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Electrodeposition and Characterization of Films of CoP

by K. Mondal, N. Sathitsuksanoh & Shashi B. Lalvani*

The influence of various parameters such as the applied current density and bath pH on the composition of CoP deposits has been studied. The data show that an increase in the current density leads to a decrease in the phosphorus content with a concomitant increase in the Faradaic current efficiency. A decrease in the solution pH results in an increase in the phosphorus content of the deposits with a corresponding decrease in the Faradaic current efficiency. The deposits were characterized by scanning electron microscopy.

Electrodeposited cobalt is crystalline in nature. However, the addition of phosphorus and other metalloids results in the formation of an amorphous phase.¹ Because of the absence of grains, amorphous alloys have low corrosion rates and magnetic properties that can be tailored by the proper addition of nickel, cobalt and phosphorus.² For example, amorphous NiP is non-magnetic³ for phosphorus contents above 15 at%. Samples of NiCoP exhibit ferromagnetic behavior for cobalt contents above 45 at%. Below this value, the dependence of magnetization on temperature shows a superparamagnetic behavior.² As the Co/Ni ratio is lowered, the cobalt content decreases. The ability to conveniently tailor magnetic properties along with the enhanced corrosion resistance of amorphous alloys makes them very suitable for numerous applications in the microelectronics industry.

In this study, we systematically investigated the influence of various process parameters on the CoP alloy formed by electrodeposition. In the past, electrodeposition of CoP has been carried out by a number of investigators.^{4,5}

Nuts & Bolts: What This Paper Means to You

Interest in ever concentrated data storage media has rekindled interest in cobalt deposit layers. At the same time, the life of that coating under less-than-perfect environmental conditions (say, under the hood of an automobile), still requires corrosion resistance. Here, the researchers have a look at the amorphous structure and corrosion resistance of cobalt-phosphorus electrodeposits.

One paper reports a method for electroless deposition as well.⁶ The influence of various process variables on the composition and properties of deposits of CoP formed under well-defined hydrodynamic conditions has been reported.

Experimental

Electrodeposition of Co-P alloys was accomplished in the reactor shown in Fig. 1. A rotating disk electrode (1500 rpm) was used as the working electrode to ensure well defined mass transfer characteristics. The anode and cathode were separated by a distance of 5 cm. The cathode and anode were a polished copper foil and platinum mesh, respectively. The plating bath composition was based upon the work of Djokic⁴ and was as follows:

Cobalt sulfate ($\text{CoSO}_4 \cdot 6\text{H}_2\text{O}$)	70 g/L (9.3 oz/gal)
Cobalt chloride ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$)	15 g/L (2.0 oz/gal)
Phosphorous acid (H_3PO_3)	25 g/L (3.3 oz/gal)
Phosphoric acid (H_3PO_4)	40 g/L (5.3 oz/gal)

The source of cobalt is a mixture of cobalt chloride and cobalt sulfate (14:3 weight ratio). Experiments were carried out under constant current conditions. The thickness of most of the deposits was approximately 50 μm (~2 mils) after 30 min of deposition. Deposit composition was determined by energy dispersive x-ray spectroscopy (EDX).

Results & discussion

A typical experiment was conducted at a solution pH of 1.4 and a temperature of 80°C (176°F). In one set of experiments, the influence of current density on the deposit composition was determined (Fig. 2). The data show that cobalt content increased with the current. For example, increasing the current density from 0.05 to 0.35 A/cm² (46 to 325 A/ft²) resulted in an increase in cobalt content from

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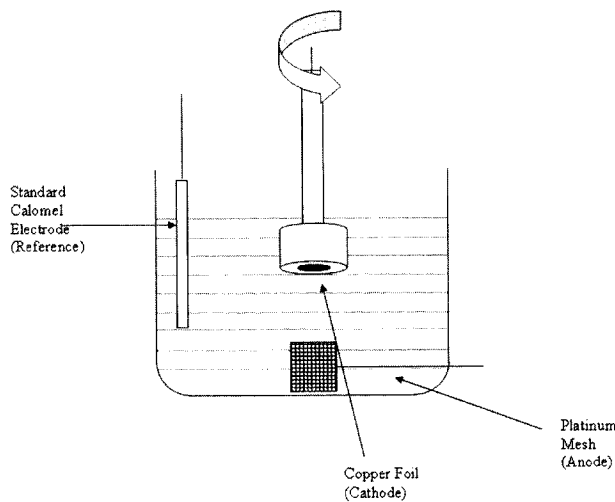


Figure 1—Experimental set-up.

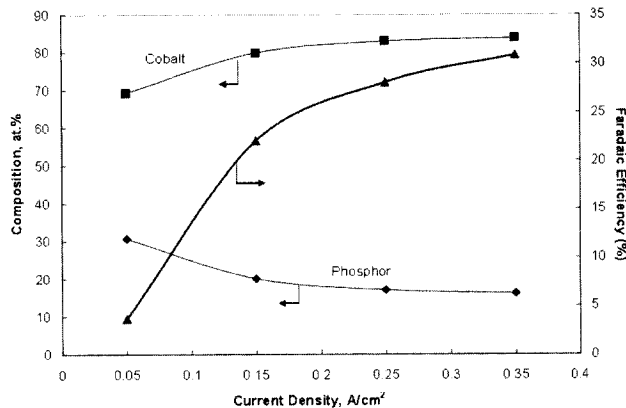


Figure 2—Composition and Faradaic efficiency vs. current; experiments were conducted at 80°C (176°F) and a solution pH of 1.4.

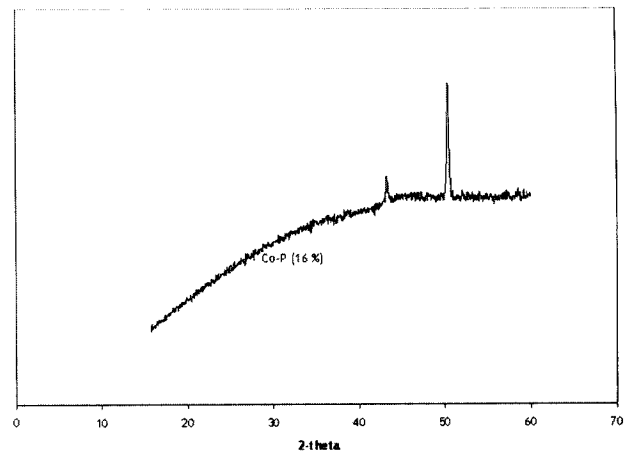


Figure 3—X-ray diffraction spectrum.

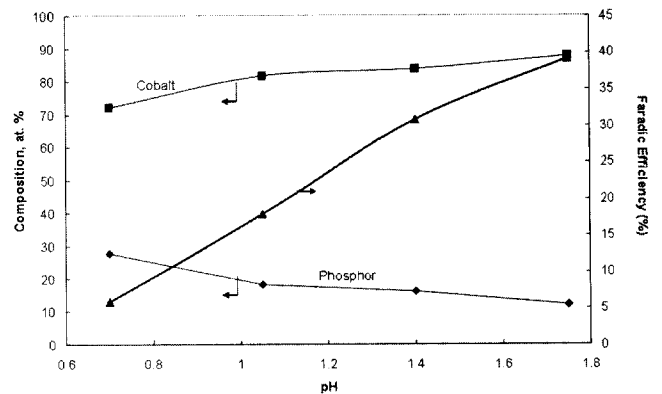


Figure 4—Composition of Faradaic efficiency vs. pH; experiments were conducted at 80°C (176°F) and a current density of 0.35 A/cm² (325 A/ft²).

69.3 to 83.9 at%. For all deposits, the phosphorus content was found to be 16.2 at% or greater. A decrease in the current led to increased phosphorus content. The Faradaic efficiency for deposition was found to increase with current density (Fig. 2). Figure 3 is the broad x-ray diffraction spectrum of the Co-P deposit except for the relatively small peak at $2\theta = 43^\circ$, which indicates that the deposit was either nanocrystalline or generally amorphous with a very small crystalline phase present. The peak at about 50° was attributed to the copper substrate.

It is known that for Ni-P alloys, with a phosphorus content above 15 at% results in amorphous phase formation. Therefore, we believe that deposits produced in this investigation with a high phosphorus content (greater than 20 at%) could be viewed as mostly amorphous, in light of the XRD analysis.

The influence of pH on the deposit composition is shown in Fig. 4. The data show that the cobalt composition increased from 72.0 to 87.9 at% with an increase in the solution pH from 0.7 to 1.75. Since the hydrogen evolution reaction is favored at low pH, the increase in bath pH also resulted in significant Faradaic efficiency.

A number of deposits were characterized using scanning electron microscopy at a 500X. Figure 5 shows the typical morphology of the electrodeposits. A phosphorus-free cobalt deposit (Fig. 5a)

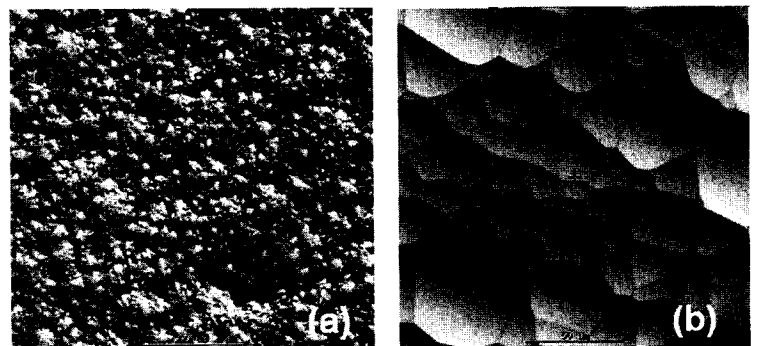


Figure 5—SEM micrographs of (a) a phosphorus-free deposit and (b) a deposit containing 14 at% phosphorus.

appears to be disordered while one with 14 at% phosphorus (Fig. 5b) shows the near absence of grain boundaries leading credence to the suggestion that the deposit was amorphous.

Acknowledgements

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About the Authors



Dr. Kanchan Mondal is a chemical engineer with expertise in electrochemical engineering, materials, energy and environmental remediation. He is currently a research scientist at the Department of Mechanical Engineering and Energy Processes at Southern Illinois University, Carbondale, IL. He has published 29 papers and has presented at several national and international conferences. He also has a patent on a low temperature electrochemical hydrogenation process for vegetable oils.

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Conversion Coatings for Aluminum and Magnesium

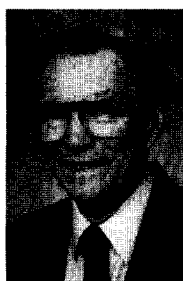
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Mr. Don Baudrand, CEF has been an independent metal finishing consultant, based in Poulsbo, Washington, since 1994. He received his B.A. in Chemistry from Whittier College, California and did Graduate Work at the University of California - Berkeley. From 1954 to 1966, he was Owner and President of Electrochemical Laboratories, and until 1994, was Vice-President at Allied-Kelite. He is a member of several professional associations including AESF, the International Microelectronics and Packaging Society, SME, SAE, and the Institute of Metal Finishing. He holds 10 U.S. patents and numerous foreign patents and has authored over 70 published papers.