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Studies and Characterization of Electroless Ni-Mo-P Alloy Coating

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ABSTRACT

An endeavor has been made to deposit ternary Ni–Mo–P coatings autocatalytically utilizing nickel sulphate and sodium molybdate as nickel and molybdenum sources, separately, and sodium hypophosphite as a lessening operator. These coatings were deposited utilizing a soluble citrate based shower and were contrasted and plain Ni–P coatings. The two coatings were described for their structure, morphology and hardness. Results obtained from EDX analysis showed that binary Ni–P alloy contains 12.74 wt.% of phosphorus. Incorporation of molybdate had reduced the phosphorus content to about 1.09 wt.% in ternary Ni–Mo–P deposits. Apart from phosphorus and nickel contents, a trace of sulphur were noticed in ternary Ni–Mo–P deposit. Structural examination carried out by XRD studies revealed the presence of a broad peak with a calculated grain size of 2.88 nm for binary Ni-P alloy, where as a sharp peak with a grain size of 27.4 nm is obtained for ternary Ni–Mo–P alloy. Microhardness measurements were made for as-deposited and heat treated coatings. Hardness is increase till 400°C and then decreases as like ternary Ni-Mo-P coatings.

I. Introduction

Materials utilized for designing application are picked by their novel properties. In any case, a large portion of the materials don't have all the necessary properties like hardness, wear, scraped area and consumption obstruction and so forth. Thus, to bestow such explicit properties surface adjustment is completed for the base materials either by altering the surface itself or by including another layer, for example, a covering. Albeit various sorts of covering strategies are accessible like physical vapor affidavit, concoction vapor statement, electro or electroless plating, electroforming and so on., electroless plating has increased extensive consideration because of its special properties like uniform thickness, promptly versatile for three dimensional inclusion and conceivable to plate both conductive and protecting surfaces.

Nickel sulphate baths are widely used for electrodepositionof nickel and Ni–P alloys in acidic baths. Ni–P alloysobtained by electrolytic deposition have been highlighted due toits good physical and chemical properties, such as highcorrosion resistance, good magnetic and thermal properties,etc. [1–3]. Ni–P alloys can also be prepared by autocatalyticprocess and are widely used for the production of uniform, lessporous, adherent deposits for many industrial applications.Generally, these binary alloys are prepared by autocatalyticmethod using nickel sulphamate or nickel chloride as a nickelsource and hypophosphite as a reducing agent along withcomplexing and buffering agents.

ENP coatings are broadly utilized by virtue of their great useful properties. It has been contemplated out that this magnificent conduct is because of the nearness of phosphorus. Prior investigations uncover that joining of molybdate into the store modifies the useful properties. The impact of sodium molybdate on a nickel compound electroless testimony process and the combination structure has been examined as of late.

By scanning through the available literature not much information is available on the studies carried out on introduce of sodium molybdate in the electroless nickel bath and the characterization of resulting deposits. Hence, the present investigation focuses on the preparation of both binary Ni-P and ternary Ni-Mo-P alloys for comparison. The obtained deposits are characterized for their structure, composition, morphology and hardness.

II. EXPERIMENTAL

The composition of the basic bath used for the preparationof ternary Ni–P and ternary Ni–Mo–P alloys is given in Table1. Nickel sulphate concentrate of 22-30 g/L was used as anickel source in the electroless bath for the deposition ofbinary and ternary alloys. Mild steel specimens (2.5 cm×2.5 cm×0.08cm) were used as substrate for binary and ternary alloydeposition. The composition of the mild steel substrate isgiven below:

C(wt. %)	Mn(wt. %)	Si(wt. %)	Fe(wt. %)
0.13	0.18	0.1	Balance

Specimens were degreased in acetone, cathodically cleanedin 10% sodium hydroxide solution for 5 min at 15 A/dm2,rinsed in running water and deionized water. The degreasedsamples were deoxidized in 50 vol.%sulphuric acid solutionfor 30s, rinsed in running water and deionized water andplaced in the electroless solution for plating. The electroless solution was taken in a 250-ml glass beaker which was keptin a constant temperature water bath (Siskin Julabo VPCmodel) to heat the solution to 90 °C. Stirring of theelectroless nickel alloy bath was not employed. Both binaryand ternary deposits were plated for 2 h with a deposition rateof approx.12μm/h. After plating, the samples were againrinsed in running water and deionized water, dried andpreserved for characterization.X-ray diffraction (XRD) measurements of the deposits weremade in as plated condition with a Rigaku

Table 1: Composition and operating conditions of the plating baths

Chemical composition	Concentration (g/L)	
	Ni-P	Ni-Mo-P
Nickel Sulphate	22-30	22-30
TriSodium Citrate	20-30	20-30
Ammonium Sulphate	25	25
Sodium Molybdate	-	1
Sodium Hypophosphite	15-25	15-25
Lactic acid	4-6 ml	4-6 ml
Operating Conditions		
pH	8 ± 0.2	11 ± 0.2
Temperature (° C)	80 ± 2	85 ± 2

Table 2: Composition of as-plated electroless nickel alloy coatings determined by EDX analysis

Type of coating	P (Wt.%)	Mo (Wt.%)	Ni (Wt.%)
Ni-P	12.74	---	87.26
Ni-Mo-P	1.09	16.25	82.66

D/max 2200 powderdiffractometer using Cu Kα radiation. Scanning electronmicroscope (SEM-Model Leo 440I) with EDX (EnergyDispersive X-ray analysis, Oxford) attachment was used todetermine the elemental composition of the deposits.

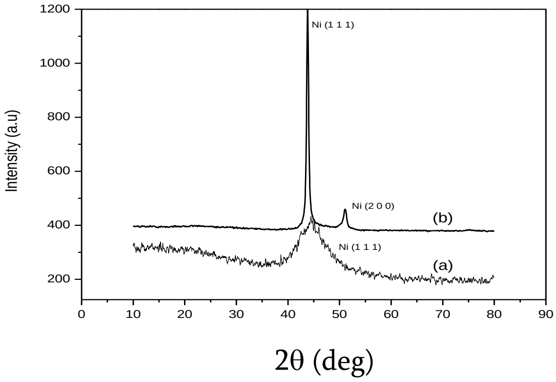

Fig 1. X-ray diffraction patterns of as-plated electroless(a) Ni-P, (b) Ni-Mo-P coatings

III. RESULTS AND DISCUSSION

As-deposited coatings of thickness 23±2 μm on mild steel samples are subjected to energy dispersive analysis of X-ray (EDAX) to find out the Mo and P elements co-deposited in EN matrix and are given in table 2. It is clear that binary Ni-P deposit contains 12.74 wt.% P. Small amount of Mo has been co-deposited due to the addition of 1 g/L of sodium molybdate in the alkaline EN bath without affecting the P content of 25 g/L. It can also be seen from the table 2 that the incorporation of sodium molybdate in the bath, P content decreased from 12.75 to 1.09 wt.%. From this it can be concluded that Mo incorporation has affected the composition of ternary Ni-Mo-P deposits. The decrease in P content withsodium salts of molybdate in EN bath could be due to the increase of metals to hypophosphite ion ratio in the EN bath.

The X-ray diffraction patterns of the as-plated Ni-P and Ni-Mo-P deposits are shown in fig 1. In both diffraction patterns, the reflections corresponding to the (111) plane of a face centered cubic (fcc) phase of nickel could be observed. From Fig 1(a) it can be observed that as-deposited binary Ni-P coating had only a single, broad peak at 44° with a calculated grain size (from Debye Scherrer formula) of 2.8 nm. Co-deposition of molybdate in Ni-P deposit has reduced the peak broadness and increased the peak sharpness fig 1(b). Apart from high intensity peak one more very low intensity peak at 51° is also noticed which can be ascribed to Ni (2 0 0). Grain size of ternary Ni-Mo-P alloy is 27 nm.

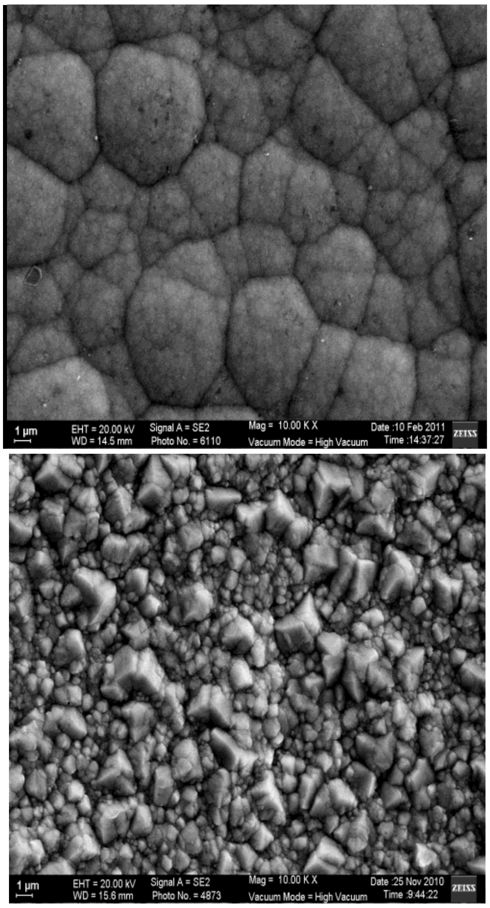

Figure 2. SEM micrographs of as-plated electroless nickel alloys at 1000X (a) Ni–P and (b) Ni–Mo–P.

Chemical resistance of electroless nickel coatings is strongly dependent on the P content of Ni-P deposits which affects the structure [10] whereas the surface morphology is influenced by the chemical constituents present in the electroless nickel bath

[11]. The effect of Mo co-deposition in electroless Ni-P matrix on the morphology of ternary Ni-Mo-P alloys is shown in fig 2. Plain Ni-P deposit exhibits a smooth morphology with fine nodules fig 2 (a).As shown in fig 2 (a) Ni-P deposits exhibited cauliflower type of morphology with smooth nodules. Pores are also visible in this deposit and appear as dark regions. However, these are very small pores and may not be penetrated to the substrate surface. Whereas Ni-Mo-P depositexhibits coarse type of morphology compared to binary Ni-P deposit as shown in fig 2 (b). Similar observations are also noticed for other ternary alloy deposit like Ni-W-P [13]. From the above it can be observed that by incorporation of Mo in Ni-P matrix has affected not only the morphology but also composition of the as-deposited ternary Ni-Mo-P deposits.

Table 3: Microhardness of electro less deposits in as-plated and heat treated at various temperatures for 1 hour.

Temperature (°C)	Ni-P (VHN50$_{gf}$)	Ni-Mo-P (VHN50$_{gf}$)	ΔH%
RT	536	664	23.88
200	621	737	18.67
250	715	814	13.84
300	813	902	10.94
350	914	994	8.75

Microhardness measurements made on the cross-sections of plain Ni-P and ternary Ni-Mo-P deposits in as-deposited and annealed at various temperature conditions for 1 hr. Table 3 shows the hardness values for Ni-P and Ni-Mo-P coatings at different heat treated temperatures. Binary Ni-P deposit exhibited microhardness value of 536 VHN in as-plated condition. The obtained hardness value is considerably high compared to that of bulk nickel (100-150 VHN) and electrodeposited nickel (250-350 VHN). Co-deposition of Mo showed an increase in hardness in all the cases. From the table it is evident that maximum hardness values are obtained at 350°C. The percentage increase in hardness due to Mo inclusion is also shown in Table 3. Both Mo and P contents influence the as-deposited hardness. It is well known that the co-deposited Mo is in solid solution form [10] and P is in supersaturated form in EN matrix. Since the Ni-Mo-P is having high Mo (16.25 Wt %) and low P (1.09 Wt %) contents and due to the heat treatment small amount of nickel phopshide could have formed.

From the table 3 it is evident that there is about 24% increase in hardness has been obtained for as plated Ni-Mo-P deposits compare to Ni-P deposits. Peak hardness of about 990 VHN has been obtained for the annealed Ni-Mo-P deposits at 350°C/1hr. In general both binary Ni-P and ternary Ni-W-P deposits exhibited the maximum hardness of 920 – 980 VHN after annealing at 400°C/1hr [10]. Whereas in the present investigation the peak hardness obtained at 350˚C could be due to the presence of low phosphorus in Ni-Mo-P deposits.

IV. CONCLUSIONS

Electroless Ni-Mo-P Ternary alloy coating has been successfully prepared. Ni-P deposits exhibited cauliflower type of morphology with smooth nodules. Whereas Ni-Mo-P deposits exhibited coarse morphology. From EDAX analysis, it is clear that Ni-P deposit contains 12.75 Wt.% P and 87.25 Wt.% Ni and the Ni-Mo-P deposit consists of 1.09 Wt. % P, 16.25 Wt. % Mo and 82.66 Wt. % Ni. Calculated grain sizes using XRD data indicated that higher grain sizes obtained for the ternary Ni-Mo-P deposits compared to binary Ni-P deposits. Microhardness measurements made on the cross-sections of plain Ni-P and ternary Ni-Mo-P deposits in as deposited and annealed at various temperatures for 1 hr indicated that at all heat treated conditions, Ni-Mo-P deposits showed better hardness than Ni-P coatings.

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