ELECTRODEPOSITION OF HEAT-TREATABLE $Ni\text{-}P\text{-}Al_2O_3$ COMPOSITE COATINGS

Raj Narayan and Surya Narayanan

Heat-treatable $Ni\text{-}P\text{-}Al_2O_3$ composite coatings have been produced so as to expand the application range of Nickel Composite Coatings. The effect of various factors e.g. surface condition & bath load of Al_2O_3 and current density on Al_2O_3 and P content in the coating and microhardness in as-plated and heat treated conditions has been studied. Under optimum conditions, microhardness was within a range of 1140 to 1300 kg/mm^2 as compared to 530 to 630 kg/mm^2 for as-plated coatings. Mechanism of codeposition was similar to that in $Cr\text{-}Al_2O_3$ composite coatings.

For more information, contact:

Dr. Raj Narayan,
Professor,
Department of Materials & Metallurgical Engineering,
Indian Institute of Technology,
Kanpur-208016,
INDIA
Email : rnarayan@iitk.ac.in

INTRODUCTION

Electroless Ni-P alloy coatings first developed by Brenner and Riddel (1) have become quite popular due to their excellent corrosion and wear resistance in as-plated and heat-treated conditions. Their wear resistance is comparable to hard chromium coatings(2). Tribological properties of these coatings have been further extended by codepositing second phase particles with electroless Ni-P; second phase particles being of Al_2O_3, Cr_3C_2, Cr_2O_3, SiC, Si_3N_4, WC, PTFE, Grphite etc.(3-9) However, the electrolytes used for electroless plating are expensive and P content of the coating is usually limited to 8%. To overcome these difficulties Ni-P coatings have produced by electrodeposition.(10,11) These electrodeposited Ni-P coating can be hardened by heat treatment. Present investigation was undertaken to examine the possibility of electrodepositing heat treatable Ni-P-Al_2O_3 composite coatings.

EXPERIMENTAL

Al_2O_3 powder particles obtained by dry grinding as-received Al_2O_3 for 12 hours and having an average particle size of 4 μm, suitably pretreated, was added to a electroplating bath containing Nickel Sulphate ($NiSO_4.7H_2O$) 150 g/l , Nickel Chloride ($NiCl_2.6H_2O$) 45 g/l , Phosphoric Acid (H_3PO_4) 50 g/l and Phosphorus Acid (H_3PO_3) 5 g/l . A magnetic stirrer was used to blend Al_2O_3 particles for 1 hour before starting of electrodeposition & for keeping the particles under suspension during plating. Water was added to make up for evaporation loss during plating. Plating was carried out for 15 minutes at 80^0C on suitably prepared mild steel specimens.

The Al_2O_3 content of the coating was determined gravimatrically by dissolving it in concentrated sulphuric acid containing few drops of formaldehyde, diluting to approximately 4:1 and filtering through a previously weighed Whatman filter paper no. 40, washing, drying and reweighing it.

Microhardness of the coating was measured using a Tukon microhardness tester by using a diamond pyramid indentor with an open angle of 136^0 at a load of 1 kgf.

RESULTS & DISCUSSIONS

Preliminary results showed that surface condition of Al_2O_3 was affecting the nature of Ni-P-Al_2O_3 composite coating. When Al_2O_3 was added in as-received condition bath pH increased and deposits obtained were black, loose and spongy. Frequent adjustment bath pH was necessary to obtain acceptable deposits. Using Ni-P coated Al_2O_3 powder also was not effective and coatings obtained were rough and porous with poor adherence. Treated Al_2O_3; produced by mixing as-received Al_2O_3 with electroplating solution at 80^0C for 4 hours followed by filtering, washing and drying at 150^0C; produced bright, smooth and adherent coatings. In the present study all further experiments were carried out using treated Al_2O_3.

With increasing Al_2O_3 content in the bath (bath load), the Al_2O_3 content in the coating increased steadily for 0.1 A/cm^2 and 0.4 A/cm^2 whereas for 0.2 and 0.3 A/cm^2 there were regions where Al_2O_3 content in the coating was almost independent of the bath load. (Fig. 1)

At all bath loads and at all current densities the amount of phosphorus in the coating was always lower than the value expected from a bath containing no Al_2O_3 particles. When the bath load was increased from 20 g/l to 40 g/l, the amount of phosphorus in the coating increased. Thereafter it either decreased (at 0.1 and 0.2 A/cm^2) or remained almost constant (at 0.3 and 0.4 A/cm^2). At 0.3 and 0.4 A/cm^2 the phosphorus content of the coating increased when bath load was increased from 100 to 120 g/l. (fig.2)

With increasing Al_2O_3 content in the bath, cathode current efficiency (CCE) decreased at 0.1, 0.2 and 0.4 A/cm^2, whereas at 0.3 A/cm^2 it increased. In all cases CCE was between 80 to 90 % (fig.3).

In the As-plated condition the microhardness of the composite coating first decreased and then increased with increasing Al_2O_3 content in the bath at all current densities except for 0.1 A/cm^2 where a reverse trend was obtained (fig. 4). The minimum microhardness observed increased with increasing current density.

For samples vacuum annealed for 1 hour at 200^0C, Al_2O_3 content in the bath versus microhardness showed a minimum at 0.1 and 0.2 A/cm^2. At 0.3 A/cm^2 it was almost constant up to a bath load of 60 g/l, thereafter it increased with increasing bath load. At 0.4 A/cm^2 microhardness of the coating increased up to about 50 g/l thereafter it remained constant up to about 100 g/l and increased thereafter (fig.5).

When samples were vacuum annealed for 1 hour at 400^0C, microhardness increased regularly with increasing Al_2O_3 in the bath at 0.1 and 0.2 A/cm^2. Whereas at 0.3 and 0.4 A/cm^2 there appeared to be a region where microhardness was independent of Al_2O_3 in the bath (fig.6).

For samples vacuum annealed for 1 hour at 600^0C, microhardness of the composite coatings increased regularly with increasing Al_2O_3 content in the bath at all current densities (fig.7).

For samples vacuum annealed for 1 hour at 800^0C, microhardness increased with increasing Al_2O_3 in the bath at 0.1 A/cm^2 whereas as 0.2, 0.3 and 0.4 a/cm^2 a maximum is observed at about 80 g/l (fig.8).

At all current densities, the plot of annealing temperature vs. microhardness resembled very much to that of Ni-P alloy coatings. With increasing annealing temperature the hardness increased reached a maximum and then dropped, optimum being observed at about 400^0C (fig. 9 to 12).

When microhardness was plotted against either Al_2O_3 or P content in the coating wide scatter in results was obtained. This was apparently due to the fact that both Al_2O_3 and P in the coating affect its hardness. Using Linear Regression Analysis following relationship was observed for samples in as-plated condition.

Microhardness (Kg/mm^2) = 714.30 + 15.49 x Al_2O_3 (wt %) – 35.77 x P (wt %)

Since bath load and current density are independent variables an attempt was made to correlate microhardness with these variables at different annealing temperatures. Following equations can be used to predict Micro-hardness of Ni-P-Al_2O_3 composite coatings in as-plated and annealed (for 1 hour) conditions using Al_2O_3 (wt.%) in the bath and Current Density (A/cm^2)

As-Plated : Microhardness = 0.31 x Al_2O_3 + 378.99 x P + 472.78
Annealed at 200^0C : Microhardness = 0.82 x Al_2O_3 + 653.30 x P + 634.50
Annealed at 400^0C : Microhardness = 3.49 x Al_2O_3 + 5864.80 x P - 662.56
Annealed at 600^0C : Microhardness = 0.47 x Al_2O_3 + 341.20 x P + 482.50
Annealed at 800^0C : Microhardness = 0.38 x Al_2O_3 + 150.50 x P + 242.56

The two stage adsorption mechanism proposed by Gugliemi(17) is not applicable in the present case since a plot of volume percent and volume fraction of Al_2O_3 in the bath and the coating respectively failed to give a sheaf of straight lines converging at a point. Also other mechanisms based purely on electrophoretic deposition and mechanical entrapment of solid particles in the electrodeposit are unable to explain all the results obtained.

A mechanism proposed by Narayan & Chattopadhyay(18) for electrodeposition of Cr-Al_2O_3 composite coatings appear to be applicable in the present Ni-P-Al_2O_3 system also. According to this mechanism the transportation of Al_2O_3 particles towards the cathode and their subsequent deposition within the Ni-P matrix would depend upon :-

1. The surface charge of Al_2O_3 particles, which may be modified due to adsorption of certain species from the plating bath.
2. Transportation of the particles towards the cathode due to hydrodynamic and electrophoretic forces.

Al_2O_3 particles, which are initially negatively charged in aqueous solution, adsorb the hydrogen produced by oxidation of hypophosphite anion to a more stable phosphite ion.

$H_2PO_2^- + H_2O = H(HPO_3)^- + 2H^+$ (adsorbed by Al_2O_3 particles)

This adsorption of H^+ ions would either neutralize the charge on Al_2O_3 particles or positively charge it. These neutral or positively charged particles move towards the cathode due to hydrodynamic and electrophoretic forces and get entrapped within the growing Ni-P matrix and the adsorbed hydrogen evolves as H_2 gas.

At a given current density increasing the bath load should increase the amount of Al_2O_3 codeposited with Ni-P, whereas increasing the current density will have the following mutually opposing effects:

- Increased production of H^+ produced by decomposition of $H_2PO_2^-$ ions, which are produced by reduction of H_3PO_3 molecules at the cathode. This would result in higher amount of codeposited Al_2O_3 due to increased chance and magnitude of H^+ adsorption on Al_2O_3 surface.
- Increased evolution of H_2 gas bubbles at the cathode and thereby making codeopsition of Al_2O_3 difficult. This would result in lower amounts of codeposited Al_2O_3.

The above explains why at low current density (0.1 A/cm^2) codeposition is negligible at 20 and 40 g/l bath loads and high as we increase the bath load from 60 to 80 g/l, whereas at higher current densities codeposition is appreciable at lower bath loads also. This will also explain why initial rate of increase of Al_2O_3 in the coating with Al_2O_3 in the bath is less at higher current densities as compared to lower current density (fig. 1). This also explains optimum codeposition at 0.2 A/cm^2 for bath loads of 40, 60 & 80 g/l and at 0.3 A/cm^2 for bath load of 20 g/l.

Effect of bath load and current density on the amount of P in the present investigation can be best explained by the effect of these parameters on reactions taking place at the cathode surface. During electrode position of Ni-P coatings following reactions occur at the cathode.

$$Ni^{2+} + 2e \rightarrow Ni \qquad (1)$$
$$H_2PO_2^- + e \rightarrow 2OH^- + P \qquad (2)$$
$$2H^+ + 2e \rightarrow H_2 \qquad (3)$$

The present observation that the amount of P in coatings containing Al_2O_3 , at all current densities and bath loads, was lower than the expected value for a bath without Al_2O_3 can be explained in terms of its effect on bath pH. It was observed that addition of Al_2O_3 to the bath increases its pH. This would tend to shift the equilibrium in the above reaction (2) towards left and result in lower P in the coating.

Similarly the present observation that increasing current density results in lower P in the coating can be explained in terms of the effect of increasing current density on the above reactions. It appears that initially increasing current density accelerates reaction (1) more than reaction (2) and thereby results in lower P in the coating. At current densities above 0.3 A/cm^2 rate of reaction (2) is also inceased in the forward direction resulting in higher P in the coating.

Ni-P-Al_2O_3 composite coatings harden on heat treatment by precipitation of Ni_3P phase as they do in any thermally prepared alloy. However, the first stage of the hardening process, high temperature heat treatment, in not necessary in case of electrodeposited coatings because in as deposited condition they are in single-phase metastable phase. When this single-phase alloy is heated in temperature range of 200 – 400^{0}C precipitation of sub-microscopic Ni_3P results in increased hardness. At higher temperatures these precipitates coarsen resulting in drop in hardness. The effect of annealing time on hardness at various temperatures has not been studied in the present investigation. However, it is reasonable to assume that it will follow the general effect observed for precipitation hardening.

CONCLUSIONS

1. It was possible to produce heat-treatable Ni-P-Al_2O_3 composite coatings.
2. Addition of as-received Al_2O_3 to the electroplating solution increases its pH, which in turn effects the nature of electrodeposited coating. Black coatings being obtained at pH higher than 1.6
3. Using treated Al_2O_3 it was possible to produce composite coatings of acceptable quality.
4. At a given current density the Al_2O_3 content in the coating increased with increase in its content in the bath.
5. P content of the coating decreased with increase in current density.
6. Microhardness of the coating was always higher than pure nickel coatings. It increased with increasing Al_2O_3 and decreasing P content in the coating.
7. Microhardness of as-plated and heat-treated coatings was strongly dependent on current density. It increases with increasing current density and then shows an optimum.
8. Microhardness of Ni-P-Al_2O_3 composite coating increased with increasing heat treatment temperature up to 400^0C, thereafter it decreased. The peak hardness was higher than Ni-P alloy coatings.
9. Mechanism proposed by Narayan and Chattopadhyay for Cr- Al_2O_3 appears to be applicable in Ni-P-Al_2O_3 system also.

REFERENCES

1. A.Brenner and G.E.Ridell, J. Res. Natl. Bur. Standard, 37 (1946), 31.
2. A.W.Ruff and D.S.Lashmore, J.Proc. ASTM 62 Sym. Dec. 1981.
3. D.J.Shen, Y.L.Wang, Z.Wang, J.W.Zhang, M.Zhang, and X.Y.Zhang, Trans. Met. Heat Treat., 1993, 14 (3), 58-60.
4. M.H.Satia, M.Jeandin, D.B.Lewis, and E.S.Puchi, Surf. Eng., 1997, 13, 335-338.
5. Y.Wu et.al., J.Nonferrous Met., Sept.,1998, 8(3), 415-419.
6. G.Shen, L.Ji and R.Yu, Rare Met. Mater. Eng., Apr.1998, 27(2), 107-111.
7. S.Li , Z.Li, H.Situ and X.Y.Ye, Heat Treat. Met.(China), Jan.1997, 1, 39-42.
8. E.D.Dovreva and Ch.Petrov, Metalloberflache, Aug.1998, 52(8), 637-639.
9. Y.Yin, X.Wang, T.Xie and Y.Zhu, Mater. Prot., July 1996, 29(7), 27-28.
10. J.N.Balaraju and S.K.Seshadari, Trans. Institute Met. Finish., Mar.1979, 72(2), 84-86
11. C.Zhang, Trans. Chin. Soc. Intern. Combust. Engines, 1998, 16(3), 365-372.
12. L.Xu, et al., Mater. Proy. (China), Nov (1997), 30(11), 9-12.
13. Y.Li, Plat. Surf. Finish, Nov.(1997), 84(1), 77-81
14. A.Brenner, D.E.Couch and E.K.Williams, J.Res. Natl. Bur. Standard, 44 (1950), 109-122.
15. Raj Narayan and M.N.Mungole, Intl. Conf. on "Progress in Metallurgical Research : Fundamental and Applied Aspects," Feb.11-15, 1985, IIT Kanpur, 514-521.
16. Raj Narayan and M.N.Mungole, Surface Technology, 24(1985) 233-239.
17. Guglielmi.N., J.Electochem. Soc. 1972, 119(8), 1009-12
18. Raj Narayan and S.Chattopadhyay, Surface Technology, 16(1982), 227-234

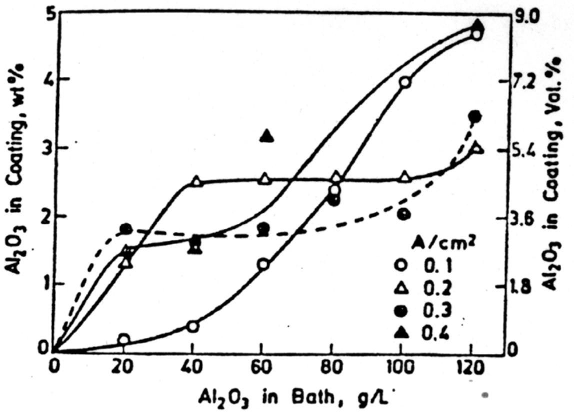

Fig 1 EFFECT OF Al_2O_3 IN THE BATH ON Al_2O_3 CONTENT IN THE COATING

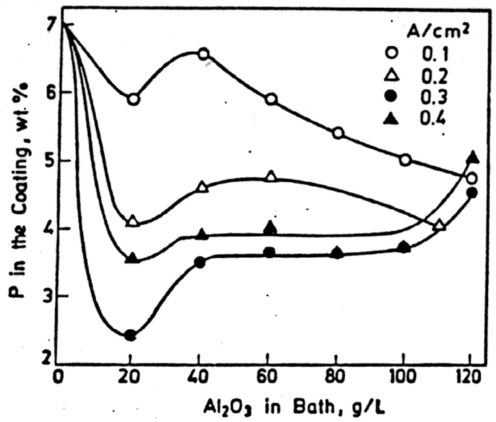

Fig 2 EFFECT OF Al_2O_3 IN THE BATH ON P CONTENT IN THE COATING

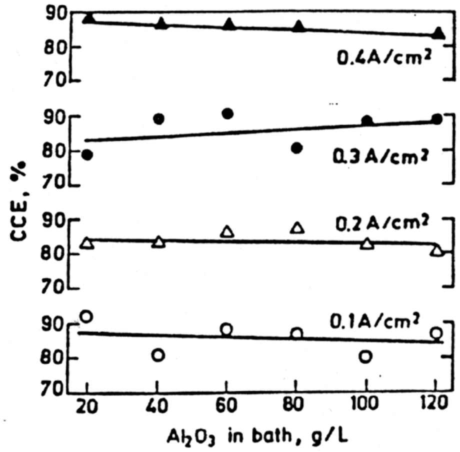

Fig 3 EFFECT OF Al_2O_3 IN THE BATH ON CATHODE CURRENT EFFICIENCY

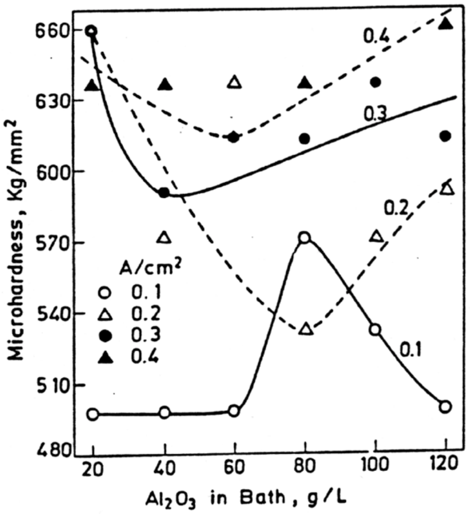

Fig 4 EFFECT OF Al_2O_3 IN THE BATH ON MICRO-HARDNESS OF AS PLATED COATINGS

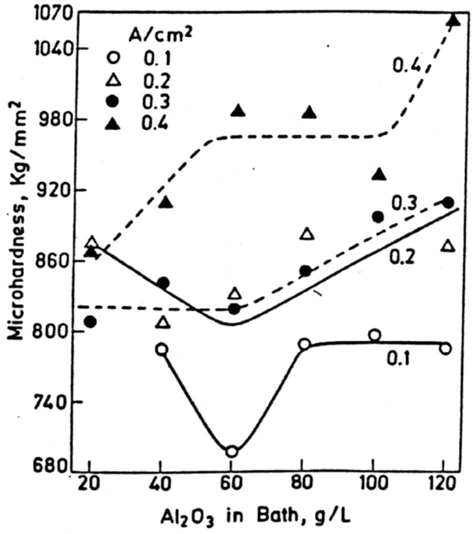

Fig 5 EFFECT OF Al_2O_3 IN THE BATH ON MICRO-HARDNESS OF COATINGS VACUUM ANNEALED FOR 1 Hr. AT 200°C

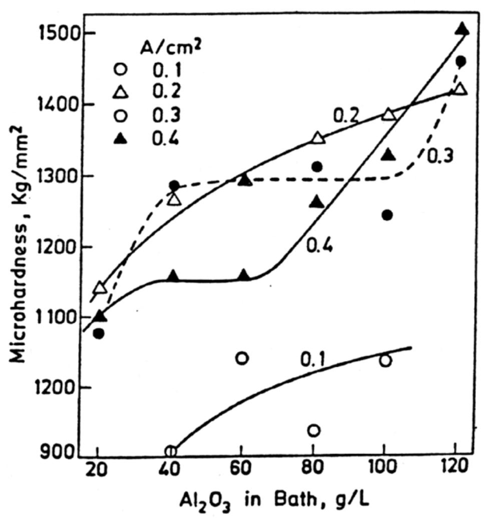

Fig 6 EFFECT OF Al_2O_3 IN THE BATH ON MICRO-HARDNESS OF COATINGS VACUUM ANNEALED FOR 1 Hr. AT 400°C

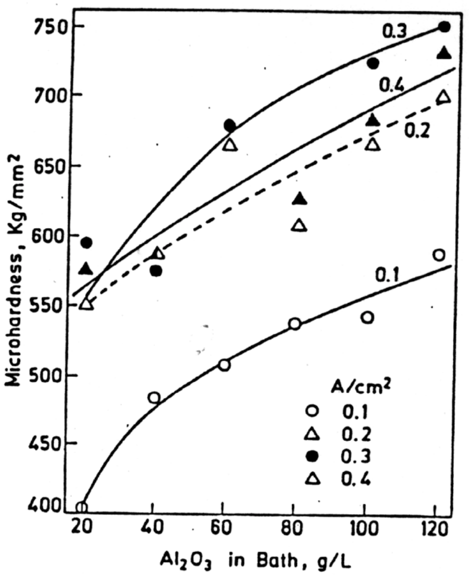

Fig 7 EFFECT OF Al_2O_3 IN THE BATH ON MICROHARDNESS OF COATINGS VACUUM ANNEALED FOR 1 Hr. AT 600°C

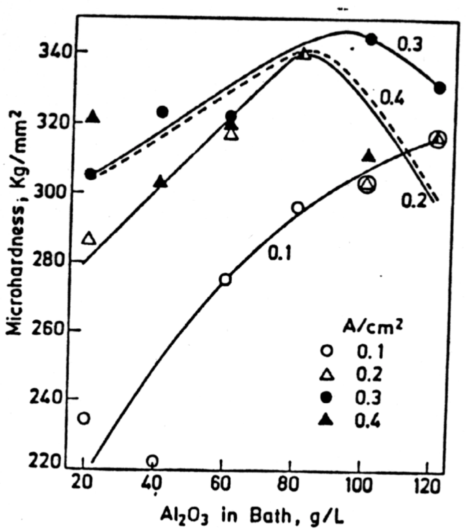

Fig 8 EFFECT OF Al_2O_3 IN THE BATH ON MICROHARDNESS OF COATINGS VACUUM ANNEALED FOR 1 Hr. AT 800°C

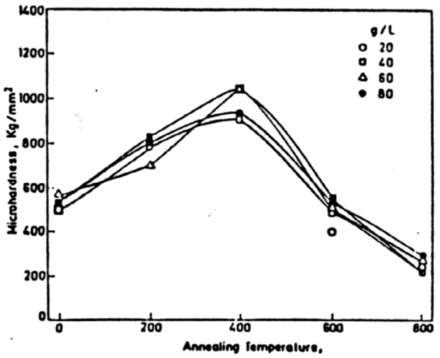

Fig 9 EFFECT OF ANNEALING TEMPERATURE ON MICROHARDNESS OF COATINGS DEPOSITED AT DIFFERENT BATH LOADS AT 0.1 A/cm^2

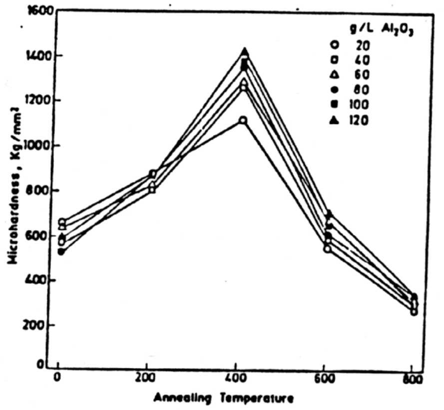

Fig 10 EFFECT OF ANNEALING TEMPERATURE ON MICROHARDNESS OF COATINGS DEPOSITED AT DIFFERENT BATH LOADS AT 0.2 A/cm^2

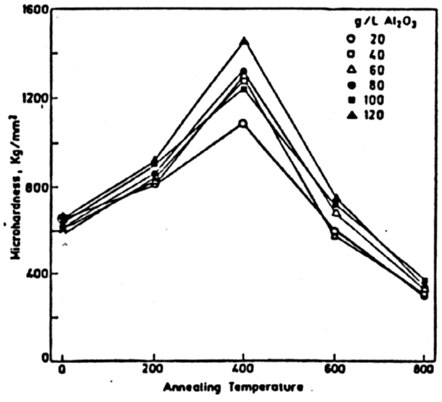

Fig 11 EFFECT OF ANNEALING TEMPERATURE ON MICROHARDNESS OF COATINGS DEPOSITED AT DIFFERENT BATH LOADS AT 0.3 A/cm^2

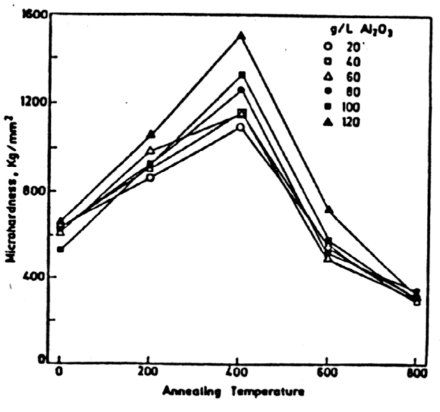

Fig 12 EFFECT OF ANNEALING TEMPERATURE ON MICROHARDNESS OF COATINGS DEPOSITED AT DIFFERENT BATH LOADS AT 0.4 A/cm^2