Electroless Deposition of Ni-Cu-P Alloys

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Electroless deposition of Ni-Cu-P alloy layers has been investigated. Using electrochemical measurements and data analysis an electrolyte composition has been developed, containing sodium hypophosphite as a reducer, and the deposition parameters have been optimized. Amorphous alloys containing 70 to 72 wt percent Ni, 13 to 15 wt percent Cu, and 12 to 15 wt percent P are obtained at 12 mg/cm²/hr at 90 °C and pH 9. Their microhardness ranges from 750 to 850 HV.

Electroless deposition of nickel layers with phosphorus or boron has found many applications, especially in the field of electronics.[1,2] So far, few investigations have been devoted to the electroless deposition of alloys.[3-5] Ni-Cu-P alloy layers containing only a few percent of either nickel or copper, have been studied and patented .[7-10] F. Matsui et al., however, pointed out the effect of Cu on the properties of Ni-Cu-P alloys which remain non-magnetic even after heat treatment and consequently could usefully replace Ni-P layers as undercoats for hard discs.” In previous work, we electrodeposited corrosion-resistant Ni-Cu alloy layers[12,13] and elucidated the codeposition mechanism.[14] The present investigation is directed at developing nickel-copper alloy layers by means of electroless deposition.

Experimental Procedure

A 250-mL cell was regulated to the desired temperature. The substrates were mild steel sheets (four cm² in area) held by a glass rod, immersed in the solution. They were mechanically polished and chemically etched in dilute sulfuric acid prior to the experiment.

For the electrochemical investigation, rotating disc electrodes (nickel, mild steel or platinum) were used. The reference electrode was a saturated sulfate electrode (SSE), the counter electrode was platinum gauze.

Variation Ranges of the Reacting Species, pH and Temp., Cone., Mol/dm³

$CuSO_4$	$NiSO_4$	Hyp.	Cit.	NH_4Cl	pH	T, °C
0.0005- 0.004	0.01- 0.057	0.11 - 0.68	0.034- 0.4	0-1.86	5.8-9	65-90

The deposition rate was calculated from sample weight gains after the given plating time (1-2 hr). Charge transfer resistance at the deposition potential, which is inversely proportional to the deposition rate,[15,16] was measured by means of impedance spectroscopy. A frequency response analyzer[a] coupled to an electrochemical interface and monitored by a microcomputer was used. The layer morphology was examined by SEM and the composition by EDX analysis or by Induced Coupled Plasma Emission. Structure was investigated by X-ray diffraction ($\lambda Co_{K\alpha 1}$ = 1.7889 Å).

Optimization of Plating Rate

Several parameters have to be adjusted to develop an appropriate stable electrolyte with an acceptable deposition rate. The classical nickel electroless electrolytes have been modified to allow copper codeposition. They contain sodium hypophosphite as a reducing agent, nickel sulfate and copper sulfate. In addition, completing agents were added, such as sodium citrate and ammonium chloride, which are known to enhance the deposition rate and electrolyte stability of electroless nickel.[17]

The table lists the variation ranges of the deposition parameters. The ranges were chosen after a preliminary investiga-

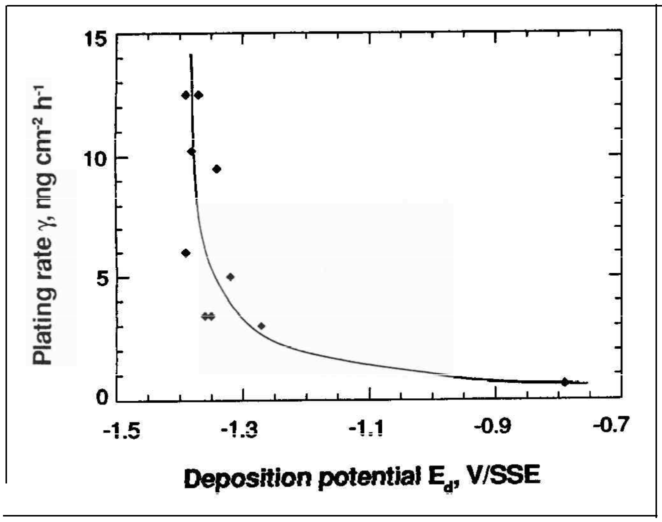

Fig. 1—Plating rare as a function or deposition potential, E_d.

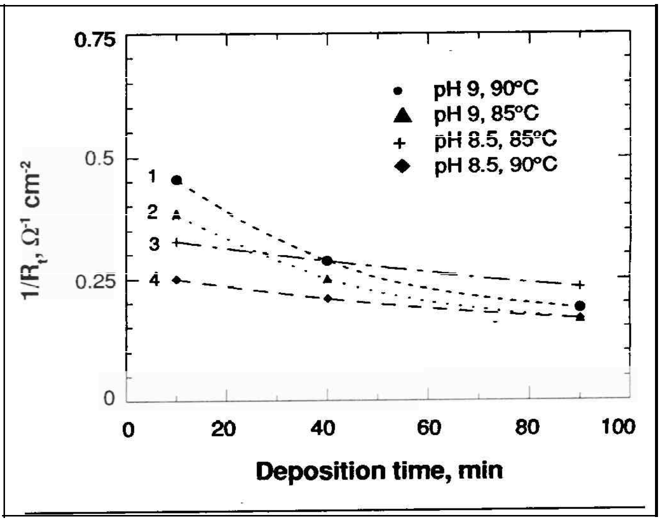

Fig. 2—Time dependence of the plating rare expressed as the inverse of the charge transfer resistance, R_t.

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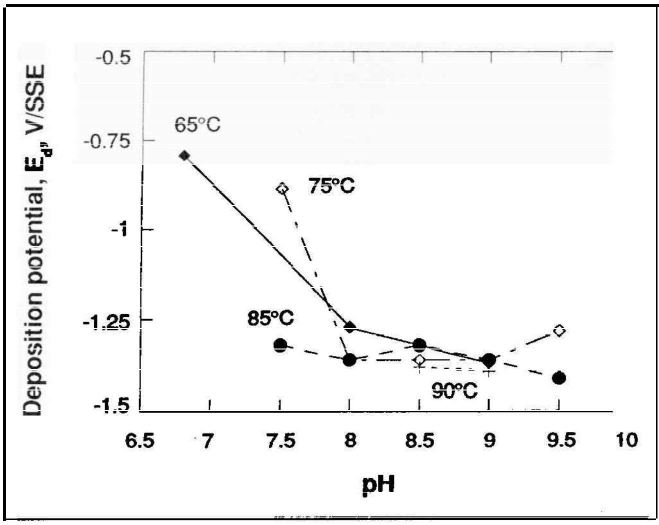
[a] *Model 1250, Solartron Transducers, Houston, TX*

[b] *Model 1186, Schlumberger, France*



g. 3—pH dependence of the deposition potential.

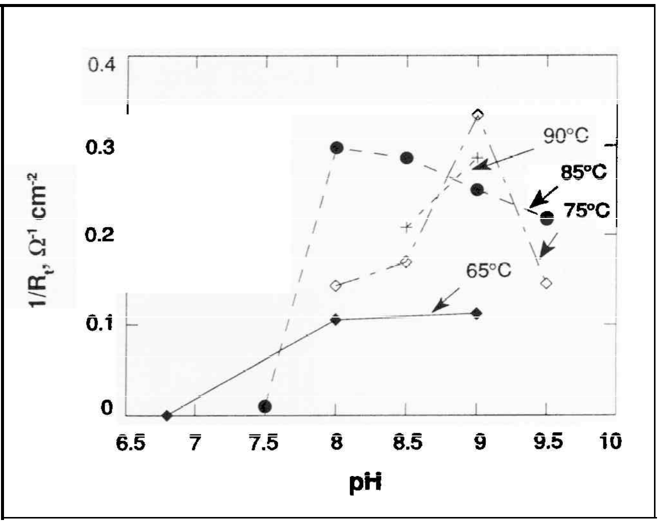


Fig. 4—pH dependence of the inverse of the charge transfer resistance, R_t.

tion of the chemical stability, so that no precipitation and no spontaneous decomposition occur.

Preliminary experiments have pointed out that the preferential deposition of copper, the most noble metal used, is more pronounced than for the electrodeposition of Ni-Cu alloys. For a Cu/Ni ratio of 5.10-2 in the solution, Ni-Cu-P alloys containing 10 to 25 wt percent Cu are obtained. It was shown, however, that the presence of cupric species in the solution inhibits the discharge of nickel; the reaction rate drops with increasing copper sulfate concentration as already pointed out.[5] It was confirmed that addition of ammonium chloride increases both the electrolyte stability and the plating rate. In the range investigated, the hypophosphite concentration does not significantly affect the plating rate.

To achieve a high plating rate the following conditions must be fulfilled:

- low copper and high nickel concentrations (the Ni/Cu ratio must be adjusted, however, to obtain the desired alloy coating composition);
- large ammonium chloride concentration (upper limit: 1 M for bath stability);
- high plating temperature.

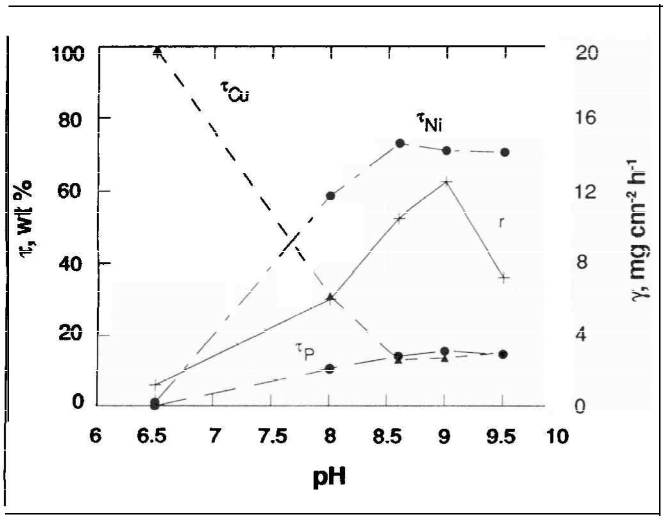


Fig. 5-pH dependence of the deposit imposition (τ_{Cu}, τ_{Ni}, τ_P) in wt percent and of the plating rate, r. Deposition temperature: 90 °C.

The following composition has been adopted: 10^{-3} M $CuSO_4$, ***5.7 x*** 10^{-2} M $NiSO_4$, 0.45 M sodium hypophosphite, 0.4 M sodium citrate, 0.93 M NH_4Cl.

Electrochemical Measurements

To achieve a more precise description of the effects of the parameters, an electrochemical investigation was carried out by means of steady state polarization and impedance measurements.

Figure 1 illustrates the correlation between the plating rate and the deposition potential, E_d: The rate markedly increases when E_d becomes more negative than about -1.3 V/SSE. For E_d in the range -0.7 to -1.2 V/SSE, powdery copper layers are obtained with a very low plating rate (0.1 - 0.8 $mg/cm^2/hr$). As for the electrodeposition of Ni-Cu alloys, the deposition potential must be more negative than a certain threshold, in the present case, -1.3 V, to obtain the Ni-Cu codeposition.[14]

Figure 2 shows the time dependence of the deposition rate, plotted by means of charge transfer measurements, R_t. Indeed, the impedance diagrams present a capacitive feature resulting from relaxation of the double layer capacitance (about 80 to 100 $\mu F/cm^2$) in parallel with the charge transfer resistance. In this case, R_t was shown to be inversely proportional to the plating rate.[16,17] The deposition rate decreases with time, especially at the beginning of the process. It then stabilizes after about 30 min. All the results reported in Figs. 4 and 5 were recorded for 40 min deposition time. The effects of pH and temperature on the plating rate are emphasized in Figs. 3 and 4. Whatever the temperature, the deposition potential, E_d, is shifted towards more negative values and the plating rate, 1/ Rt, increases when the pH is raised from 6.5 to 8. The optimum pH range is between 8 and 9.5. In the pH range 8-9.5, the deposition potential is not much affected by temperature, however the plating rate increases markedly with temperature, especially between 65 and 85 °C. Under optimal conditions (90 °C, pH 9), the plating rate is about 12 $mg/cm^2/hr$, which is comparable to that of Kanigen nickel.[1,17] Ni-Cu-P deposits with a thickness up to 40 µm can be obtained.

The pH dependence of the plating rate results from its influence on both anodic and cathodic reactions. The pH affects the nature of the complexed species which controls the cathodic reaction (co-discharge of nickel and copper). Indeed, it is known that the characteristics of the citrate complexes with copper and, to a lesser extent with nickel, depend on pH and are stabilized at high pH values.[18] It has been shown that for Ni-Cu electrodeposition, an alkaline pH brings the discharge potentials of nickel and copper closer, enabling deposition of alloy layers.[14] Increasing pH may also increase the oxidation reaction of hypophosphite because hydroxyl ions are involved in some of the transfer steps.

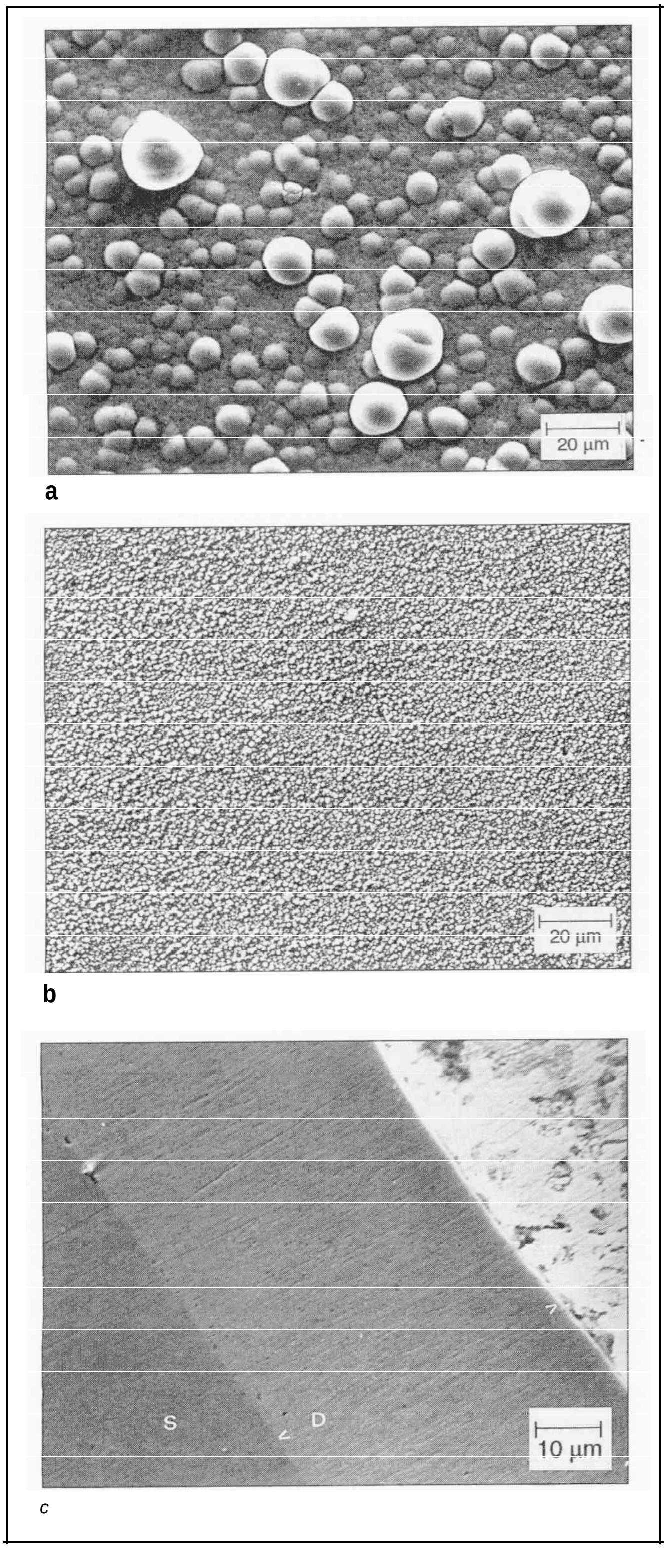


Fig. 6—SEM photographs of Ni-Cu-P layers: (a) τ_{Cu}, 4 wt %; τ_{Ni}, 84.5 wt %; τ_{P}, 11.5 wt %; (b) τ_{Cu}, 20 wt %; τ_{Ni}, 66 wt %; τ_{P}, 12 wt %; (c) Cross section (τ_{Cu}, 12 wt %; τ^{Ni}, 63 wt %; τ_{P}, 22 wt %); S denotes the substrate and D the deposit.

Deposit Composition

The deposit composition also strongly depends on bath composition, pH and temperature. A Ni/Cu ratio between two and five atomic percent in the alloy layers can be obtained from solutions having a Ni/Cu ratio of 115 atomic percent, pH 8.5 to 9.0, at 85 to 90 “C. It indicates that copper is strongly preferentially deposited; the effect is much more pronounced than for Ni-Cu electrodeposition in which a Ni/Cu electrolyte ratio of 5 to 15 atomic percent allows a Ni/Cu ratio of two to five atomic percent in the alloy layers.[12, 13]

Figure 5, corresponding to alloys deposited at 90 “C, shows that the copper content markedly decreases with increasing pH. For pH 6.5, powdery copper deposits are obtained (E_d= -0.78 V). For pH values above 7.5, the deposition potential lies between -1.3 and -1.4 V, and alloys with increasing nickel and phosphorus content may be obtained. The plating rate exhibits a maximum for pH values around nine. With increasing bath temperature, the copper and phosphorus contents increase as well as the deposition rate, whereas nearly no effect on nickel content is observed.

Deposit Characteristics

For electrodeposited Ni-Cu alloys, the color of the layers depends on their compositions-pink when the copper content is larger than 60 wt percent and gray for nickel content over 40 wt percent. Their surface morphology is nodular (Fig. 6a). Nodule diameter increases when the copper content decreases (Fig. 6a: $\tau_{Cu}=4$ wt percent; Fig. 6b: $\tau_{Cu}=20$ wt percent). Their cross sections do not show any laminations, even after chemical etching (Fig. 6c). Microhardness of Ni-Cu-P, mea-

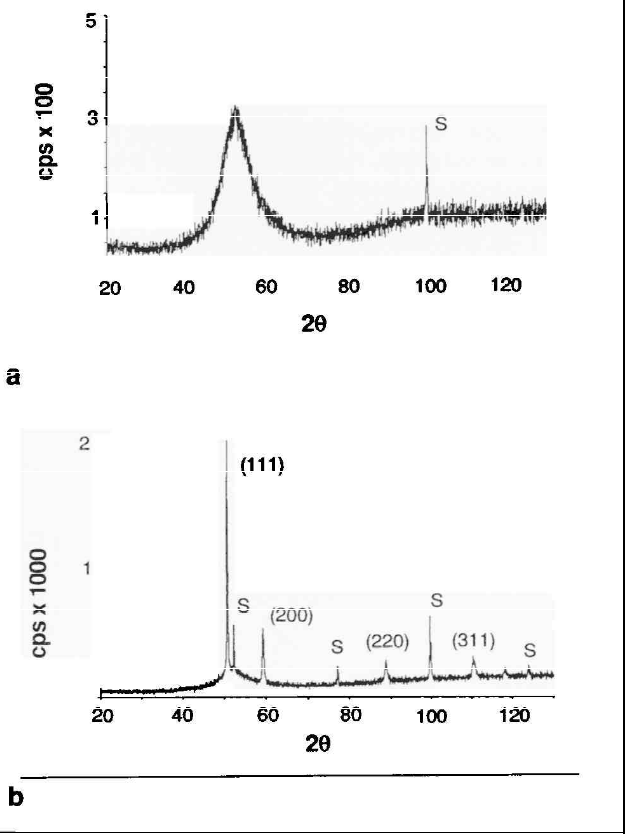


Fig. 7—X-ray diffraction patterns of Ni-Cu-P layers (index S denotes peaks related to iron substrate): (a) τ_{Cu}, 5.1 wt %; τ_{Ni}, 71.7 wt %; τ_{P}, 23.2 wt %; (b) τ_{Cu}, 21.4 wt %; τ_{Ni}, 70.4 wt %; τ_{P}, 8.2 wt %.

sured at 25-g load, ranges between 750 and 850 HV, which is significantly greater than the value for the d-c plated Ni-Cu layers (about 500 HV) and still much greater than for the massive Ni-Cu alloys, like Monel 400 (about 200 HV).[13]

The crystalline state of the Ni-Cu-P layers depends on the phosphorus content, as it does for electroless nickel layers. The X-ray diffraction patterns of deposits containing more than about 10 wt percent phosphorus exhibit only a broad halo with a half-height width larger than 9° (in 2θ), indicating an amorphous state (Fig. **7a).** For lower P content, the X-ray patterns are characteristic of the fcc Ni-Cu solid solution (Fig. 7b). The lattice parameter lies between 3.61 and 3.62 A [i.e., larger than for the Ni-Cu solid solution (3.55 to 3.57 Å for 50 to 30 wt percent Cu)], probably because of the presence of phosphorus.”

Conclusions

Compact Ni-Cu-P alloy layers have been deposited by an electroless process. They contain 70 to 72 wt percent nickel, 13 to 15 wt percent copper and up to 15 wt percent phosphorus. The composition can be varied by adjusting solution pH and temperature. The deposition rate is comparable to that of electroless nickel. The color can be changed from pink to gray and the surface morphology is more or less nodular, depending on the copper content. The crystalline state depends on the phosphorus content.

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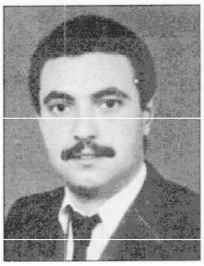
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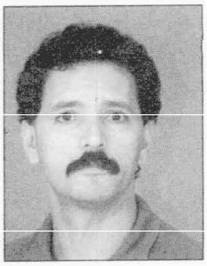
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