

Structural and Corrosion Behavior of Nanocrystalline Ni-P Deposits on Aluminium with Heat Treatment

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Abstract

Nanocrystalline nickel-phosphorus (NC-Ni-P) coatings were prepared from aluminium alloy in an acidic electroless glycine bath in the heat treated condition. Nickel sulphate was used as metal ion source and sodium hypophosphite was used as a reducing agent. Surface morphology, nanostructure and corrosion resistance properties coatings were studied by SEM, AFM, XRD and potentiodynamic polarization method. From the XRD, the phase structure of the coating was ascertained to be nanocrystalline. AFM, SEM observation revealed that dense, uniform spherical nodular structure present in the heat treated Ni-P deposit. The electrochemical analysis in 3% sodium chloride solution provided that the nanocrystalline Ni-P coating exhibited better corrosion resistance than the bare aluminium alloy substrate.

Keywords: NC-Ni-P, SEM, XRD, AFM, Corrosion.

Introduction

Aluminum is one of the widely used substrate material in industrial applications, especially in aerospace and household industries due to its light weight, low price, recyclability, malleability, easy to fabrication, thermal and electrical conductivity [1]. The main features of aluminum are its corrosion resistance in aqueous solutions except for pitting corrosion due to the presence of a thin, adherent and passive film on its surface [2, 3]. There are several electrochemical plating methods to increase the materials performance for different applications.

Electroless deposition is one of the most popular methods for the formation of nanocrystalline nickel deposit of different grain sizes were considered for various applications [4, 5]. The structure and morphology of the Ni-P deposit can be modified on heat treatment [6] with different deposition time. The effect of coating time on corrosion resistance of Ni-P alloy on mild steel deposits was analyzed by H. Ashassi-Sorkhabi and S. H. Rafizadeh [7].

However, the effect of coating time on corrosion and structural behavior of nanocrystalline nickel deposit on aluminium, after heat treatment has not been studied widely. The present work aims to study the formation of electroless NC-Ni-P coating in the heat treated condition and to evaluate its structural characteristics, morphology and corrosion resistance.

Experimental

Heat treated electroless nickel deposit specimen were prepared from optimised electroless bath containing Nickel sulphate-0.15 M, glycine -0.15 M and sodium hypophosphite - 0.2 M at a constant temperature of 80 °C and a pH of 4.0 for different deposition time. Heat treatment was carried out from Muffle furnace at 400 °C for 1 h.

Surface morphology of the deposits was examined by scanning electron microscopy (SEM, JEOL-Japan-JSM-840A) and atomic force microscopy (AFM) (Digital Instruments CP-II Veeco Company, USA). All AFM images were acquired in tapping mode. The phase evolution of the NC-Ni-P deposits was determined from a Philips X'pert X-ray diffractometer (XRD) with Cu K α radiation ($\lambda=0.15418$ nm). The corrosion studies were carried out using electrochemical workstation (CHI, Model 760) in 3wt.% NaCl solution at 30 °C using potentiodynamic polarization method. The corrosion potential (E_{corr}), corrosion current density (i_{corr}) and polarization resistance (R_p) were obtained from the Tafel plot (log current versus potential) using Stern-Geary equation [8].

$$I_{\text{corr}} = [b_a b_c / 2.303 \times R_p (b_a + b_c)] \quad (1)$$

Where, b_a and b_c are the Tafel slopes expressed in volts/decades and R_p is the polarization resistance expressed in Ω/cm^2 . Corrosion rate (C_R) was calculated by using the formula

$$C_R \text{ (mpy)} = 0.129 \times i_{\text{corr}} \text{ (}\mu\text{A}/\text{cm}^2\text{)} \times \text{Equivalent weight (gm)} / \text{Density (gm cm}^{-3}\text{)} \quad (2)$$

Results and discussion

SEM analysis

The SEM images of heat treated Ni-P coatings formed at 400 °C for 1 h for the deposition time of 30 s, 600 s and 1800 s are given in Fig. 1(a, b & c) at X 40,000 magnification respectively. It is observed from SEM images that crystalline growth is formed after heat treatment at the deposition time of 30 s which has the tiny and large number of homogeneous grains. Heat treated coatings formed at the deposition time of 600 s (Fig. 1b) has finer, compact nanocrystalline deposits and uniformly

distributed grains are observed and the deposition time of 1800 s (Fig. 1c) the size of the nodular grains becomes larger and more compact.

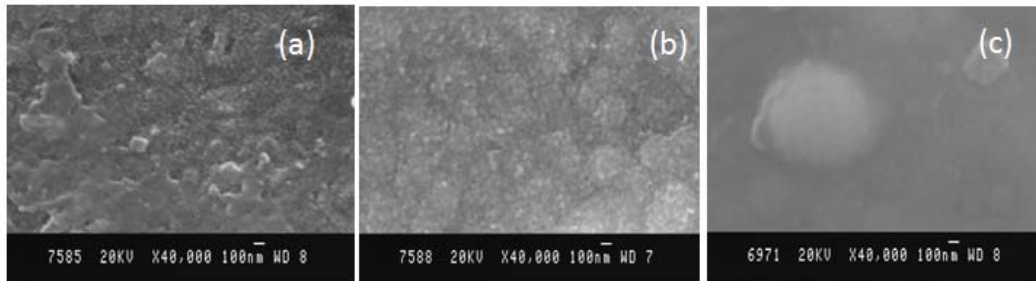


Figure 1: SEM images of nanocrystalline nickel phosphorus deposits on zincated aluminium at various deposition time (a) 30 s, (b) 600 s, (c) 1800 s in the after heat treatment at 400°C for 1 h.

AFM analysis

Fig. 2(a, b) and Fig. 3(a, b) shows the topographic and three dimensional AFM images of electroless Ni-P deposits obtained at the deposition time of 30 s and 1800 s after heat treatment at 400 °C for 1 h. After heat treatment, the electroless Ni-P deposit formed at 30 s (Fig. 2a, b) produces larger number of clusters of tiny Ni-P crystals. These nanocrystals are highly dense, compact and uniformly present on the surface. But in 1800 s (Fig. 3a, b) diffused like morphology was observed. The average surface roughness (Ra) of the heat treated electroless NC-Ni-P coating is 22.8 nm for 30 s deposition time and 2.7 nm for 1800 s deposition time and the corresponding root mean square (RMS) values are 28.5 nm and 3.5 nm respectively. As the deposition time increases, roughness decreases, because of increase in smoothness of the coating.

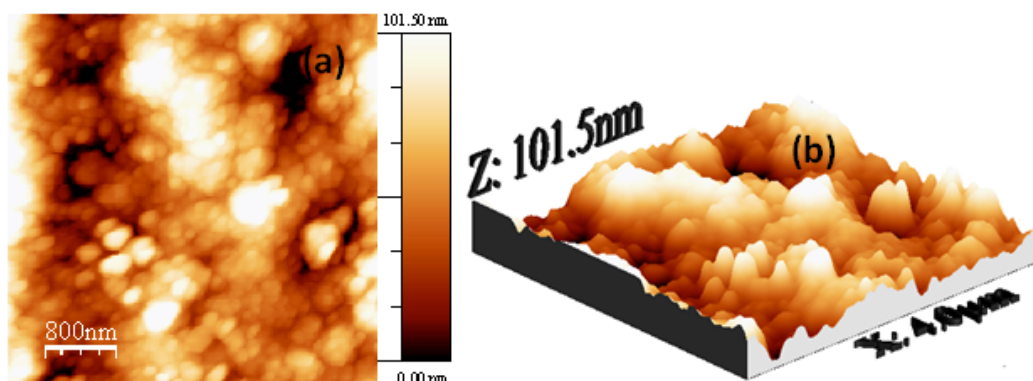


Figure 2: AFM images of heat-treated electroless NiP coating on zincated aluminium for the deposition time of 30 s (a) Topographic image (b) 3-Dimensional image.

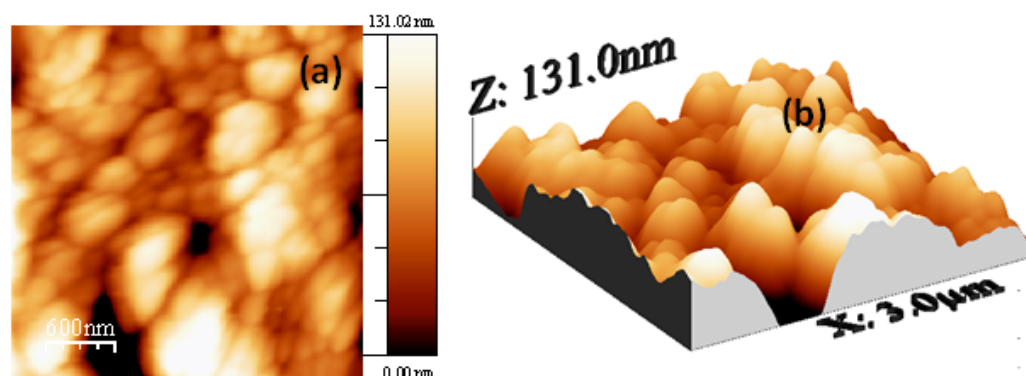


Figure 3: AFM images of heat-treated electroless NiP coating on zincated aluminium for the deposition time of 30 s 1800 s (a) Topographic image (b) 3-Dimensional image.

X-ray diffraction analysis

Fig. 4(a- c) shows the XRD patterns for Ni-P deposits formed at different deposition time after heat treatment at 400 °C for 1 h. From the Fig. 4(a), it can be found that, the deposit formed at 30 s gives a meta-stable Ni_{12}P_5 peak (1 1 2) (JCPDS card No. 74-1381) at 38.6° and Ni peak at two positions 44.84° and 78.32° with (1 1 1) and (2 2 0) plane orientations (JCPDS card No. 03-1051, 88-2326) and Ni_3P stable phase with (1 0 3) plane orientation at 65.18° (JCPDS card No. 65-2778).

Fig. 4(b) shows the XRD patterns of the deposit formed at 600 s after heat treatment, which give the crystallization of meta stable Ni_{12}P_5 phase with (1 1 2) (JCPDS card No. 74-1381) at 38.52°, stable Ni_3P peak with (3 2 1) orientation (JCPDS card No. 65-2778) at 41.8° and Ni peak with (1 1 1) orientation (JCPDS card No. 03-1051) at 44.77°, Ni_3P peak with (1 0 3) orientation at 65.14° (JCPDS card No. 65-2778) and Ni peak with (2 2 0) plane orientation at 78.27° (JCPDS card No. 88-2326).

Fig. 4(c) depicts the XRD patterns of heat-treated electroless nickel deposits formed at 1800 s. The sharp meta stable Ni_{12}P_5 (1 1 2) peak (JCPDS No. 74-1381) appears at 38.46°. Broad diffraction peak occurred in the as-deposited condition at around 45° are converted into multiple new low intensity peaks. The newer peaks at 41.77° corresponds to stable Ni_3P (3 2 1) (JCPDS No. 65-2778), the peak at 43.73° corresponds to meta stable Ni_5P_4 (2 1 2) peak (JCPDS No. 89-2588), the peak at 44.68° corresponds to Ni (1 1 1) (JCPDS No. 03-1051), the peak at 46.57° corresponds to Ni_3P (1 4 1) (JCPDS No. 34-0501) and the peak at 51.93° corresponds to Ni_3P (1 5 0) (JCPDS No. 89-2743). The larger peak appearing at 65.08° corresponds to Ni_3P (1 0 3) (JCPDS No. 65-2778) and Ni (2 2 0) (JCPDS No. 88-2326) peak appears at 78.21°. These diffraction peaks are sharper with narrower full width at half maximum indicating a better crystallization of the alloy. The presence of these phase have been reported by other workers in the early stages of crystallization of nickel phosphorus deposits [9, 10]. The detailed analysis of the X-ray diffraction patterns of the heat-

treated Ni-P deposit is reported in the literature [11-13]. After heat treatment, the average calculated crystal size of electroless deposit is 75.7 nm, 64.5 nm and 40.1 nm for the deposition time of 30 s, 600 s and 1800 s, respectively.

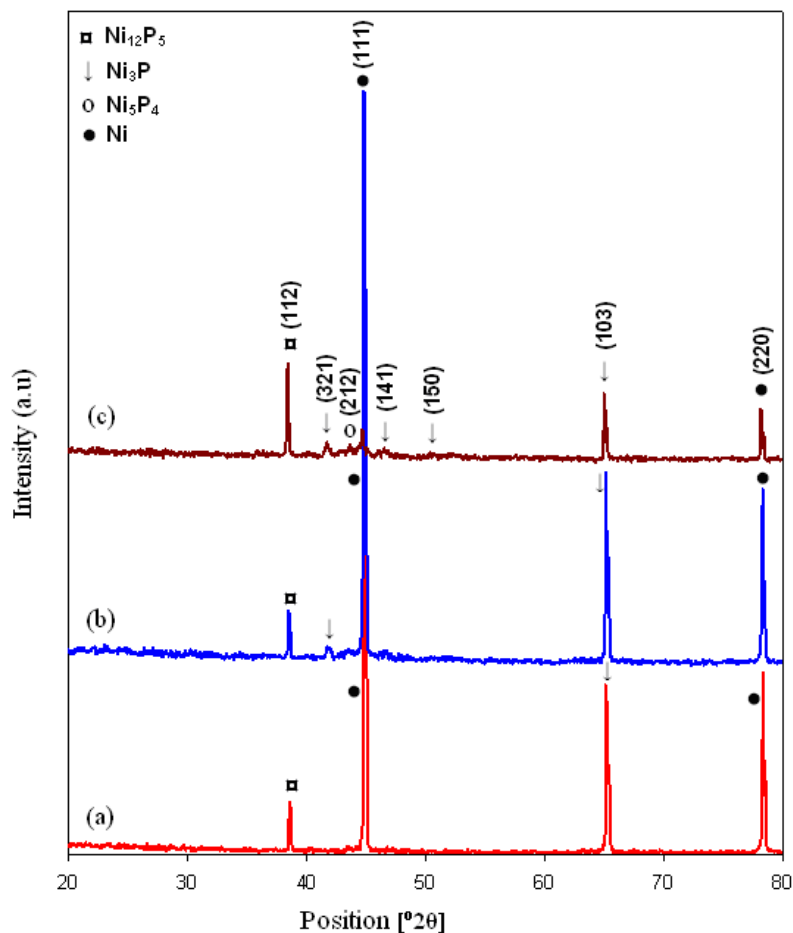


Figure 4: X-ray diffraction patterns of the electroless nanocrystalline Ni-P deposit heat treated at 400°C / 1 h for the deposition time of a) 30 s; b) 600 s; c) 1800 s.

Corrosion studies – Potentiodynamic polarization method

Potentiodynamic polarization curves of heat treated electroless nickel phosphorus coatings obtained at various deposition times of 30 s, 600 s and 1800 s are presented in Fig. 5 and the corresponding corrosion parameter values are summarized in Table 1. The heat treatment at 400°C for 1 h shifts the corrosion potential to a very low value and increases the corrosion current density. High temperature heat treatment results in the formation of Ni-P phases with the help of phosphorus diffusion [14, 15]. This diffusion process may decrease the stability of the adsorbed hypophosphite film. Therefore the removal of the adsorbed layer may cause a further decrease in the corrosion resistance of the deposit.

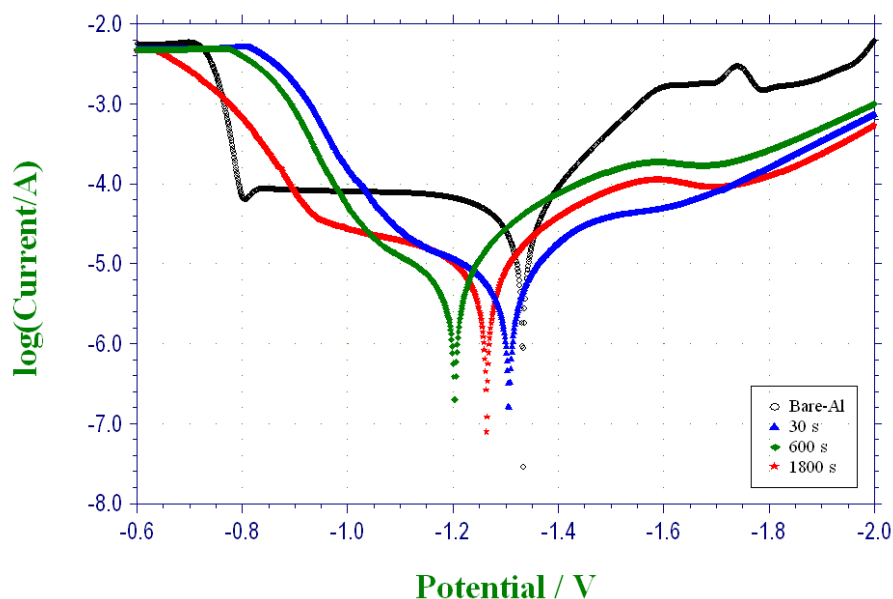


Figure 5: Tafel polarization curves of after heat treated electroless nanocrystalline nickel phosphorus on aluminium for various plating time.

Table 1: Effect of plating time on corrosion parameters for Ni-P deposits after heat treatment.

| Plating time | E_{corr} (V) | i_{corr} ($\mu\text{A}/\text{cm}^2$) | b_a (V/dec) | b_c (V/dec) | R_p (ohm cm^{-2}) | C_R (mpy) |
|--------------|-----------------------|---|---------------|---------------|--------------------------------|-----------------------|
| Bare-Al | -1.334 | 6.61 | 20 | 23.15 | 70.51×10^4 | 2.83 |
| 30 s | -1.308 | 0.501 | 61.11 | 64.28 | 2.71×10^7 | 2.36×10^{-1} |
| 600 s | -1.2 | 0.63 | 70 | 40 | 1.75×10^6 | 2.97×10^{-1} |
| 1800 s | -1.26 | 1.58 | 28.66 | 18.75 | 3.10×10^6 | 7.47×10^{-1} |

Conclusion

NC-Ni-P deposits were produced by heat treatment at 400°C for 1 h for different deposition time. Upon heat-treatment Ni-P deposits crystallize to produce meta-stable Ni_{12}P_5 , Ni_5P_4 peak and stable Ni_3P , Ni peak as major compound constituents has different plane orientations. According to corrosion studies, NC-Ni-P deposits have lower i_{corr} , corrosion rates and better corrosion resistance than that of bare aluminium substrate.

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