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STUDIES OF ELECTROLESS NICKEL-MOLYBDENUM-PHOSPHORUS DEPOSITION

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Electroless Ni-Mo-P alloys deposition has been obtained from a bath based on nickel sulphate, sodium hypophosphite, sodium gluconate, sodium molybdate and lactic acid. It was found that the addition of sodium molybdate decreases the hardness, wear resistance and increases the corrosion resistance of the deposits.

Keywords: Electroless deposition, Ni-Mo-P, Alloy deposition.

INTRODUCTION

In general, until 1963, electrolessdeposition was limited to binary alloys [1]. It is well known that electroless binary Ni-P alloy is a relatively new protective coating, which improves the mechanical properties, such as hardness, wear and corrosion resistance to a wide range of engineering components [2]. The articles and patents describing the electroless poly alloys have been concerned primarily with the operating parameters affecting their deposition [3-6]. The intention of this paper is to discuss the effects of molybdenum incorporation in the electroless Ni-P alloys deposits.

ENP coatings are widely used on account of their excellent functional properties. It has been reasoned out that this excellent behaviour is due to the presence of phosphorus. Earlier studies reveal that incorporation of molybdate into the deposit alters the functional properties. The effect of sodium molybdate on a nickel alloy electroless deposition process and the alloy composition has been investigated recently [9]. Controlling the molybdate concentration to give a MoO_4^{2-}, Ni^{2+} ratio in the range 0.034-0.045 produced an alloy (Ni-Mo-P) with improved corrosion resistance. Structure and corrosion behaviour of electroless Ni-Mo-P deposits with 20 to 25 micron thickness were studied by controlling concentration of sodium molybdate which varies from 0 to 0.01 *M*. Both amorphous and crystalline structures were obtained by changing concentration of sodium molybdate. Maximum molybdate content of 19.4 wt% was obtained at 0.01 *M* concentration. Deposits of higher P and lower Mo content showed less weight loss after immersion in acidic neutral and alkaline solutions during corrosion tests. This behaviour is believed to be correlated with change from crystalline to amorphous structure.

EXPERIMENTAL

Various complexing agents reported in the literature such as sodium citrate, EDTA, tartarate, gluconate and lactate were tried for getting electroless Ni-Mo-P. Among them sodium gluconate and lactic acid were found to be very effective complexing agents and gave bright and adherent deposits. The electroless bath had the following composition:

Nickel sulphate	29 gl^{-1}
Sodium hypophosphite	21 gl^{-1}
Sodium gluconate	50 gl^{-1}
Lactic acid	30 ml l^{-1}
Sodium molybdate	0-2 gl^{-1}
*p*H	8.5
Temperature	353-355 K

Mild agitation was given to the bath periodically. Stainless steel panels of size 5 x 3 cm and brass 10 x 10 cm were used for the analysis of nickel, molybdenum and phosphorus content in the deposit and rate of deposition, hardness and wear resistance respectively. Both the panels were sensitized and activated and then electrolessly plated for a period of 3 hrs. The deposits had a thickness of about 36 micron.

The deposits from stainless steel panels were removed and dissolved in 40% nitric acid for analysis. Nickel content in the alloy was determined by EDTA complexometric method and phosphorus by coulorimetric method.

The electroless deposits were heat treated in vacuum at 673 K for one hour and the hardness was compared with panels in the plated condition. The hardness was calculated on Vicker's scale.

Wear resistance of the deposit was measured (with heat treated and as plated condition) using Taber Abraser. The measurement was carried out for 1000 cycles with a load of 1000 g. The experiment was repeated for the second 1000 cycles and the average value was taken. The value was indication of wear resistance of the coating.

Abrasion resistance = Weight loss (in mg) per 1000 cycles

Polarisation measurements were carried out galvanostatically by exposing one square centimeter of the plated specimens using constant current regulator. Platinum was used as an auxiliary electrode and saturated calomel electrode was used as reference electrode with a sweep rate of 1 mV/ sec. The electrolyte used in the study was 3% sodium chloride. Graph was drawn with potential against current density using Tafel extrapolation method. Corrosion current and corrosion potentials were determined.

TABLE I: Effect of sodium molybdate on the percentage of nickel, phosphorus and molybdenum in the deposit

Sodium molybdate (gl^{-1})	Percentage of nickel	Percentage of phosphorus	Percentage of molybdenum
0.00	89.62	10.38	00.00
0.36	82.52	3.52	13.96
1.00	78.02	2.51	19.47
2.00	78.03	2.48	19.49

RESULTS AND DISCUSSION

The analysis of the electroless alloys foils revealed the percentage of nickel to be 78.01% and phosphorus 2.48% and the rest being molybdenum. In the case of 19% molybdenum content, the hardness of the plated Ni-Mo-P deposit was found to be 640 VHN with an indentation load of 50 g. Heat treatment in vacuum at 673 K for one hour decreased the hardness to 575 VHN. The decrease in hardness can be attributed to a structural change. When the temperature is too low, the critical dispersion of the Ni_3P phase is never achieved. On the other hand, when the temperature is too high, the precipitate of the Ni-P phase and crystalline Ni grains are too coarse, and the initial increase in hardness is wiped out [7]. In addition, it can also be seen from Table II that the Ni-P deposit, possesses the highest hardness level of the coatings. This may be due to the fact that the alloy has the larger amount of Ni_3P, which will make the film hardened [8]. Wear resistance of the as plated alloys was found to decrease after heat treatment at 673 K. This may be due to the softness of the deposits because molybdenum is a soft metal. As the concentration of the molybdenum increases, its incorporation into the deposit also increases. Hence the softness increases thereby decreasing the wear resistance of the coating. Table III shows the wear resistance data of the deposits. The corrosion resistance of the as plated alloy deposits are found to increase after heat treatment at 673 K. It is found from Table IV that the increase in corrosion resistance may be due to the lower porosity of the alloy deposits. As the concentration of molybdenum increases, the porosity is reduced and hence the corrosion resistance increases.

TABLE II: Micro hardness of Ni-Mo-P alloy plating at a load of 50 gms

Sodium molybdate (gl^{-1})	Hardness (V H N)	
	As plated	After heat treatment (673 K)
0.00	675	890
0.36	660	597
1.00	640	575
2.00	630	550

TABLE III: Wear resistance of Ni-Mo-P alloy plating

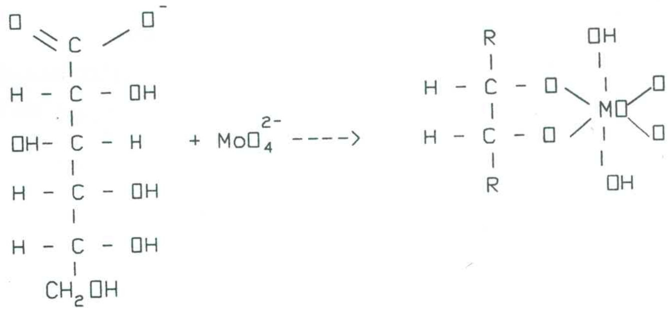
Sodium molybdate (gl^{-1})	As plated	After heat treatment (673 K)
0.00	14.8	13.9
0.36	15.1	20.4
1.00	15.7	21.6
2.00	15.8	21.8

TABLE IV: Corrosion measurements in 3% Nacl w.r.t SCE

Sodium molybdate (gl^{-1})	As plated		After heat treatment 673 K	
	E_{corr} ($mV.cm^{-2}$)	I_{corr} ($mV.cm^{-2}$)	E_{corr} ($mV.cm^{-2}$)	I_{corr} ($mV.cm^{-2}$)
0.00	-359	5.300×10^{-6}	-263	4.33×10^{-6}
0.36	-330	4.830×10^{-6}	-250	3.23×10^{-6}
2.00	-301	2.253×10^{-6}	-246	1.43×10^{-6}

Mechanism of electroless nickel deposition

The addition of sodium molybdate to both acid and alkaline bath gluconate/hypophosphite forms a complex (See scheme 1).



Scheme 1

In alkaline *p*H ranges the rate of deposition is higher and the stability of bath is also found to be good. During the course of the reduction, four completing reactions such as nickel ion reduction, hydrogen ion reduction, phosphorus reduction and molybdenum reduction are to take place.

$$H_2PO_2^- + H_2O \longrightarrow H_2PO_3^- + 2H^+ + 2e^- \quad (1)$$

$$Ni^{2+} + 2e^- \longrightarrow Ni \quad (2)$$

$$2H^+ + 2e^- \longrightarrow H_2 \quad (3)$$

$$H_2PO_2^- + e^- \longrightarrow 2OH^- + P \quad (4)$$

$$Mo^{6+} + 6e^- \longrightarrow Mo \quad (5)$$

This molybdenum is co-deposited with Ni - P system.

CONCLUSION

A suitable electroless Ni-Mo-P alloy bath has been standardised and the bath composition is:

Nickel sulphate	29 gl^{-1}
Sodium hypophosphite	21 gl^{-1}
Sodium gluconate	50 gl^{-1}
Lactic acid	30 $ml.l^{-1}$
Sodium molybdate	0-2 gl^{-1}
Temperature	353-385 K
*p*H	8.5

Increase in concentration of molybdenum in the deposit decreases the hardness and wear resistance and increases the corrosion resistance as in plated condition and after heat treatment at 673 K.

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