Mechanism of Nickel-Phosphorus-Aluminum Oxide Composite Coatings by Electroless Process

by Z.A. Hamid & R.A. El-Adly

Electroless nickel-phosphorus composite coatings incorporating aluminum oxide were obtained from an acidic bath. Sodium benzene sulfonate was added as stabilizer and chelating agent. Codeposition of aluminum oxide particles in a composite depends on the concentration of both Al_2O_3 and reducing agent, as well as on pH and temperature. Microhardness and wear resistance of the composite were investigated. The mechanism of incorporation of Al_2O_3 and other ions was suggested and confirmed in view of the calculated free energy of adsorption of Al_2O_3 and the activation energy of the composite.

Composite coatings are prepared by suspending micron or submicron particles in the plating solution and codepositing these particles with the metal. These particles are generally considered insoluble, although some undergo surface modifications resulting from slow chemical interactions with the plating solutions. Composite coatings possess enhanced mechanical properties relative to conventional coatings.[1,2] Electroless composite coatings containing ceramic particles are very promising as protective coatings. Electroless composite deposits that include particulates such as alumina, carbides and diamond particles have been reported.[3-5] Excellent corrosion resistance with good wear resistance are two major reasons for the widespread use of electroless nickel deposits in the fabrication of components for the automotive, oil and aircraft industries. Nickel deposits find many other applications, such as the manufacture of electronic and computer parts, because of magnetic and electrical properties of electroless deposits. Many techniques could be used to produce composite coatings (*e.g.*, electroplating and electroless).[6-8] In a previous study, the mechanism of co-deposition of various particles, such as SiC and Al_2O_3 was studied in view of the electrokinetic charge characterizing the solid particle.[9]

This paper reports study of the formation of Ni-P-Al_2O_3 composites by electroless process in the presence of sodium benzene sulfonate in comparison with the conventional coating. It also attempts to clarify the mechanism of codeposition of Al_2O_3 in view of the free energy of adsorption AG_{ads}°. Microhardness and wear resistance of Ni-P-Al_2O_3 composite coatings are also investigated in comparison with those of Al_2O_3 free nickel deposits.

Experimental Procedure

Codeposition of Al_2O_3 particles with a Ni-P alloy was performed by electroless coating technique. The plating bath consisted of 35 g/L nickel sulfate, 15 g/L sodium citrate, 5 g/L sodium acetate, 5-20 g/L sodium hypophosphite, 5-20 g/L Al_2O_3 particles and 0.2 g/L sodium benzene sulphonate at 99 percent purity. Steel specimens 7 x 3 x 0.06 cm were used. The plating process took place under the following conditions: temperature range 65-85 °C, pH 3-6 and plating time 1.5 hr. The process proceeded with mild stirring of the bath. The mass of the plated composite deposited on the steel samples was calculated from the difference in the weight of the steel samples before and after coating (W_2-W_1). The Al_2O_3 content in the composites were determined gravimetrically.[8]

The microhardness measurements of the deposits were determined by an indentation technique, using a diamond pyramid indenter at 200 gf load. The indentation measurement of microhardness was carried out at the matrix area only (Ni-P deposit) and far from the particles of aluminum oxide.

The abrasion wear resistance of the as-plated composites was determined by a standard test method for measuring abrading, using a dry sand/rubber wheel apparatus (ASTM G 65-91) at 1000 gf load. The test sample (6 x 3 x 0.06 cm) was weighed before and after abrasion. The weight loss in g/m of abrasion was calculated.

Results & Discussion

The influence of the different parameters on the electroless nickel deposition and incorporation of Al_2O_3 in the deposit

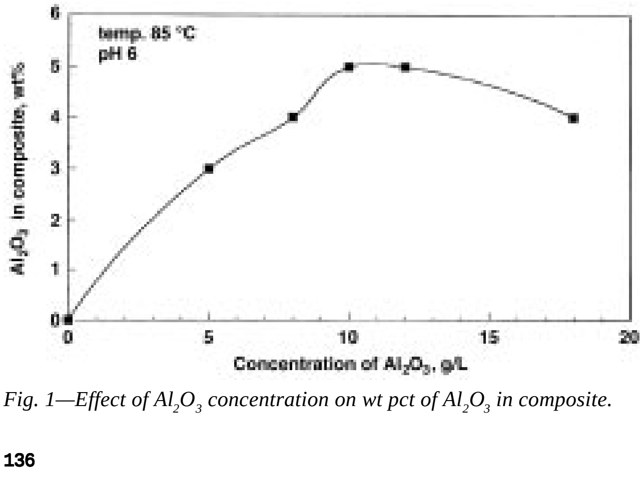

Fig. 1—Effect of Al_2O_3 concentration on wt pct of Al_2O_3 in composite.

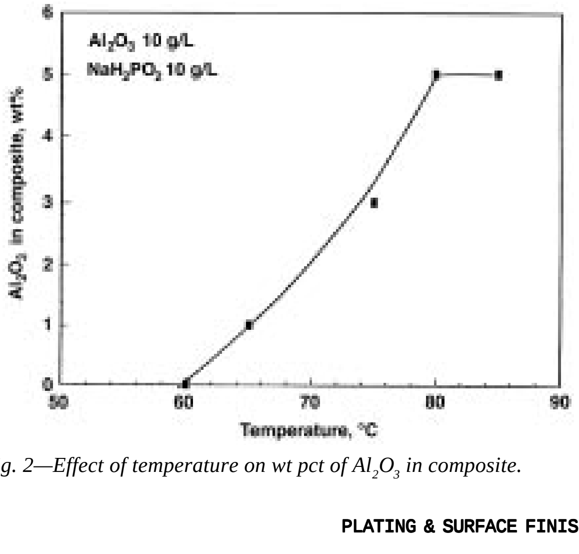

Fig. 2—Effect of temperature on wt pct of Al_2O_3 in composite.

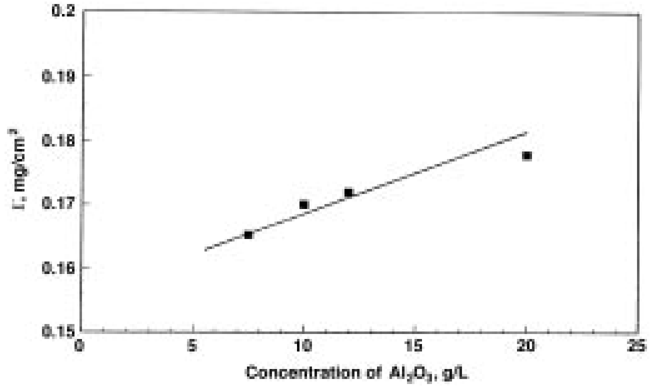

Fig. 3—Langmuir adsorption isotherm for sodium benzene sulfonate with Al_2O_3.

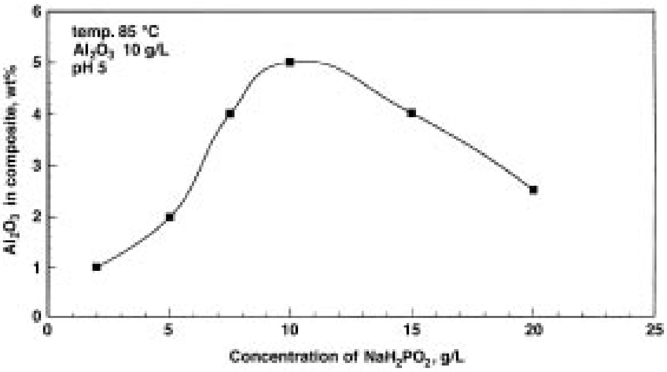

Fig. 4—Effect of concentration of reducing agent on wt pct of Al_2O_3 in composite.

was studied. Figure 1 shows the variation of the weight percent of the incorporated Al_2O_3 with suspension concentration of Al_2O_3 particles at 85 °C. As can be seen, particle incorporation increases with suspension concentration and attains an optimum value at 12 g/L. This limiting concentration may correspond to steady state equilibrium. With further additions, the particles appeared to agglomerate in the bath and a decreasing trend was observed.

The effect of temperature on the weight percent of Al_2O_3 in the deposit is shown in Fig. 2. The extent of codeposition is markedly influenced by the temperature of the plating bath. The percent of Al_2O_3 in the composite increases with temperature increase. The minimum temperature at which the bath can be operated is about 65 °C.

The mechanism of incorporation of Al_2O_3 particles in the composite may be illustrated as follows: Ni^{+2} cations in solution are adsorbed on Al_2O_3 particles which have a partial negative charge. This is in agreement with Berkh *et al.*[10] The benzene sulfonate anion acts as a chelating agent for the Ni^{+2} cations with alumina and forms a complex. On reaching the steel surface, nickel ions will be deposited while Al_2O_3 is adsorbed on the surface with benzene sulfonate by electrostatic attraction. This mechanism can be confirmed by the increase in the value of adsorption free energy of Al_2O_3 ($\Delta G_{ads}°$) on the substrate surface. $\Delta G_{ads}°$ is calculated from the following equation:[11]

$$\theta/1-\theta \exp(A\theta) = KC \qquad (1)$$

where $K = 1/55.5 \exp(\Delta G_{ads}°/RT)$, C is the concentration of Al_2O_3 in g/L, θ is the fractional surface coverage of Al_2O_3 in the deposit and A is the lateral interaction of adsorbed benzene sulfonate. Figure 3 shows the relation between surface density (Γ) and the concentration of Al_2O_3 particles. It yields the Langmuir-type adsorption isotherm. Data given in Table 1 reveals that the free energy of adsorption attains the highest negative value at 85 °C. This observation strongly suggests physical adsorption on the steel surface. As $-\Delta G_{ads}°$ increases (*i.e.*, the driving force for the adsorption process increases), the weight percent of the incorporated Al_2O_3 in the deposit increases. Moreover, the activation energy of composite coatings is calculated from the Arrhenius equation, which describes the dependence of the deposition rate on temperature. The values of the activation (E_a) is calculated from the Arrhenius equation:

$$dw/dt = Ae^{-Ea/RT} \qquad (2)$$

where A is the Arrhenius constant, R is the gas constant (8.314 J), T is the absolute temperature and dw/dt is the rate of deposition. The activation energy of the deposition reaction of $Ni\text{-}P\text{-}Al_2O_3$ composite from a bath containing 10 g/L NaH_2PO_2 is 19.3 kJ/mol.

Table 1

Effect of Concentration of Al_2O_3 on Adsorption Free Energy of Composite Deposition at Different Temperatures

Temperature, °C	Concentration of Al_2O_3	G_{ads}, kJ/mol
65	8	-11.38
	10	-11.52
	12	-11.60
	20	-11.30
75	8	-16.7
	10	-16.92
	12	-16.94
	20	-16.35
85	8	-17.19
	10	-17.31
	12	-17.32
	20	-17.10

The effect of concentration of reducing agent NaH_2PO_2 on the weight percent of Al_2O_3 in the deposit is shown in Fig. 4. The results indicate that the weight percent of Al_2O_3 increases with increasing hypophosphite concentration and the maxi-

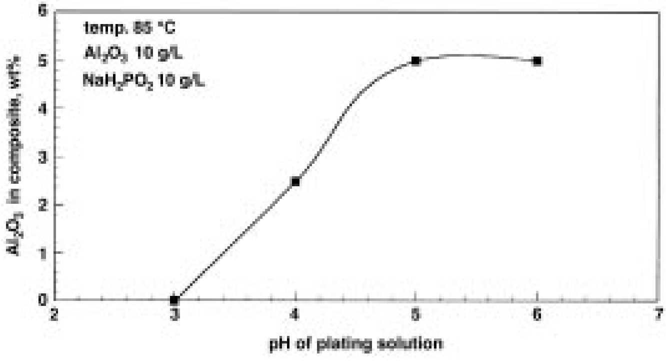

Fig. 5—Effect of pH on wt pct of Al_2O_3 in composite.

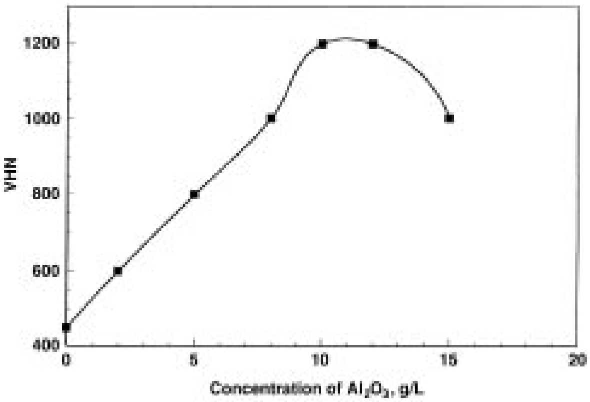

Fig. 6—Effect of concentration of Al_2O_3 on microhardness of the composite.

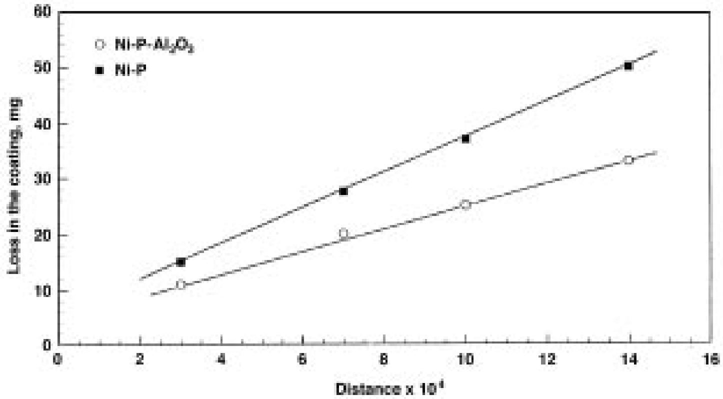

Fig. 7—Relation between sliding distance and loss of coating weight.

mum value corresponds to a concentration of 10 g/L. This result may be attributed to the proton availability as the hypophosphite concentration increases. Proton availability depends on the oxidation rate of hypophosphite to orthophosphite:

$$H_2PO_2 + H_2O \rightarrow HPO_3^{-2} + 2H^+ + 2e^-$$

which represents the rate determining step in the deposition reaction.[12] Further increase in the hypophosphite concentration leads to variation in Ni^{+2} concentration. The above observation is confirmed by the variation of $G_{ads}°$ and E_a with the concentration of NaH_2PO_2. E_a has the lowest value at the concentration of 10 g/L of NaH_2PO_2; however, $\Delta G_{ads}°$ attains tile highest negative value (Table 2). The influence of pH on Al_2O_3 incorporation is shown in Fig. 5. The results indicate that the weight percent of Al_2O_3 increases with increasing pH, reaching a maximum value around pH 5-6. At pH less than 3, there is no deposition because of complete hindrance of the reduction process at this pH.

Table 2

Effect of Concentration of NaH_2PO_2 on Adsorbed Free Energy & Activation Energy of the Composite at Constant Al_2O_3 Content (10 g/L)

Concentration of NaH_2PO_2, g/L	Temperature °C	G_{ads} kJ/mol	E_a kJ/mol
2	65	-14.11	38.5
	75	-14.51	
	85	-14.61	
5	65	-15.9	25.5
	75	-16.11	
	85	-16.20	
10	65	-16.52	19.2
	75	-16.94	
	85	-17.32	
20	65	-15.65	25.5
	75	-15.91	
	85	-16.11	

Properties of the Composite

The microhardness of the Ni-P deposit is 450 (HV). It can be increased to approximately 950 (HV) by heat treatment at 400 °C for 2 hr. The variation in microhardness of the Ni-P-Al_2O_3 composite, without heat treatment, vs. the Al_2O_3 concentration in the bath is shown in Fig. 6. The results indicate that the hardness increases gradually and reaches a maximum value of 1200 (HV) at 10 g/L Al_2O_3 concentration in the electrolyte. Further increase of Al_2O_3 in the electrolyte is accompanied by decrease in microhardness. This is a result of agglomeration of the particles in the bath, as illustrated in Fig. 1. The increase in microhardness with increase of Al_2O_3 concentration may be attributed to the presence of dispersed particles in the Ni-P alloy, which obstruct the movement of dislocations and resist plastic flow. This result is in agreement with Ramesh Bapu.[13]

The wear resistance and hardness of composite coatings were found to be related to each other as well as to the particle content in the coating. Figure 7 shows the relation between the sliding distance and the loss in coating weight. It was found that the wear rate of the Ni-P-Al_2O_3 composite and Ni-P deposits were 2.1×10^{-7} and 3.44×10^{-7} g/m, respectively. The wear resistance was estimated by calculating the reciprocal of the wear rate. As can be seen, incorporation of Al_2O_3 was found to improve significantly the wear resistance of nickel-phosphorus coatings.

Conclusions

From the above results we can conclude that:

- Uniform thickness of Ni-P-Al_2O_3 composites are formed by controlling the variables of the deposition process (*i.e.*, pH, temperature, concentration of Al_2O_3 and a reducing agent in the presence of sodium benzene sulfonate).

- The suggested mechanism of Ni-P-Al_2O_3 was discussed in view of the free energy of adsorption ($\Delta G_{ads}°$) and the activation energy (E_a).

- Codeposition of Al_2O_3 powders with Ni-P alloys is attributed to strong physical adsorption.

- Incorporation of Al_2O_3 powders with Ni-P alloys improves microhardness and wear resistance.

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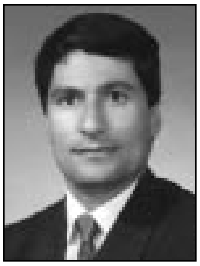

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