cr (III)", AES 69th Annual Technical Conference Proceedings, vol. 2, paper U4, San Francisco, June 1982, with A. Kasaaian.

5. "Use of Alcohol for Increasing the Current Efficiency of Chromium Plating", U.S. Patent No. 4,447,299, with A. Kasaaian. Application also filed for Canadian patent.

6. "Influence of Magnetic Fields on the Electrodeposition of Chromium", AES 70th Annual Technical Conference Proceedings, vol. 1, paper A4, Indianapolis, June 1983, with Ru-Tsin Chen and K. Housen.

7. "Effect of Magnetic Fields on the Morphology of Electro-deposited Copper," Proc. 41st Annual Meeting of EMSA, Phoenix, 1983 (San Francisco Press), with H. Takeo and S. Mal.

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10. "Magnetic Effects on Electroplating of Copper," Proc. AES 11th Plating in the Electronics Industry Symposium, Orlando, Feb. 1984. With H. Takeo and C. Tam.

11. "High Efficiency Chromium and Chromium-Iron Plating", AES 71st Annual Technical Conf. Proc., N.Y., July 1984, with A. Kasaaian.

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16. "Effect of Methanol and Formic Acid on Chromium Plating", Plating and Surface Finishing, 71, No. 11, p. 66 (Nov. 1984). With A. Kasaaian.

17. "Effects of Chromium Electroplating Solution Composition on Properties of the Deposts", AES 72nd Annual Technical Conf. Proc., Detroit, July 1985. With A. Kasaaian and W. Lanford.

D. List of participating scientific personnel

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