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Characterization of Electroless Deposition of Ni-P-Al2O3 and Ni-P-TiO2 from Alkaline Hypophosphite Baths in the Presence of Gluconate as a Complexing Agent

by

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ABSTRACT

Electrodeposition of Ni-P-Al₂O₃ and Ni-P-TiO₂, in the presence of gluconate as a complexing agent, on copper substrates was studied. The dependence of the composite formation on different plating variables was investigated. The deposited coatings were characterized using different techniques, including energy dispersive x-ray spectroscopy (EDX), x-ray diffraction (XRD), scanning electron microscopy (SEM), hardness and corrosion resistance testing. The amount of particles incorporated in the coatings increased with increasing particle concentration in the bath. However, the particle size greatly affected the amount incorporated. The addition of these particles changed the microstructure of the Ni-matrix, and enhanced the hardness and corrosion resistance.

Keywords: complexing agent, electroless deposition, copper substrate, matrix composite, corrosion resistance, polarization curves.

Introduction

By coating metals with a metallic matrix composite containing particles of Al₂O₃ or TiO₂, they can be protected from abrasion. These hard materials are too brittle and offer little or no adhesion potential to be used alone as a coating material. Therefore, a metal matrix is used to hold Al₂O₃ or TiO₂ particles together and facilitate good adhesion to the metal surface being coated. These composites have a considerably higher yield strength and hardness than what the pure metal exhibits.¹ Composite coatings can also reduce the corrosion of low alloys.² The high temperature oxidation resistance of Ni-P alloys has been significantly increased by the addition of Al₂O₃, matching a decrease in the rate of oxidation with increasing volume percent of Al₂O₃ in the composite.³ This suggests that electroless Ni-P-Al₂O₃ composite coatings should offer good wear and corrosion properties at high temperatures.⁴

The structure of as-deposited electroless Ni-P is amorphous with high phosphorus content. However, this amorphous structure is metastable and undergoes a crystalline transition with increasing temperature. After adequate heat treatment, the coating becomes crystalline and its hardness and wear resistance are greatly improved.⁵

Embedding particles in electroless deposited metals is a convenient method of preparing composite coatings, and the particles increase the mechanical and physical properties of the coating.⁶ The activation energy of crystallization is lowered due to the presence of co-deposited particles in composite coating.⁷ The effect of particle size has been studied.⁸ Greater particle incorporation and uniform distribution was found in composite coatings obtained with 1.0 μ m than with 50 nm or 0.3 μ m particle sizes.

Using a complexing agent such as citrate in electroless Ni-P such as citrate,⁹ propylene glycol and urea¹⁰ is found to induce stability during plating. A survey of the literature shows that gluconate electrolytes have been used to electroplate metals such as nickel,¹¹ copper,¹² tin¹³ and zinc.¹⁴ No literature reference was found on the use of gluconate in electroless nickel plating.

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The objective of the present study is to obtain Ni-P-Al₂O₃ and Ni-P-TiO₂ composites from alkaline gluconate baths, studying the dependence of coating characteristics on several electroless plating variables. Our work also characterizes the coatings by using different analytical techniques such as SEM, EDX and XRD and examines the coating hardness and corrosion resistance.

Experimental

Pretreatment and activation of copper substrate

Copper sheets of dimensions 2×2 cm were used as substrates. They were mechanically polished with different grade emery papers and then immersed in a pickling solution (300 mL H₂SO₄ + 100 mL HNO₃ + 5 mL HCl + 595 mL doubly distilled water) for 1 min, washed with distilled water and rinsed with acetone. After treatment, the copper substrate was immersed for 20 sec in a dilute acidic solution of PdCl₂ (0.1 g/L PdCl₂ + 0.2 ml/L 36% HCl), followed by thorough rinsing. Finally, the substrates were dried and weighed.¹⁵

Electroless nickel deposition

The three bath compositions listed in Table 1 were used in this study. They were freshly prepared from analytical grade chemicals and doubly distilled water. The electrochemical cell was connected by immersing the copper substrate in 250 mL of the electroless solution for 60 min. The pH was measured using a Microprocessor pH/mV/°C Meter (Model CP 5943-45USA) and adjusted with NH₄OH solution. The temperature was controlled by using a thermostatically-controlled bath. From the change in weights of the substrates before and after the electroless process, the deposit weight was calculated.

	Bath A	Bath B	Bath C
Nickel sulfate	25 g/L	25 g/L	25 g/L
Sodium hypophosphite	15 g/L	15 g/L	15 g/L
Sodium gluconate	15 g/L	15 g/L	15 g/L
Ammonium sulfate	15 g/L	15 g/L	15 g/L
Alumina (70 nm)	-	10-90 g/L	-
Titania (50 nm)	-	-	1-6 g/L
Succinic acid	0.3 g/L	0.3 g/L	0.3 g/L
Sodium dodecyl sulfate	0.1 g/L	0.1 g/L	0.1 g/L
Lead acetate	2 mg/L	2 mg/L	2 mg/L
Time	60 min	60 min	60 min
Temperature	90°C	90°C	90°C
pН	9	9	9
Stirring speed	150 rpm	150 rpm	150 rpm

Table 1 - Bath composition and operating conditions for (a) Ni-P, (b) Ni-P-Al₂O₃ and (c) Ni-P-TiO₂ electroless deposition.

The composition of the coatings was examined using the following procedure:

- 1. The coating layer was stripped using 10% H₂SO₄ solution. The specimen was made the anode in an electroplating cell in which the coating layer is dissolved in the solution, which is then diluted to 250 mL with doubly-distilled water.
- 2. The analysis was done using atomic absorption spectrophotometry (Perkin-Elmer 3100, Germany).
- 3. The solution obtained in (1) was further diluted by dissolving 5 mL in doubly-distilled water to 250 mL.
- 4. Nickel standard solutions for the elements to be detected were prepared (1.0 g Ni metal in (1+1) HNO₃. Diluted to 1.0 L with 1.0 vol% HNO₃), Ni, air-acetylene flame gases and standard wavelength of 232 nm.
- 5. The phosphorus weight was calculated by subtracting the nickel and alumina or titania weights from the total deposited weight.

The results were confirmed for some samples with EDX analysis.





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The deposited mass of nickel m on the unit surface during the plating time represents the deposition rate:¹⁶

$$dR = dm/dt$$

(1)

The surface morphology of the as-deposited Ni-P-Al₂O₃ and Ni-P-TiO₂ composites on copper was studied using scanning electron microscopy (SEM)(JEOL-5410 attached to an EDX unit). The surface phases and phase changes of the different coated substrates was studied with an x-ray diffractometer (Broker AXS-D8 x-ray diffractometer, ADVANCE, Germany), with a copper target (Cu λ = 1.54060Å) and a nickel filter. The Vickers microhardness of the deposits and the specimen material was measured under a 50-gram load, using a Shimdzu hardness tester. The electrochemical experiments were performed using a Volta Lab 40 (Model PGZ301) with the aid of commercial software (Volta Master 4, V 7.08). A saturated calomel electrode (SCE) and a platinized platinum black were used as the reference and auxiliary electrodes, respectively, with different deposited plated specimens as the working electrode. The electrolyte used in the electrochemical cell was a 3.5% NaCl solution. Volta Master 4 calculates and displays the corrosion rate in µm/yr. This rate is calculated from the corrosion current density *i*_{corr}, the density *D*, the atomic mass *M* and the valence *V*. The calculation is performed as follows:

Corrosion rate, μ m/yr = [i_{corr} (A/cm ²) × M (g)] / [D (g/cm ³) × V) × 3270	(2)
 3270 = 0.01 × [1 year (sec) / 96497.8] and 	
96497.8 = 1 Faraday (Coulombs)	(3)

Results and discussion

Effect of alumina and titania on Ni-P electroless deposition

Figure 1 shows that the deposition rate increased with increasing alumina concentration up to 70 g/L, and then decreased as the alumina content in the bath increased further. The alumina content in the deposit also increased in the same manner as shown in Fig. 2. This limiting content corresponds to steady state equilibrium, whereby the number of co-deposited particles equals the number approaching the substrate surface. Beyond the optimum concentration, suspended particles appeared to agglomerate in the bath. Accordingly, the decreasing trend of incorporation of alumina particles was observed.

The effect of TiO₂ content in the bath on the deposition rate of Ni-P-TiO₂ alloy is illustrated in Fig. 3. The deposition rate increased with increasing titania content in the bath. Figure 4 shows the TiO₂ content in the deposit increased with increasing TiO₂ nanoparticle concentration in the plating bath. The nickel films from the alkaline bath contained significantly higher amounts of particles.



Figure 1 - Effect of alumina concentration in the plating bath on the deposition rate from a bath containing 25 g/L NiSO_{4.6}H₂O, 15 g/L sodium hypophosphite, 15 g/L ammonium sulfate, 0.1 g/L sodium dodecyl sulfate, 0.3 g/L succinic acid, 15 g/L sodium gluconate, time = 60 min, pH 9, temperature = 90°C.





Figure 2 - Effect of alumina concentration in the plating bath on the alumina content in the Ni-P-Al₂O₃ alloy from a bath containing 25 g/L NiSO₄.6H₂O, 15 g/L sodium hypophosphite, 15 g/L ammonium sulfate, 0.1 g/L sodium dodecyl sulfate, 0.3 g/L succinic acid, 15 g/L sodium gluconate, time = 60 min, pH 9, temperature = 90°C.



Figure 3 - Effect of TiO₂ concentration in the plating bath on the deposition rate from bath containing 25 g/L NiSO₄.6H₂O, 15 g/L sodium hypophosphite, 15 g/L ammonium sulfate, 0.1 g/L sodium dodecyl sulfate, 0.3 g/L succinic acid, 15 g/L sodium gluconate, time = 60 min, pH 9, temperature = 90°C.



Figure 4 - Effect of TiO₂ concentration in the plating bath on the titania content in the Ni-P-TiO₂ alloy from a bath containing 25 g/L NiSO₄.6H₂O, 15 g/L sodium hypophosphite, 15 g/L ammonium sulfate, 0.1 g/L sodium dodecyl sulfate, 0.3 g/L succinic acid, 15 g/L sodium gluconate, time = 60 min, pH 9, temperature = 90°C.





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There seems to be a tendency that negatively-charged oxide particles are preferentially codeposited in cathodic processes, at least in solutions containing divalent cations. To explain this counter-intuitive behavior, an electrostatic model has been proposed¹⁷⁻¹⁹ that takes into account the charge distribution on the particle and the electrode surface. In the alkaline electrolyte the TiO₂ nanoparticles are negatively charged, whereas in the acidic one they bear a positive charge. Under the conditions of the nickel electroplating process, the electrode bears negative excess charges.¹⁹ According to the model, negatively charged particles are preferentially attracted by the positive excess charges in the electrolytic part of the electrical double layer of the electrode (EDL). When the particle has come close to the electrode, the shell of adsorbed ions on the particle is stripped off within the EDL of the electrode. Finally the particle becomes incorporated into the growing metal layer.

The major challenges for the codeposition of ceramic particles seem to be the occlusion of a sufficient number of nonagglomerated particles combined with a good dispersion of the particles in the metal matrix. In general, it has been observed that the amount of embedded ceramic particles increases with increasing concentration of suspended particles in the electrolyte.²⁰ Additionally, the reduction of particle size increases the agglomeration tendency of the particles, due to their enhanced surface energy, while decreasing their codeposition content in the metal matrices and the mean grain size of the matrix crystallites.²¹ Moreover, research has pointed out that the physico-chemical properties of the ceramic particles are crucial to the understanding of the codeposition mechanism of each type of particle.²²

The EDX chart in Fig. 5 shows the pattern 90% Ni-6% P-4% Al₂O₃ alloy with 40 g/L alumina in the bath. By contrast, a 6.0 g/L TiO₂ load in the bath can yield Ni-P-TiO₂ with 2% titania as indicated in Fig. 6. The reason that the titania incorporation from the bath (40 g/L \rightarrow 4%; 10:1) is higher than alumina (6 g/L \rightarrow 2%; 3:1) can be explained from the difference in particle size (50 nm versus 70 nm, respectively). The particle size is a very important factor in the composite coatings formation.⁸

The addition of alumina nanoparticles to the bath obviously affects the crystal orientation of the coatings as indicated from the xray diffraction spectra (Fig. 7). The peak width for the alumina (Fig. 7, Sample A) was narrower than the peak obtained for the Ni-P alloy (Fig. 7, Sample C), indicating a change from the amorphous structure. The appearance of the different peaks of Ni-P and Al₂O₃ without heat treatment is not fully understood. The grain size was 34.5 nm for the alumina sample versus 16.84 nm in the case of the Ni-P alloy. In the XRD pattern of the Ni-P-TiO₂ alloy (Fig. 7, Sample B), the reflections corresponding to the (111), (200) and (220) planes of a face centered cubic (fcc) phase of nickel could be observed. The broad peak is evidence of an amorphous structure. The crystal size was 24 nm.



Figure 5 - EDX chart of 90% Ni-6% P-4% Al₂O₃ deposit from a bath containing 25 g/L NiSO₄.6H₂O, 15 g/L sodium hypophosphite, 40 g/L alumina, 15 g/L ammonium sulfate, 0.1 g/L sodium dodecyl sulfate, 0.3 g/L succinic acid, 15 g/L sodium gluconate, time = 60 min, pH 9, temperature = 90°C.





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Figure 6 - EDX chart of 90% Ni-8% P-2% TiO₂ alloy from a bath containing 25 g/L NiSO₄.6H₂O, 15 g/L sodium hypophosphite, 6.0 g/L TiO₂, 15 g/L ammonium sulfate, 0.1 g/L sodium dodecyl sulfate, 0.3 g/L succinic acid, 15 g/L sodium gluconate, time = 60 min, pH 9, temperature = 90°C.





Characterization of the coatings

Surface morphology

It is clear from Fig. 8 that the amorphous structure of the Ni-P alloy (Fig. 8a) was changed to a uniform distribution of embedded particles on the coating surface in the case of Ni-P-Al₂O₃ (Fig. 8b) and Ni-P-TiO₂ (Fig. 8c). It has been shown that the structure and morphology of the nickel matrix composites depend on the physicochemical properties, and the particle size and concentration in the bath. A parallel study by Zhou, *et al.*²³ showed the same results.





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Figure 8 - SEM of (a) 82% Ni-18% P alloy; (b) 89% Ni-5.5% P-5.5% Al₂O₃ coating; (c) 90.1% Ni-8% P-1.9% TiO₂ coating.





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Microhardness

The hardness of 86.5% Ni-5% P-Al₂O₃ with 8.5% alumina was observed to be 620 HV₅₀. For Ni-P-TiO₂ with 2% titania, the hardness was 450 HV₅₀ without heat treatment. The hardness of Ni-P for a 96 Ni-4 P coating without heat treatment was 490 HV₅₀ was increased in the case of the Al₂O₃ addition. The particle percentage in the coatings also affects the hardness value.

Corrosion behavior

It is clear from the potentiodynamic curves of Fig. 9, and the data in Table 2, that the corrosion current density of the Cu-base $(k_{corr} = 6.2359 \ \mu A/cm^2)$ was lowered by coating the copper substrate with Ni-P alloy $(k_{corr} = 0.2848 \ \mu A/cm^2)$. The incorporation of Al₂O₃ or TiO₂ particles in the coating decreased the corrosion current density to $k_{corr} = 0.2848 \ \mu A/cm^2$ and $k_{corr} = 0.17229 \ \mu A/cm^2$, respectively. This implies that the anodic dissolution reaction of the composite coatings was restrained, which effectively decreased the corrosion resistance due to the formation of a protective layer of metallic nickel and nickel phosphide that act as barrier to oxygen diffusion to the metal surface.

The order of corrosion rate is $Ni-P-TiO_2 < Ni-P-Al_2O_3 < Ni-P < Cu$ -base, respectively, with a protection efficiency of 97.21, 95.86 and 94.58, respectively.



Figure 9 - Corrosion behavior, of the Cu-base, Ni-P, Ni-P-Al₂O₃ and Ni-P-TiO₂ in 3.5% NaCl solutions.

	<i>E</i> _{corr} (<i>i</i> =0), mV	/ _{corr} , μΑ/cm²	Rp kΩ·cm²	Beta <i>a</i> , mV/decade	Beta <i>c</i> , mV/decade	Corrosion µm/yr
Cu-base	-315.0	6.2359	1.93	73.40	-82.7	72.40
Ni-P	-225.0	0.2848	57.64	72.74	-89.7	3.296
Ni-P-Al ₂ O ₃	-233.71	0.2584	32.323	56.517	-64.0696	2.9998
Ni-P-TiO ₂	-323.9	0.17229	0.3191	57.3	-71.6	2.0170

Table 2 - Corrosion data, of the Cu-base, Ni-P, Ni-P-Al₂O₃ and Ni-P-TiO₂ in 3.5% NaCl solutions.

Conclusion

Electroless deposition of Ni-P-Al₂O₃ and Ni-P-TiO₂ in the presence of gluconate as a complexing agent shows that the percentage of incorporated particles in the coating increased with increasing the concentration of particles in the bath. The incorporated alumina and titania particles changed the structure of the Ni-matrix and enhanced the hardness and the corrosion resistance of the coated substrates.





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