

ELECTROLESS Ni-P-Al₂O₃ COMPOSITES

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Electroless Ni-P- γ -Al₂O₃ and Ni-P- α -Al₂O₃ composites have been successfully produced. It was observed that with lesser quantity of particulate matter in solution, deposits with higher hardness compared to electrocomposites can be produced. Hardness of the composites was enhanced by annealing.

Key words: Electroless composites, electro composites, Ni-P- γ -Al₂O₃ Ni-P- α -Al₂O₃.

INTRODUCTION

An electrodeposited composite plating is defined as the one in which an uniform dispersion of small discrete particulate matter is deliberately codeposited within a metallic coating [1–3]. Electroless nickel phosphorus coatings have many properties that are superior to those of electrodeposited nickel [4]. Because of the phosphorus content, electroless nickel is harder and has better corrosion resistance [5]. Electroless nickel composites combine the unique properties of conventional electroless nickel deposit such as uniformity of deposition over complex geometries, high hardness and good corrosion resistance comparing with that of the abrasive materials possessing high temperature resistance and other tribological properties.

It has been indicated that it is difficult to obtain stable electroless nickel solutions to produce the composites since the inclusion of particulate matter is quite likely to destabilise the bath [6]. More research into the basic theory of electroless nickel deposition and the inclusion of particulate matter from plating baths [7, 8] has led to the conclusion that the normal working conditions of an electroless nickel bath are ideal for achieving particulate inclusion in them. Reports on the occlusion of inert particles into the metal matrix have shown that their codeposition in nickel electroplating is favoured at a relatively high solution pH, 4.5–5.0 and at high solution temperature [9] which are exactly the operating conditions for many of the electroless nickel plating baths. This paper deals with the production of electroless Ni-P-Al₂O₃ composite and its special properties.

EXPERIMENTAL

γ and α varieties of alumina were ground in a ball mill till their particle sizes were in the range of 1.0–1.6 μ m and 2.0–3.0 μ m respectively. They were leached in 50% hydrochloric acid twice, then in 10% sulphuric acid and filtered thoroughly till there was no traces of acidity, chloride or sulphate in the wash water. The powders were then dried and used for the experiments.

Electroless nickel electrolyte of the following composition was used. Nickel sulphate, 24 g.l⁻¹; Sodium hypophosphite, 21 g.l⁻¹; Lactic acid 30 ml.l⁻¹; Propionic acid 2 ml.l⁻¹; Lead nitrate 0.0001. The temperature range was 358–363K and pH was maintained at 4.4–5.0.

The above solution was taken in a graduated vessel, and heating was effected by using a thermostated water bath. The evaporation loss of the electrolyte was compensated by controlled flow of water. The pH of the bath was maintained at 4.5 electrometrically. Fresh electrolyte was used for each set of experiment.

In order to prevent agglomeration of the particles and to obtain uniform dispersion of alumina in the bath, the required amount of the particulate matter was first blended in a mortar with small amount of the electrolyte and the slurry was then added to the bulk. The particles were kept in suspension by impeller agitation and the deposition was carried out for an hour. Polished stainless steel cathodes with a cyanide copper strike were used for preparing the composites.

The volume percent of aluminium oxide was determined by gravimetric method [9]. The concentration of the particulate matter was varied from 5 to 25 g.l⁻¹ and the pH from 2 to 5 using dilute sodium hydroxide or sulphuric acid. The hardness of the composites was measured by knoop indentation method with a load of 25 g. Annealing of the specimens was done in an inert atmosphere at temperatures varying from 673 to 1273 K.

RESULTS AND DISCUSSION

As in many electrocomposite systems, increase in the inert particle concentration increases the volume percent of inclusion in the deposit up to 10 g.l⁻¹ (Fig. 1). Once this critical concentration is exceeded, further additions have negligible influence on the incorporation density. The rate of deposition of nickel decreases with high particulate volume in suspension (Table I) which also tends to destabilise the electrolyte easily. It was also observed that the rate of deposition of electroless nickel composite was only 50% compared to that of electro composites (Fig. 1). But, for obtaining the same volume percent of particulate incorporation in the deposit, only 10% of their concentration need to be suspended in the electrolyte.

TABLE-I: Mass And Thickness Of Electroless Composite Obtained By Varying γ -Alumina Concentration

	γ - Al ₂ O ₃ g.l ⁻¹					
	0	5	10	15	20	25
Mass gms. dm ² / hr (average)	2.40	2.22	1.96	1.7	1.36	1.05
Thickness/hr (average)	27.0	25.1	22.0	19.15	15.30	11.80
Temperature = 363K; pH = 4.5						

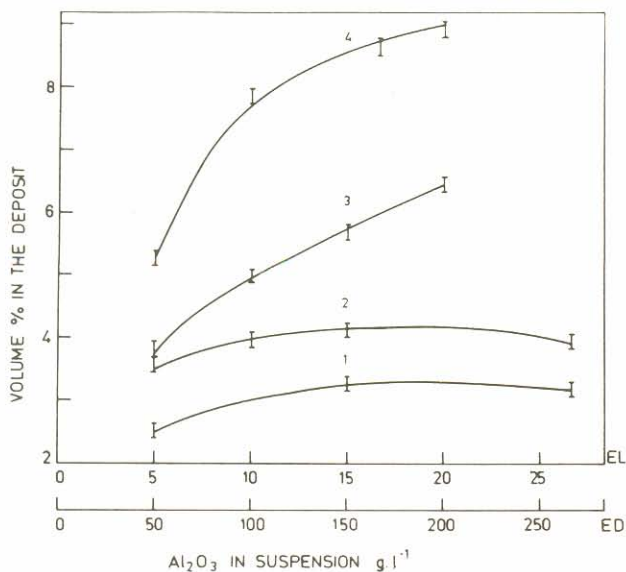


Fig. 1: Effect of concentration of dispersoid in solution on the percentage incorporation in the deposit. (1) Electroless Ni-P- γ -Al₂O₃; (2) Electroless Ni-P- α -Al₂O₃; (3) Electrodeposited Ni- γ -Al₂O₃; (4) Electrodeposited Ni- α -Al₂O₃

At low solution pH, the rate of nickel deposition was very low and only in the pH range of 4.4–4.8, maximum rate could be obtained (Table II). High pH values not catalyse autoreduction of the bath itself.

Electroless Ni-P- α -Al₂O₃ composites show a higher degree of hardness compared to Ni- γ -Al₂O₃ and Ni- α -Al₂O₃ electrocomposites and Ni-P- γ -Al₂O₃ electroless deposits, as shown in Fig. 2. Maximum hardness obtained is in the range, 600–650 KHN for Ni- γ -Al₂O₃ and Ni- α -Al₂O₃ electrocomposites respectively while for electroless nickel, it is around 480 KHN. Production of a much harder coating with minimum expenditure on the abrasives makes this process more cost effective.

TABLE II: Effect Of Solution pH On The Rate Of Electroless Composite Deposition

pH	Mass (g.dm ⁻² h ⁻¹)	Thickness (μ m. h ⁻¹)
2.5	1.08	12.1
3.5	1.52	17.1
4.5	1.96	22.0
5.5	1.96	22.0

Temperature = 363K

The outstanding feature of the composite coatings is their greater retention of strength even after annealing. Hardness values of the Ni-P-Al₂O₃ composites, as shown in Fig. 3, increase drastically after annealing at 673 K similar to electroless Ni-P deposits which has been explained as due to precipitation hardening by the formation of Ni₃P phase. Maximum hardness obtained after heat treatment ranged from 920 to 980 and 990–1200 KHN for Ni-P- γ -Al₂O₃ and Ni-P- α -Al₂O₃ respectively whereas that obtained for electroless Ni-P ranged from 750 to 800 KHN. Table III compares the variation in hardness of electrodeposited nickel, Ni-Al₂O₃, electroless Ni-P and electroless Ni-P- γ -Al₂O₃ and Ni-P- α -Al₂O₃. Hardness of the electroless composites reach low values if annealed at still higher

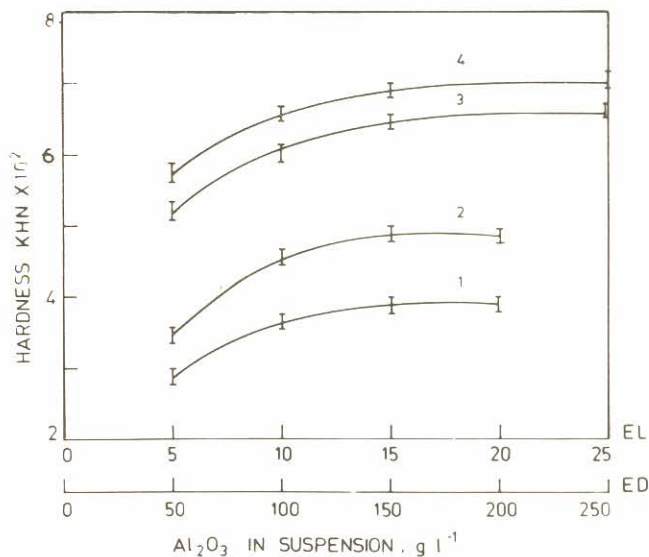


Fig. 2: Effect of concentration of Al₂O₃ in suspension on the hardness of deposits (1) Electrodeposited Ni- γ -Al₂O₃; (2) Electrodeposited Ni- α -Al₂O₃; (3) Electroless Ni-P- γ -Al₂O₃; (4) Electroless Ni-P- α -Al₂O₃

temperatures, though they maintain their superiority over other coatings. However, above 1073 K, the deposits turn grey black making the measurements difficult.

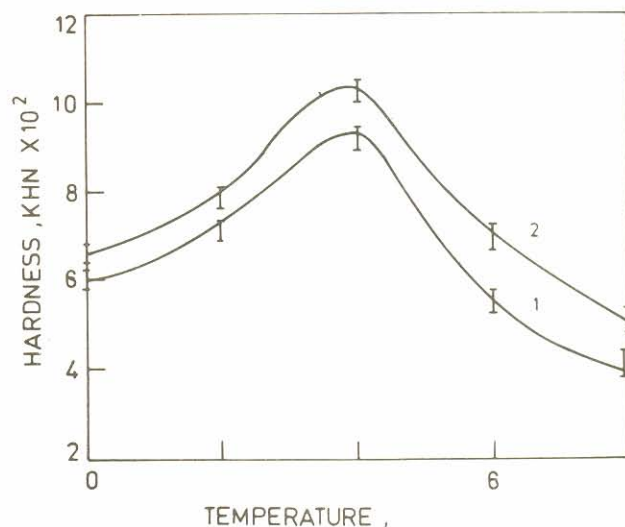


Fig. 3: Effect of annealing on the hardness of deposits. (1) Electroless Ni-P- γ -Al₂O₃ (2) Electroless Ni-P- α -Al₂O₃

Photomicrographs of the electroless Ni-P- γ -Al₂O₃ and Ni-P- α -Al₂O₃ in Fig. 4 (a to f) illustrate that the latter exhibit marginal structural variation compared to the former.

CONCLUSION

Electroless nickel-phosphorous-alumina composites can be produced from a conventional electroless nickel plating electrolyte. The hardness of the deposits are nearly three times that of electrocomposites.

TABLE-III: Effect of Annealing Temperature on the Hardness of Various Nickel Deposits

	Hardness in KHN					
	As plated	473K	673K	873K	1073K	1273K
Watts nickel	260	225	185	140	105	75
Electrodeposited	380	365	315	235	205	195
Ni- γ -Al ₂ O ₃ 5%						
Electrodeposited	450	410	340	275	245	210
Ni- α -Al ₂ O ₃ 8%						
Electroless	480	—	800	520	450	—
Ni-P						
Electroless	600	700	920	580	450*	—
Ni-P- γ -Al ₂ O ₃ 3.2%						
Electroless	650	750	1020	645	520*	—
Ni-P- α Al ₂ O ₃ 4.2%						

* Not consistent

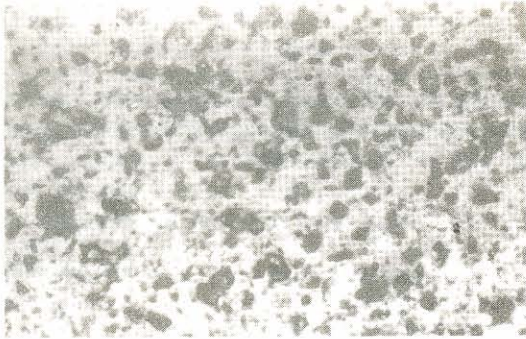
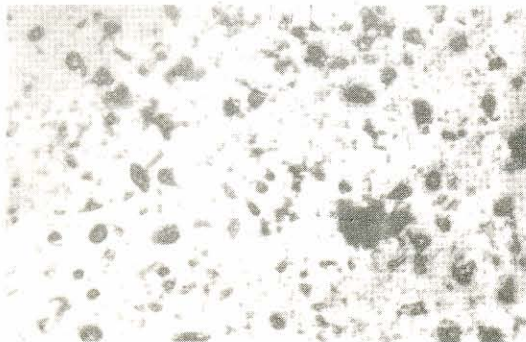
Fig. 4 (a): Photomicrograph of Ni-P- α Al₂O₃ composite after annealing at 673K.

Fig. 4 (b): Photomicrograph of the above deposit after annealing at 873K.

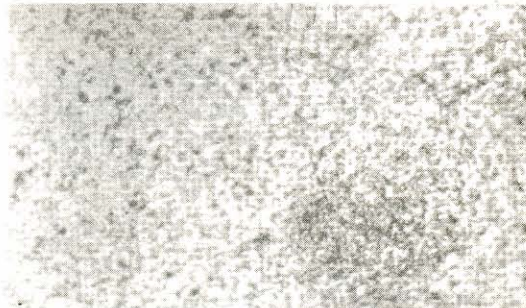
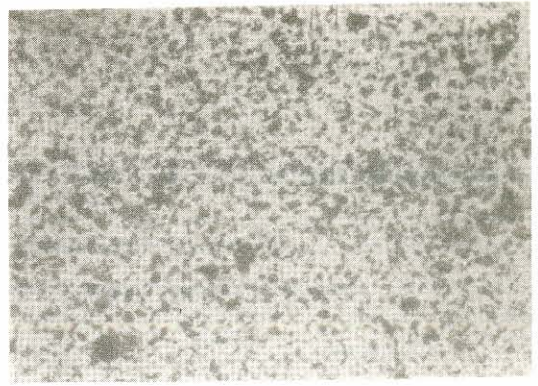
Fig. 4(c): Photograph of Ni-P- γ Al₂O₃ composite after annealing at 673K.

Fig. 4(d): Photomicrograph of the above deposit after annealing at 873K.

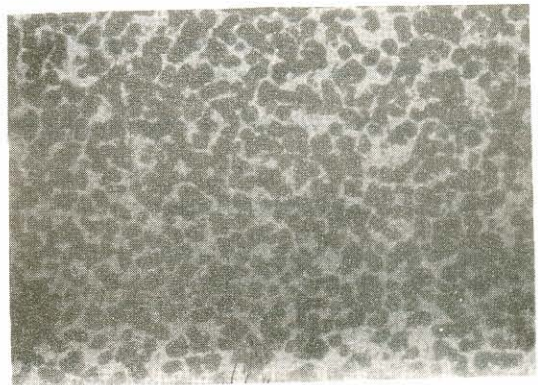


Fig. 4(e): Photomicrograph of the above deposit after annealing at 1073K.



Fig. 4(f): Photomicrograph of the above deposit after annealing at 1273K.

REFERENCES

1. E C Kedward, *Electroplating Metal Finish*, **20** (1972) 25.
2. Malathy Pushpavanam, S Gowri, S Krishnamoorthy, R Thangappan and B A Shenoi. *Electroplating Metal Finish*, **27** (1972) 24.
3. F J Honey, V Wride and E C Kedward, *Plating and Surf Finish*, **42** (1986) 73.
4. R A Jeanmenne, *Products Finish*, **84** (1990) 1.
5. F A Lowinheim, *Modern Electroplating*, John Wiley and Sons, New York, (1974) p. 591.
6. F N Hubbal, *Trans Metal Finish*, **65** (1978) 56.
7. C White and J Foster, *Trans Inst Metal Finish* **92** (1978) 59.
8. C White and J Foster, *ibid*, **8** (1981) 59.
9. Malathy Pushpavanam and B A Shenoi. *Metal Finish*, **39** (1947) 30