STUDIES ON ELECTROLESS NICKEL - PHOSPHOROUS MOLYBDENUM SULPHIDE COMPOSITE COATINGS

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The deposition of Ni-P-MoS_2 composite coatings gives formidable problems due to the fact that MoS_2 particles are weakly cataphoretic and strongly hydrophobic and has the tendency to agglomerate. It was found from the study that MoS_2 incorporation in electroless nickel-phosphorous system reduced the hardness both in the plated and heat treated conditions. An optimum concentration of 10g/l of MoS_2 is recommended for getting good lubrication properties. SEM studies indicated that under heat-treated condition one could see crowding of MoS_2 particles on the surface, which accounts for the lubricity of the coating.

INTRODUCTION

Electroless nickel composite materials are gaining importance in recent years in engineering industry involving high technological applications. Examples can be cited in the areas of applications like aero engines, modern gas turbines and the automobile industry. It is well known that powdered oxides, carbides, nitrides and silicides of Al, Ba, Cr, Mo, Si, Ca, Ta, V, Ni etc can be co-deposited with electroless nickel to improve the hardness, wear and corrosion resistance as well as lubrication properties. For their co-deposition the particles of size in the range of 1 to 12 microns must be present as the dispersed phase in the deposition bath. In the case of electroless nickel composites the matrix is not pure nickel, but it is either Ni-P or Ni-B depending upon the type of reducing agents used. In the case of hydrazine as the reducing agent, pure nickel is obtained which is highly stressed. S. Karthikeyan (1999) presented in a recent review article literature details of some of the nickel composites. Development of Ni-P-MoS_2 composite coatings is fairly difficult for the reasons that MoS_2 particles are weakly cataphoretic and strongly hydrophobic and have easier tendency to agglomerate. This affects the bath stability. Use of surfactants help to solve these problems. Grosjean etal.(1996) have reported the deposits to be rough and of higher hardness than nickel. Ghouse et al.(1980) have compared Ni-graphite and Ni-MoS_2 composites and showed the coefficient of friction to be less with the MoS_2 composites. These authors have studied the effect of various parameters such as temperature, pH and plating time on the rate of deposition of MoS_2 in electroless nickel - phosphorous system. They also studied the effect of MoS_2 on the hardness, corrosion resistance, impedance measurements and wear resistance of the coating both in the as plated and heat treated conditions. SEM and XRD studies were carried out to characterise the deposits.

EXPERIMENTAL

The bath used for the development of electroless composites had the following compositions:

Nickel sulphate 25 g/L

Sodium hypophosphite 20g/L

Sodium gluconate 52g/L

Lactic acid 10ml/L

Lead nitrate 0.5ppm

The MoS_2 composite particles used in the present study were made in the form of slurry through mixing with bath electrolyte and kept in dispersion in the bath through mechanical agitation at 240rpm. The temperature of the bath was maintained through a heater and relay system. The pH of the solution was frequently monitored by using pH meter and the pH was controlled by suitable additions of sulphuric acid or ammonia. Nickel sulphate and sodium hypophosphite in the bath were replenished depending upon the residual nickel content in the solution. The bath container was cleaned periodically with concentrated nitric acid. The bath was periodically filtered through G-4 crucible to avoid contamination with any suspended impurities. Copper panels of size 10 cm x 10 cm were used. The panels were subjected to the pretreatment processes of degreasing, rinsing, pickling, rinsing, activating, drying and weighing. Then the panels were subjected to EN composite plating at different temperatures (65°C, 70°C, 80°C, 90°C) for 6 hours at a pH value of 5.2. Mechanical agitation at 240 rpm was provided to keep the suspended composite particles in dispersion in the bath. Before plating, one side of the panels were masked by using lacquer while the other side was free for plating. After 6 hours the panels were taken out, rinsed, dried and again weighed. The difference in weight indicate the weight of nickel/composite deposited. From the weight, area and density of the deposits, the thickness was calculated.

The influence of pH on the plating rate was studied by varying the pH of the medium to different values in the range 4 to 7. The optimum pH for the superior quality deposits was found to be 5.2. At pH value of 5.2, the plating duration was varied from 1 to 6 hours with step of 1 hour intervals. This is done to understand the inhibitive or catalytic role played by the deposits on further plating. The concentration of the composite particles on the deposit was varied by loading the bath with 0 to 25 g/l of the particular composite. The composites developed were tested for their microhardness and Taber abrasion resistance in the as-plated and heat-treated conditions at 400°C for one-hour duration. The electrochemical polarisation measurement and impedance studies were made with the electroless nickel composite electrodes of $1cm^2$ area using 3.5% NaCl electrolyte.

The phosphorous estimation is based on precipitating phosphorous completely as ammonium phosphomolybdate, dissolving the precipitate in standard NaOH solution and estimating the excess NaOH through back titration procedure. The nickel is analysed through EDTA complexometric titration method. In the case of the composites, the amount of composite particles in the deposit is simply obtained as the differences between the total weight and sum of the weights of phosphorous and nickel. XRD and SEM studies were made for the electroless nickel composites both in the as-plated and heat-treated conditions.

RESULTS AND DISCUSSIONS

Influence Of Temperature, pH And Deposition Time

The effect of various parameters such as temperature, pH and plating time on rate of deposition are given in Tables I, II and III. The rate of deposition increases with increase in temperature due to increased mobility of the ions and composite particles. pH also increased the rate of deposition. An optimum pH of 5.2 is recommended considering the bath stability. It was observed that as the deposition time increases the thickness of the coating also increases due to the auto-catalytic nature of the process.

Table - I Effect of temperature on rate of deposition obtained in the presence of 10g/l of MoS_2 particles

Sr. No.	Temperature (°C)	Rate of deposit (μm/hr)
1.	60	5.3
2.	70	5.8
3.	75	6.5
4.	80	9.3
5.	85	11.2
6.	90	12.0
7.	95	13.5

Table - II Effect of pH on rate of deposition in the presence of 10g/l of MoS_2 particles

Sr. No.	pH	Rate of deposition (μm/hr)
1.	4.0	5.5
2.	4.5	6.4
3.	5.0	9.6
4.	5.2	10.5
5.	6.0	11.3
6.	6.5	13.8

Table-III Effect of deposition time on rate of deposition in the presence of 10g/l of MoS_2 particles

Sr. No.	Deposition time (min.)	Rate of deposition (μm/hr)
1.	10	9.4
2.	15	10.8
3.	20	11.2
4.	25	11.6
5.	30	12.8
6.	45	13.3
7.	60	12.4
8.	90	11.0
9.	120	10.2

Studies on Hardness : Table IV gives the micro hardness values for the electrolessly deposited Ni-P-MoS_2 composite coatings both in the as plated as well as heat treated conditions. For any composition of the deposits under heat treated condition the coatings are found to be harder than in the as plated condition. But the incorporation of MoS_2 particles in the Ni-P matrix in both cases is found to reduce its hardness.

Table IV - Effect of concentration of MoS_2 particles in the bath on the hardness of the coating

Sr. No.	Concentration of MoS_2 in the bath (g/l)	Vicker's hardness (load 50g)	
		As plated	After heat treatment at 400°C
1.	0	495	613
2.	2	325	527
3.	5	302	508
4.	10	286	490
5.	15	270	472
6.	25	266	454

It is also observed from the table that the hardness is decreased as the MoS_2 content in the bath is increased, as would be expected due to the incorporation of more of the soft particles in the deposit. Similar observation has been made by Izzard (1987) in the case of graphite composites. After the heat treatment at 400°C, the MoS_2 particles may get sintered, leaving larger MoS_2 films on the surface of the deposit accounting for dry lubrication - a speciality of this composite. As the heat treatment process emanates more MoS_2 particles on to the surface from the bulk of the deposit, it may become the cause for the lowering of hardness. Wear resistance of the coatings is very much improved in the presence of MoS_2.

Studies On Wear Resistance : Table V gives

Table V - Effect of concentration of MoS_2 particles on the abrasion resistance of the coatings (Cs 10 wheel and 1 kg weight)

Taber wear index (in g)		
MoS_2	As plated	After heat treatment
0	0.075	0.069
2	0.063	0.060
5	0.047	0.029
10	0.034	0.028
15	0.032	0.021
25	0.022	0.018

the value of wear resistance taken by Taber abraser at a load of 1000g for about 2000 cycles on the as plated as well as heat treated surfaces. It is seen from the table that the wear resistance is more for the coatings containing MoS_2 particles than with Ni-P alloy. It is also noted that as the concentration of MoS_2 in the bath increases its content in the deposit also increases at the cost of nickel and phosphorous. The increase in MoS_2 content, increases the softness of the coatings and there by increases the wear resistance. Sheng (1992) also reported a good reciprocal correlation between the hardness and wear resistance values.

Potentiodynamic Polarisation And Impedance Studies : Ni-P-MoS_2 composites are seen to be more corrosion resistant than Ni-P alloy in sodium chloride environment. The potentiodynamic polarisation and impedance measurements of the composites are given in Table VI, VII. The AC impedance analysis also confirms this trend. The corrosion resistance of this coatings are due to the uniform dispersion of particles which ensure pore-free deposit and also the tendency to form passive film on the surface.

Influence Of MoS_2 Concentration : It can be seen from the Table VIII that there is an increase in concentration of MoS_2 particles in the matrix as the particulate concentration in the bath is increased. Increasing concentration of MoS_2 particles cause a decrease in the percentage of nickel and phosphorous content in the deposits. An optimum concentration of 10g/l of MoS_2 particles is recommended. Beyond this concentration collision among

Table VI - Evaluation of corrosion resistance in 3.5% NaCl solution by potentiodynamic polarisation

Nature of deposit	E_{corr} (mV Vs SCE)	Tafel slopes		I_{corr} ($\mu A.cm^{-2}$)
		ba V dec^{-1}	be V dec^{-1}	
Ni- P	-350	0.168	0.156	505
Ni-P-MoS_2 (10g/l)	-343	0.198	0.165	21

Table VII - Evaluation of corrosion resistance of the coatings by impedance measurements in 3.5% NaCl solution

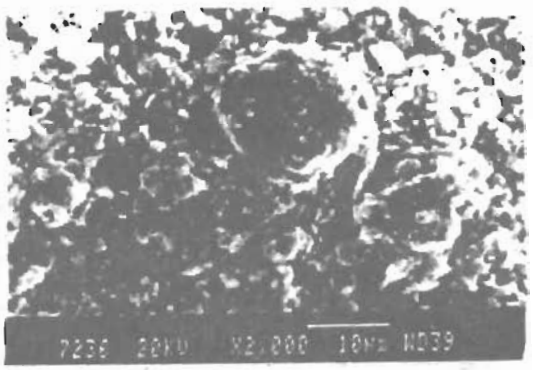
Nature of deposit	R_t ohm cm^2.	C_{dl} $\mu A/cm^2$
Ni - P	939	154
Ni - P -MoS_2 (10g/l)	3780	38

Table VIII - Effect of concentration of MoS_2 particles in the bath on the percentage of Ni-P and MoS_2 in the coating

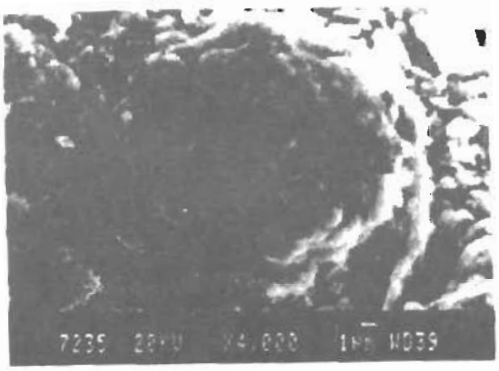
Concentration of MoS_2 in the bath (g/l)	Composition of the deposit		
	Nickel (%)	Phosphorous(%)	MoS_2(%)
0	89.8	10.2	-
2	88.61	9.42	1.97
5	87.30	10.45	2.25
10	83.94	7.41	8.65
15	83.48	7.30	9.22
25	83.63	6.49	9.88

moving particles inhibit the plating process.

XRD And SEM Studies : The XRD studies of Ni-P-MoS_2 revealed that MoS_2 particles are included in the matrix which is confirmed from the ASTM data (2 ∅=14.16, d=6.18) as against the experimental value (2 ∅= 14.16, d=6.249) SEM analysis indicated that the crowding of MoS_2 particles on the surface leading to MoS_2 film formation which accounts for dry lubrication property of the composites (Fig. 1).



a) 2000 X



b) 5000 X

ig. 1 - SEM photographs of Ni-P-MoS_2 composite oating

CONCLUSION

The following bath composition and operating conditions are recommended for obtaining Ni-P-MoS_2 composite coatings.

Nickel sulphate25g/L

Sodium hypophosphite 20 g/L

Sodium gluconate 52 g/L

Lactic acid 10ml/L

Lead nitrate 0.5ppm

pH 5.2 ± 0.2

Temperature 82 ± 2°C

Optimum concentration of 10g/l of MoS_2 is recommended for obtaining good lubrication properties. At this concentration of MoS_2 the deposit is found to contain 7.4% phosphorous and 8.65% MoS_2. It was found from the study that MoS_2 incorporation increases the corrosion resistance of the electroless nickel phosphorous system and reduces the hardness both in the as plated and heat treated condition.

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