Effect of Agitation in Electroless Nickel Deposition

By K. Sevugan, M. Selvam, K.N. Srinivasan, T. Vasudevan and P. Manisankar

Agitation of an electrolyte brings more of the active species to the electrodes, where a reduction or oxidation process takes place, and leads to improved rate of reaction. Agitation may be by forced air or by mechanical stirring or controlled flow, or by ultrasonic effects. The main purposes of agitating the electrolyte are to improve the rate of reaction, to get reproducible values and to relieve adsorbed hydrogen or oxygen if any, on the surface of the electrodes. Adsorption of gases can lead to pitting or holes in the deposit. It was found that agitation improved the rate of nickel deposition and affects to some extent the phosphorus content of the deposit.

lectroless nickel coatings have several advantages over electrodeposited nickel.⁴⁴ Because the physical and mechanical properties are important in engineering applications, electroless nickel (Ni-P or Ni-B) has become significant in these applications. Several acid or alkaline types of baths to deposit Ni-P coatings have been developed. Careful control of variables is necessary to obtain reproducible coatings having the same composition and the same physical and mechanical properties, because of the effect of each variable on the deposition process. In electroless nickel, concentrations of bath constituents, pH, temperature and agitation affect the phosphorus content of the deposit, the rate of deposition and the nature of the deposit.

When using hypophosphite as reducing agent, increasing electrolyte pH increases the rate of deposition, decreases the phosphorus content of the deposit and decreases the tolerance limit of impurities for spontaneous decomposition of the bath. Because electroless nickel deposition is always accompanied by hydrogen evolution at the electrode, there is always a change in pH (*i.e.*, between the electrode and the diffusion layer, even if it is operated in a highly acid pH range). Another possibility for change in the nature of the deposit maybe a result of diffusion of ions through the diffusion layer if the system is under diffusion control. Depending upon the operating variables, the film thickness varies, leading to a change in the rate

Table 1								
Effect	of	Agitation	on	Rate	of	Deposition		

of diffusion of ions to the electrode site. Accordingly, agitation is an important variable for maintaining the electrolyte pH, temperature and concentrations of active species at the electrode at a constant level. Different types of agitation, such as mechanical, ⁵air, ⁶rotation ⁷and ultrasonic vibration⁸¹³ have been used to study the rate of deposition in electroless baths. In the present study, the effect of mechanical, ultrasound and air agitation on a lower-temperature (70 °C) electroless nickel bath was investigated for the rate of deposition and phosphorus content of the deposit.

Experimental Procedure

Electroless Bath

The bath composition and its optimum operating conditions are given below:

Nickel sulfate	40 g/L
Trisodium citrate	50 g/L
Sodium hypophosphite	35 g/L
pH	6to12
Temperature	60 "C.

Copper sheet/caps were used as the substrate material. The pretreatment for the copper included mechanical buffing, decreasing with trichloroethylene, acid dipping in five-percent sulfuric acid for 60 to 120 see, activation treatment in a solution of 0.5 g/L palladium chloride and 10 ml/L of hydrochloric acid and, finally, electroless deposition with intermediate rinsings. Agitation in this study included air, to-and-fro motion, ultrasound, mechanical, and rotation of the electrode.

Air Agitation

Air agitation is normally implemented by passing compressed air through small nozzles. In this study, to get more or less uniform agitation under air flow, a constant volume and height of the electrolyte, constant pressure of air, same tank and position of electrodes and other immersed objects, such as the heater, thermometer and agitation coils, were maintained for all experiments.

Table 2Effect of Agitation on Phosphorus Contentof the Deposit

рH		Rate o	of deposition	µm/hr	рН	Percentage of phosphorus (wt.)			
	Mechanical Agitation	Air Agitation	Ultrasonic Agitation	Rotating disc electrode agitation		Mechanical Agitation	Air Agitation	Ultrasonic Agitation	
6	2.172	2.41	1.464	1.898	6	8.278	11.417	12.09	
8	9.294	10.14	9.708	8.033	8	4.11	4.54	6.51	
10	15.797	11.42	16.92	14.15	10	3.282	4.72	4.58	
12	10.88	6.16	16.47	10.09	12	2.74	3.596	3.35	

Table 3Effect of AgitationEnhancement Factor on Rate of Deposition

Table 4Effect of Agitation Enhancement Factorof Phosphorus Content in the Deposit

рН	Mechanical Agitation	Air Agitation	Ultrasonic Agitation	RDE	рН	Mechanical Agitation	Air Agitation	Ultrasonic Agitation
6	1.47	1.59	1.0	1.27	6	0.57	0.78	0.83
8	1.39	1.52	1.45	1.19	8	0.41	0.46	0.65
10	1.3	0.94	1.39	1.16	10	0.57	0.81	0.79
12	0.81	0.46	1.24	0.75	12	0.78	1.03	0.95

Mechanical Agitation

In mechanical stirring, an ordinary small blade with a motor was used by rotating a small fan inside the electrolyte through a long shaft. In to-and-fro motion, the electrode was hung from a bar coupled with a set-up to make to-and-fro motion from rotation of the shaft of a reduction gear motor. For a rotating disc electrode, the hydrodynamic conditions are well known and the experimental set-up is simple. The flow of an incompressible fluid is caused by the rotation of a disc about an axis through its center.

Ultrasonic Agitation

The electrolyte was placed in a glass beaker and kept in a water bath of an ultrasonic agitation unit. The electrolyte was heated via the water bath by an immersion heater coupled with a constant temperature controller and a thermometer.

Rate of Deposition

The rate of deposition was calculated by the weight gain method. In this method, a known area and weight of the activated copper panel was plated with electroless nickel for a specific time under constant operating conditions. From the weight of the deposit, the area of the panel, the time of deposition and density of the coating, the rate of deposition in μ m/hr was calculated using the relation

Rate of deposition =
$$\frac{w \times 10^4}{ad}$$

where W = weight of deposit in grams

a = area in cm²

d = density in glee

Analysis of Phosphorus Content

For phosphorus analysis, stainless steel panels were used to obtain only the electroless deposit. The known amount of deposit was dissolved in 20-percent nitric acid and used for analysis. The phosphorus in the deposit was oxidized with potassium permanganate and precipitated as ammonium phosphomolybdate. The precipitate was separated by filtration and dissolved in a known excess volume of standard sodium hydroxide. The excess sodium hydroxide was titrated against standard sulfuric acid. From this titration, the phosphorus content of the deposit was calculated using the relation

$$\mathsf{P}_{(\text{percent})} = \frac{[\mathsf{V}_{\text{NaOH}} \times \mathsf{N}_{\text{NaOH}}) - (\mathsf{v}_{\text{H}_2\text{SO}_4} \mathsf{X} \mathsf{N}_{\text{H}_2\text{SO}_4})] \ 1.3478}{\text{Weight of deposit in grams}}$$

Results and Discussion

During agitation of the electrolyte, the rate of deposition and phosphorus content of the deposit, plus electrolyte pH, were studied. The results are reported in Tables 1 and 2. Table 1 shows that in low electrolyte pH (6.0 to 8.0), air agitation yields a high rate of deposition, whereas at a higher pH (10.0), ultrasonic agitation yields a high rate of deposition. With increasing electrolyte pH, up to 10.0, irrespective of the type of agitation, the rate of deposition is increased. At a pH of 12.0, however, all types of agitation slightly reduced the rate of deposition.

For low pH (6.0 to 8.0), ultrasonic agitation produces higher phosphorus content in the deposit and at high pH (10.0 to 12.0), air agitation yields higher phosphorus content than other types of agitation. Reduction in phosphorus content in the deposit with agitation is noted in Table 2. Increasing the pH of the solution also decreases the phosphorus content of the deposit during agitation.

The enhancement of the rate of deposition and the percent phosphorus in the deposit for various types of agitation are given in Tables 3 and 4 respectively. The enhancement factor for the rate of deposition is the ratio of the rate of deposition while agitated to the rate of deposition under still conditions; the enhancement factor for phosphorus content is the ratio of phosphorus present in the deposits produced while agitated to the phosphorus present in the deposit under still conditions. This clearly indicates that, in general, agitation increases the rate of deposition and reduces the phosphorus content of the deposit. It explains that, during electroless deposition, a film is formed over the electrode. The thickness of the film varies, depending on the operating variables. Electrolyte agitation reduces the film thickness and brings more nickel, hydrogen and hypophosphite ions to the electrode site, leading to high rate of deposition, because it favors diffusion of these ions from the bulk electrolyte through the films to the electrode surface where they are discharged or reduced or oxidized.¹⁴⁻¹⁶This clearly indicates that the electroless nickel deposition of interest is under diffusion control. At pH 12.0, the slight reduction in rate, irrespective of the agitation used, is probably a result of loss of ammonia by evaporation. At pH 12.0, ultrasound yields 1.24 as the enhancement factor of the rate of deposition-less than the factor for deposition at pH 10.0. It can be seen from the data that ultrasound has no effect at low pH (6.0). It has better effect on the rate of deposition only at pH greater than 8.0. In ultrasonic agitation, because of its cavitation effect on the substrate, if the coating is not adherent, it may peel/span off. In the present study, no such negative result was observed, suggesting that the coating is quite adherent.

Conclusions

The nickel ion reduction process is under diffusion control. Agitation of the electrolyte improves the rate of deposition, but at the same time reduces the phosphorus content of the deposit. At low pH (6 to 8) air agitation improves the rate of deposition and at high pH (1 O to 12), ultrasonic agitation improves the rate of deposition.

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