International Research Journal of Engineering and Technology (IRJET) e-ISSN: 2395-0056
Volume: 08 Issue: 08 | Aug 2021 www.irjet.net p-ISSN: 2395-0072

Hardness and corrosion behavior of electroless quaternary Ni-Cr-Mo-P alloy coatings

Vinod Kumar G S[1], Srikantappa A S[2]

[1]*Assistant Professor, Department of Mechanical Engineering, New Horizon College of Engineering, Karnataka, India*
[2]*Principal, Cauvery Institute of Technology, Karnataka, India*

Abstract – *Electroless quaternary Ni-Cr-Mo-P alloy deposits were produced in an alkaline bath and characterised to determine parameters such as composition, structure, microhardness and corrosion behaviour in the current research. The effect of various anions from metallic sources on the structure and characteristics of quaternary deposits was investigated. FESEM and XRD were used to evaluate the composition, morphology, and structure of the deposits, respectively. Hardness and corrosion resistance of coatings were also tested. The surface of the as-plated deposit exhibits a coarse type morphology. X-ray diffraction pattern of as-prepared deposit contains a sharp crystalline nickel peaks. With an increase in the annealing temperature, the hardness improves and reaches the maximum value at 350°C. Further, it is found that Ni–Cr–Mo-P coatings have superior corrosion resistance than Ni–P deposits after the analysis of electrochemical measurement.*

Key Words: *Quaternary Ni-Cr-Mo-P, FESEM, XRD, Hardness, corrosion resistance*

1. INTRODUCTION

Mild steel alloy is a widely used metal due to its many features and benefits [1]. However, to further extend its applications, it is necessary to overcome some certain shortcomings such as poor corrosion resistance in seawater and marine atmosphere [2]. Electroless Ni–P alloy coatings provide considerable improvement of desirable qualities such as non-magnetic properties and excellent resistance properties [3–6]. To improve the surface characteristics of mild steel alloy, Ni–P coatings were deposited on the substrates by an electroless deposition process [7–10].
In recent years, more in-depth studies on electroless coatings have been carried out, especially in terms of corrosion resistance. Compared with binary Ni–P alloy coatings, ternary Ni–Mo–P alloy coatings provide more extensive usage and wider application range. However, electroless ternary Ni–Mo–P deposition process is still slow, easily led to low hardness and poor corrosion resistance, which makes the process unable to meet the practical application [11, 12]. As far as we known, few researchers have reported about the quaternary deposits by an electroless process until now. Therefore, electroless plating Ni–Mo–Cr–P coatings has considerable novelty and remarkably important research significance. In the present investigation, the quaternary Ni–Cr–Mo-P alloy coatings were deposited by introduction of Cr and Mo into electroless Ni–P deposits. Contemporaneously, Ni–P alloy coatings were also prepared for comparative analysis. Afterwards the effects of heat-treatment of Ni–Cr–Mo-P deposits on mild steel alloy were examined. Finally, the related mechanisms of the improvement of microhardness and corrosion resistance of the alloy coatings were also discussed.

2. EXPERIMENTAL DETAILS

In this study, square specimens of mild steel alloy (2.5cmX2.5cmX0.8cm) were used as substrates. The surface coatings, Ni–Cr–Mo-P alloy coatings, were deposited on the substrate with certain concentrations of the depositing bath and appropriate pH values by an electroless deposition process to improve the surface characteristics of mild steel alloy. For comparison, we also prepared Ni–P deposits. Prior to the electroless deposition process, the substrate samples were degreased in acetone and thoroughly cleaned with de-ionized water. The substrate is then cathodically cleaned in 10% sodium hydroxide solution for 3 min at 15 A/dm^2, rinsed in running water and again cleaned by de-ionised water. Then the substrate is dipped in 50% H2SO4 solution for 1min, rinsed in running water and again cleaned by de-ionized water, then placed into the electroless solution for plating.
In Ni-P bath (bath 1) uses nickel sulphate as nickel source, while sodium hypophosphite served as the reducing agent and source of phosphorus. In Ni-Cr-Mo-P bath (bath 2) same as Ni-P but sodium molybdate used as a source of molybdenum and Chromium chloride used as a source of chromium. Besides this the bath also contains suitable amounts of complexing agents and stabilizers. The bath 1 was operated at a pH range of 8±0.2 and at temperature of 80±2°C. The bath 2 was operated at a pH range of 8±0.2 and at temperature of 80±2°C. The composition of all the baths are given in the table 2.1. About 250ml of solution was taken in a beaker and placed in a chemical bath to maintain the temperature. Under optimized control of bath parameters and operating conditions, the bath was capable of depositing at a rate of 12µm/hr.

Table -2.1: The plating bath conditions for preparing Ni–P and Ni–Cr–Mo-P deposits

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

Experimental setup used for the preparation of Ni-P and Ni-Cr-Mo-P coating as shown in the figure 2.1. The plating solution is placed in the hot bath. Then the pretreated mild steel coupons fitted in the holder are placed in the bath such that coupons are held 45º to the vertical. This helps to achieve uniform electroless Ni-P coatings with a more uniform distribution.

Figure 2.1: Experimental setup used for the preparation of electroless Ni-P and Ni-Cr-Mo-P coatings.

Elemental compositions of the deposits were examined by means of scanning electron microscope with EDAX attachment. As-deposited coatings of Ni-Cr-Mo-P and plain Ni-P on mild steel coupons are subjected to EDAX to find out the Cr, Mo and P elements co deposited in EN matrix. To determine the structure of electroless Ni-Cr-Mo-P and plain Ni-P deposits in as-plated conditions, X-ray diffraction (XRD) measurement were made with a powder diffractometer using Cu-Kα radition. Vickers test is often easier to use than other hardness tests since the required calculations are independent of the size of the indenter, and the indenter can be used for all materials irrespective of hardness. The basic principle, as with all common measures of hardness, is to observe a material's ability to resist plastic deformation from a standard source. Electrochemical measurements were carried out by using an electrochemical work station, CH600D-series, U.S. Model with CH instrument beta software. The electrochemical cell used was a conventional three-electrode compartment having glass cell with a platinum counter electrode and a saturated calomel electrode (SCE) as reference. The working electrode was made up of Al 2024. All the values of potential were measured with reference to the saturated calomel electrode. Finely polished electroless plain Ni-P and Ni-Cr-Mo-P alloy specimens with 2.5cmX2.5cmX0.8cm surface area were exposed to corrosion medium of sulphuric acid (1M) separately at a laboratory temperature. The potentiodynamic current-potential curves were recorded by polarizing the specimen to -250 mV cathodically and +250 mV anodically with respect to open circuit potential (OCP) at a scan rate of 0.01 V/s.

3. RESULTS AND DISCUSSIONS

3.1 SEM analysis of electroless Ni–Cr–Mo-P deposits

Figure 3.1 shows SEM topographies of the surface of Ni-Cr–Mo-P coating under as-deposited condition prepared in this experiment. Surface morphology of the deposit is uniform, inseparably close and less porous. Additionally cracks are not observed on the surface of the coatings. The surface morphology of Cr and Mo coating is characterised by coarse microstructure. It is well known that a crack free deposited of Cr and Mo coating can be obtained by proper optimisation of the plating condition.

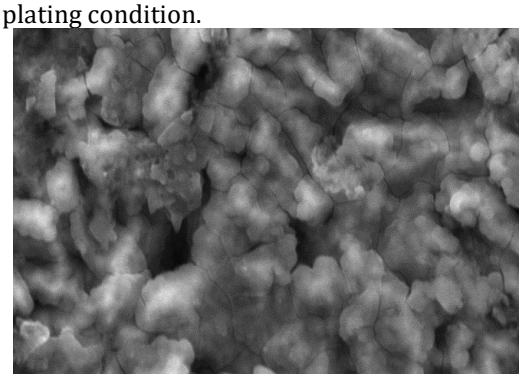

Figure 3.1: SEM micrographs of as-plated electroless Ni-Cr-Mo-P coating

In the present study using an alkaline citrate bath we could find that maximum reduction in P content was obtained due to the co-deposition of Cr and Mo in Ni-P matrix. Hence we believe that there might have been competitive reaction between Mo and P species or formation of a complex compound during autocatalytic plating and it could have inhibited the P species to co-deposit in the alloy matrix.

Table 3.1: Weight % of Ni-Cr-Mo-P coating

Element	Weight%	Atomic%
P K	2.04	3.75
Ni K	80.88	82.73
Mo L	8.89	5.29
Cr K	8.19	8.23
Totals	100.00	

3.2 XRD analysis of electroless Ni–Cr–Mo-P deposits

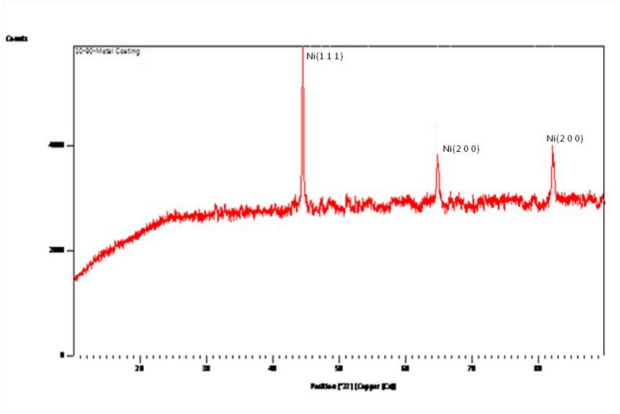

Figure 3.2: X-ray diffraction patterns of as-plated electroless Ni-Cr-Mo-P coatings

The X-ray diffraction patterns of the as-plated Ni-Cr-Mo-P deposits are shown in figure 3.2. In the diffraction patterns, the reflections corresponding to the (111) plane of a face centered cubic (fcc) phase of nickel could be observed. From figure it can be observed that co-deposition of molybdate and chromium in plain Ni-P deposit also reduced the peak broadness and increased the sharpness. Apart from high intensity peak two more low intensity peaks at 65° and 82° which can be ascribed to Ni (2 0 0). Grain size of quaternary Ni-Cr-Mo-P alloy is 41.30 nm (from Debye Scherrer formula).

3.3 Hardness of electroless Ni–Cr–Mo-P deposits

Microhardness measurements made on the cross-sections of plain quaternary Ni-Cr-Mo-P deposits in as-deposited and annealed at various temperature conditions for 1 hr. Table 3.2 shows the hardness values for Ni-Cr-Mo-P coatings at different heat treated temperatures.

Table 3.2: Vicker's microhardness test for Ni-Cr-Mo-P coatings

Microhardness - VHN50gf	
Temperature	Ni-Cr-Mo-P
30°	670
200°	739
250°	810
300°	905
350°	980

From the table it is evident that there is about peak hardness of about 980 VHN obtained for Ni-Cr-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/hr. Where as in the present investigation the peak hardness obtained at 350°C could be due to the presence of low phosphorus in Ni-Cr-Mo-P deposits.

3.4 Corrosion reistance of electroless Ni–Cr–Mo-P deposits

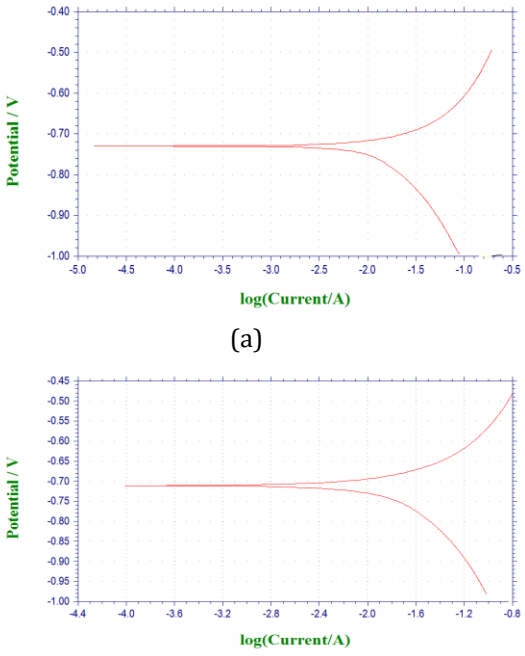

Figure 3.3 : Potentiodynamic polarization curves of the as-plated electroless (a)Ni-P (b)Ni-Cr-Mo-P coating

The effect of sulphuric acid medium on the corrosion rate of electroless plain Ni-P and Ni-Cr-Mo-P alloy coatings was studied using Tafel polarization technique. Figure 3.3

represent the potentiodynamic polarization curves of electroless plain Ni-P and Ni-Cr-Mo-P alloy coatings in concentration of lM sulphuric acid medium at lab temperature. Corrosion parameters such as corrosion potential (E_{corr}), corrosion current density (I_{corr}) anodic slope and cathodic slope are obtained from Tafel polarisation curves. The corrosion rate directly obtained from CH software. Corrosion resistance of electroless nickel and its alloys depends on the phosphorus content, alloying elements and also on the porosity of the coatings. Higher corrosion current density values are obtained for plain Ni-P deposits. Corrosion resistance of the reported coatings is very good considering the fact that the thickness of the coating is only 23±2 µm.The amount of phosphorus present in Ni–P deposit was about 12.74 wt.%, where Ni–Cr-Mo–P deposits contained around 1.5-2 wt.% phosphorus. The decrease in phosphorus content in the deposits was mainly due to the presence of molybdenum. In the present study it has been observed that the addition of Cr and Mo has shown very good improvement in the corrosion resistance of the coating as compare to that of binary Ni-P coatings.

Table 3.3: Corrosion rate of Ni-P and Ni-Cr-Mo-P alloy coatings

Type of coating	Ecorr (V)	Icorr (A)	Corrosion rate (mpy)
Ni-P	-0.502	$3.11x10^{-2}$	$1.376x10^{4}$
Ni-Cr-Mo-P	-0.500	$2.712x10^{-2}$	$1.198x10^{4}$

4. CONCLUSIONS

Electroless quaternary Ni-Cr-Mo-P alloy coating has been successfully prepared using alkaline sulphate bath containing nickel sulphate as the nickel source. From EDAX analysis, it is clear that quaternary Ni-Cr-Mo-P deposit consists of 2.04 Wt. % P, 8.89 Wt. % Mo, 8.19 Wt. %Cr and 80.88 Wt. % Ni. Surface morphology of the deposit is uniform, inseparably close and less porous. Additionally, cracks are not observed on the surface of the coatings. Ni-Cr-Mo-P exhibits coarse type of morphology. Microhardness measurements made on the cross-sections of Ni-Cr-Mo-P deposits in as deposited and annealed at various temperatures for 1 hr indicated that at all heat treated conditions Ni-Cr-Mo-P deposits showed better hardness than asplated. Using XRD data indicated that in the diffraction patterns, the reflections corresponding to the (111) plane of a face centred cubic (fcc) phase of nickel could be observed. In the present study it has been observed that the addition of Cr and Mo has shown very good improvement in the corrosion resistance of the coating as compare to that of binary Ni-P coatings.

REFERENCES

[1] S. Kuyucak, M. Sahoo, Can. Metall. Q. 1996, 35, 1.
[2] A. Kawabe, Electrochemistry 2003, 71, 681.
[3] A. Kro´likowski, P. Butkiewicz, Electrochim. Acta 1993, 38, 19793.
[4] A. R. Rahimi, H. Modarres, M. Abdouss, Sur. Eng. 2009, 25, 367.
[5] L. L. Wang, H. J. Chen, L. Hao, Sur. Eng. 2011, 27, 57.
[6] J. N. Balaraju, T. S. N. Sankara, S. K. Seshadri, J. Solid State Electrochem. 2001, 5, 334.
[7] N. K. Myshkin, A. Y. Grigoriev, D. M. Gutsev, M. Ignat, E. Chainet, V. Grandvallett, J. Sautel, J. Friction Wear 2010, 31, 413.
[8] L. L.Wang, H. J. Chen,W. Q. Huang, L. Hao, Sur. Eng. 2009, 25, 376.
[9] A. Brenner and G. Riddell: 'Nickel plating on steel by chemical reduction', J. Res. Nat. Bur. Stand., 1946, 37, 31–34.
[10] A. Riedel: 'Electroless nickel plating', 1991, London, Finishing Publication Ltd.
[11] Sankara Narayanan, T. S. N., Selvakumar, S., Stephen, A., "Electroless Ni-Co-P ternary alloy deposits: preparation and characteristics", Surface and Coatings Technology, Vol. 172, (2003) pp. 298-307.
[12] Balaraju, J. N., Anandan, C., Rajam, K.S., "Electroless deposition of ternary Ni-W-P alloys from sulphate and chloride based baths", Surface Engineering, Vol. 21, (2005) pp. 215-220.