Studies on Autocatalytic Deposition of Ternary Ni-Mo-P Alloys Using Nickel Sulphate Bath

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Abstract – An attempt has been made to deposit ternary Ni–Mo–P coatings autocatalytically using nickel sulphate and sodium molybdate as nickel and molybdenum sources, respectively, and sodium hypophosphite as a reducing agent. These coatings were deposited using an alkaline citrate based bath and were compared with plain Ni–P coatings. Both deposits were characterized for their structure, morphology, surface roughness. 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 was 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. The AFM images of the Ni-P and Ni-Mo-P deposits shows that the Molybdenum increased the roughness value from 24 to 40 nm.

1. INTRODUCTION

Materials used for engineering application are chosen according to their unique properties. But most of the materials do not possess all the required properties like hardness, wear, abrasion and corrosion resistance etc. Hence, to impart such specific properties surface modification is carried out for the base materials either by modifying the surface itself or by adding another layer such as a coating. Although different types of coating methods are available like physical vapor deposition, chemical vapor deposition, electro or electroless plating, electroforming etc., electroless plating has gained considerable attention due to its unique properties like uniform thickness, readily adaptable for three dimensional coverage and possible to plate both conductive and insulating surfaces.

Nickel sulphate baths are widely used for electro deposition of nickel and Ni–P alloys in acidic baths. Ni–P alloys obtained by electrolytic deposition have been highlighted due to its good physical and chemical properties, such as high corrosion resistance, good magnetic and thermal properties, etc. [1–3]. Ni–P alloys can also be prepared by autocatalytic process and are widely used for the production of uniform, less porous, adherent deposits for many industrial applications. Generally, these binary alloys are prepared by autocatalytic method using nickel sulphamate or nickel chloride as a nickel source and hypophosphite as a reducing agent along with complexing and buffering agents.

ENP coatings are widely used on account of their excellent functional properties. It has been reasoned out that this excellent behavior 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.

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, phase transformation behavior.

2. PROPOSED MODELLING

The composition of the basic bath used for the preparation of ternary Ni–P and ternary Ni–Mo–P alloys is given in Table 1. Nickel sulphate concentrate of 22-30 g/L was used as a nickel source in the electroless bath for the deposition of binary and ternary alloys. Mild steel specimens (2.5 cm×2.5 cm×0.08 cm) were used as substrate for binary and ternary alloy deposition. The composition of the mild steel substrate is given below:

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

Specimens were degreased in acetone, cathodically cleaned in 10% sodium hydroxide solution for 5 min at 15 A/dm2, rinsed in running water and deionized water. The degreased samples were deoxidized in 50 vol.% sulphuric acid solution for 30s, rinsed in running water and deionized water and placed in the electroless solution for plating.

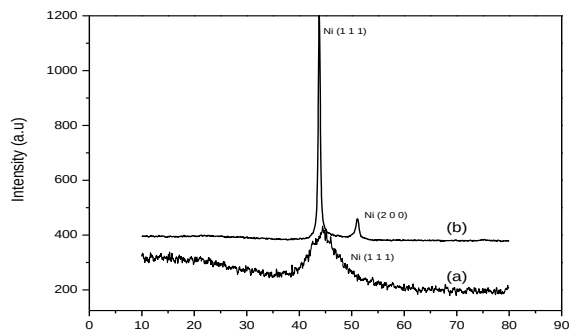
Table 1 Composition and operating conditions of the plating baths

Chemical composition	**Concentration (g/L)**	
	Ni-P	**Ni-Mo-P**
Nickel Sulphate	22-35	22-35
TriSodium Citrate	22-30	22-30
Ammonium Sulphate	28	28
Sodium Molybdate	-	1
Sodium Hypophosphite	18-25	15-25
Lactic acid	4-6 ml	4-6 ml
Operating Conditions		
pH	8 ± 0.2	11 ± 0.2
Temperature (º 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

The electroless solution was taken in a 250-ml glass beaker which was kept in a constant temperature water bath (Siskin Julabo VPC model) to heat the solution to 90 °C. Stirring of the electroless nickel alloy bath was not employed. Both binary and ternary deposits were plated for 2 h with a deposition rate of approx. 12 µm/h. After plating, the samples were again rinsed in running water and deionized water, dried and preserved for characterization. X-ray diffraction (XRD) measurements of the deposits were made in as plated condition with a Rigaku D/max 2200 powder diffractometer using Cu Kα radiation. Scanning electron microscope (SEM-Model Leo 440I) with EDX (Energy Dispersive X-ray analysis, Oxford) attachment was used to determine the elemental composition of the deposits. For AFM studies the specimens of 12 mm diameter and 5 mm thick were polished in the following sequence 400, 600, 800, 1000 and 1200 grit polishing sheets. Again these specimens were ground on sylvet cloth mounted on rotating disc using 1, 0.3, and 0.05 µm Alumina (Buhler make, USA) respectively as abrasive material. These specimens were ultrasonically cleaned in Acetone solution for 5 min and roughness was measured using atomic force microscope before plating. Morphology of the deposits was studied by depositing 15 mins duration on mild steel samples, which were metallographically polished to a roughness level of 10-12 nm. Deposit structure was examined by atomic force microscopy (AFM) (Model SSI, CSEM make). The maximum scan range for AFM in X, Y-directions was 20 µm × 20 µm and in the vertical direction was 2 µm. AFM images were obtained on an area of 10 µm × 10 µm.



2θ (deg)

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

3. RESULTS AND DISCUSSIONS

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 with sodium 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.

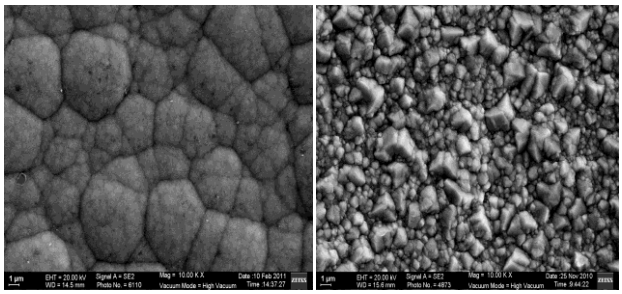


Fig.2. SEM micrographs of as-plated electroless nickel alloys at 1000X (a) Ni–P and (b) Ni–Mo–P.

Chemical resistance of electroless nickel coatings is strongly dependent on the P content of Ni-P deposits which affects the structure [10] where as 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 deposit exhibits 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.

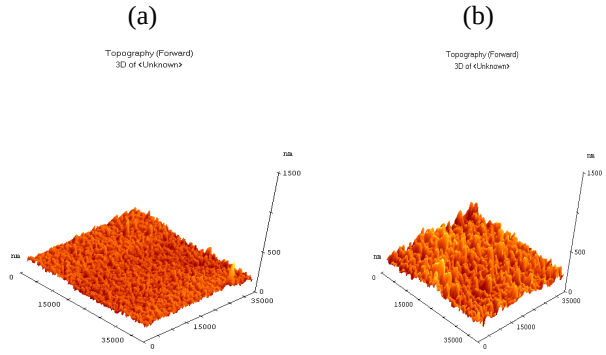


Fig 3: AFM morphologies of the as-plated electroless Nickel coating (a) Ni-P, (b) Ni-Mo-P

Fig 3 (a,b) shows the three dimensional AFM images for the as-deposited electroless Nickel and its alloy coatings deposited for duration of 15 minutes on mild steel coupons. These mild steel coupons had an initial roughness of 12 nm. By comparing the two images, it is clear that deposits have different surface roughness values due to the different growth pattern of the Ni-P and Ni-Mo-P coatings.The average roughness value obtained for Ni-P deposit is 24 nm. Roughness value has been increased to 40 nm due to the co-deposition of molybdate in Ni-P matrix.

4. CONCLUSION

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. The AFM images of the Ni-P and Ni-Mo-P deposits showed that the Molybdenum increased the roughness value from 24 to 40 nm.

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