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Crystallization mechanism and corrosion property of electroless nickel phosphorus coating during intermediate temperature oxidation

M. Sribalaji [a], P. Arunkumar [b], K. Suresh Babu [b], Anup Kumar Keshri [a,*]

[a] Materials Science and Engineering, Indian Institute of Technology Patna, Navin Government Polytechnic Campus, Patliputra Colony, Patna, Bihar, 800013, India

[b] Centre for Nanoscience and Technology, Madanjeet School of Green Energy Technologies, Pondicherry University, Puducherry 605014, India

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ABSTRACT

Electroless Ni–P coating was deposited on steel substrate and the effect of intermediate temperature oxidation on crystallization mechanism and corrosion properties of the coating was investigated. Ni–P coatings were annealed at three different temperatures, viz. 200 °C, 400 °C and 600 °C for 2 h in air. Formation of nickel oxide (NiO) was observed in the coating upon annealing beyond the crystallization temperature (330 °C). Crystallization mechanism provided insight about the step by step formation of long range ordered Ni,Ni_3P and NiO phases.Improvement in the corrosion resistance of Ni–P coating compared to bare steel was found to be ~21% on annealing at 400 °C in air which gradually increased to ~31% on annealing the coating at 600 °C in air. Increasedcorrosion resistance at 400 °C annealed coating was attributed to the formation of crystalline Ni and Ni_3P phases. Two simultaneously effects have been identified for the increased corrosion resistance of the coating annealed at 600 °C in air. (a) Formation of NiO layer which acts as a passivation layer and protects the underlying P enriched layer and (b) absence of an interdiffusion layer from substrate to coating.

1. Introduction

Electroless nickel-phosphorus (Ni–P) coatings have gained lots of interest in various industrial components such as valves, pipes, pumps in automobile, aerospace and petroleum industries because of their excellent corrosion resistant property [1–4]. In particular, these coatings are extensively being used in heat exchangers in petroleum industries, where the coating is exposed to harsh environment such as high temperature and corrosive environment [4]. However, Ni–P coatings start getting oxidized at temperature ≥400 °C in air which in turn impacts on the crystallization mechanism and ultimately affect the corrosion property of the coating. There are several studies which report the enhanced corrosion resistance of Ni–P coating on annealing at temperature range of 400–600 °C [5,6]. Increased corrosion resistance was attributed to the formation of the crystalline Face Centered Cubic (FCC)Ni and phosphorous rich Body Centered Tetragonal (BCT)Ni_3P (nickel phosphide) phases [6]. Unfortunately, almost all of the studies report the annealing of the coating in *vacuum* or in *controlled atmosphere* which resists the oxidation of the coating. However, this is far away from the practical consideration where the engineering components are exposed at intermediate/high temperature in an *air*. Few researchers have attempted the annealing of electroless Ni–P coating in air and investigated the corrosion properties of the coatings [7–9].

Singh et al. reported ~72% reduction in corrosion resistance on annealing the electroless deposited Ni–P coating at 600 °C for 15 min in air. Reduction in the corrosion resistance was due to the contamination of the coating by Fe and Si diffused from the steel substrate [7]. Bai et al. reported the corrosion resistance of electroless Ni–P coatings annealed at four different temperatures (i.e.100 °C, 200 °C, 300 °C, and 400 °C) in air [8]. Maximum corrosion resistance was observed for the coating annealed at 300 °C, while the coating annealed at 400 °C showed ~8% decrease in the corrosion resistance. Loss in corrosion resistance at 400 °C was attributed to the interdiffusion of Cu atoms from Cu substrate to coating [8]. However, both of the above mentioned studies did not report about the intermediate temperature oxidation of the coating, which might affect the crystallization mechanism and corrosion properties of the coating.

Recently, Eraslan et al. studied the high temperature (600–800 °C) oxidation behaviour of the electroless Ni–P, Ni–B and Ni–W–B coatings deposited on steel substrate in a temperature controlled tube furnace in air [9]. Their results indicate that, iron

* Corresponding author. Tel.: +91 612 2552184.
E-mail address: anup@iitp.ac.in (A.K. Keshri).

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Table 1
Chemical compositions of the electroless nickel plating bath and its operating condition.

Chemical compositions	Concentrations
Nickel sulphate ($NiSO_4{\cdot}6H_2O$)	5.5–6.5 g/l
Sodium hypophosphate ($NaH_2PO_2{\cdot}2H_2O$)	18–22 g/l
Complexing agents	$PbCl_2$
Operating conditions	
pH	4.6–5
Temperature	85–90 °C
Plating duration	1–2 h
Plating rate	10–12 μm/h

from the steel substrate starts diffusing in the oxide structure during heat treatment at 700 °C resulting in a loss of protective nature of the oxides [9]. Tomlinson et al. also studied the high temperature oxidation (800–1000 °C) of electroless Ni–B and Ni–P coatings and reported that, oxidation of Ni–P coating is approximately 1000 times faster than pure nickel at high temperature [10]. In these studies, high temperature oxidation of electroless Ni–P coating has been investigated. However, its effect on crystallization mechanism and corrosion properties of the coatings has not been discussed.

Several researchers have reported that nickel oxide (NiO) enhances the corrosion resistance of the substrate significantly [11–13]. Romero et al. found ~7 times increase in corrosion resistance of the galvanized steel substrate on coating with NiO [11]. NiO coating delay the rate of corrosion by forming a passivation layer over the substrate. Ma et al. found the relative enhancement of ~75% in the corrosion resistance of electrodeposited $NiO/NiFe_2O_4$ coating compared to Ni coating at 900 °C [12]. Improvement in the corrosion resistance was attributed to the formation of dense NiO layer which inhibited the corrosion rate at high temperature [12]. Yuan et al. found ~42% enhanced corrosion resistance in nanocrystalline Ni coating compared to coarse grained Ni coating [13]. The significantly enhanced corrosion resistance was attributed to the formation of stable passive NiO films on the surface of nanocrystalline nickel coating [13].

Since, NiO acts as passivation layer and delay the rate of corrosion, it is envisaged that formation of NiO in electroless Ni–P coating would further improve the corrosion resistance. Motivated by this scenario, the objective of the present study is to fabricate the electroless Ni–P coating followed by annealing of the coating at three different temperatures, viz. 200 °C, 400 °C and 600 °C in air. Effect of the oxidation, as a result of annealing in air, on the crystallization mechanism has been investigated. Further, the correlation between crystallization mechanism and corrosion properties of the coating has been elucidated.

2. Experimental procedure

2.1. Electroless deposition of nickel-phosphorous coatings

Ni–P coating was deposited on the 4140 steel substrate (70 mm × 25 mm × 15 mm) using an acid bath containing nickel sulphate as a source of nickel and sodium hypophosphate as a reducing agent. Table 1 lists the bath composition and the operating conditions of the deposition process. Prior to deposition, substrate was mechanically polished and degreased in an alkaline solution and further rinsed with deionized water for 30 s. The pH was controlled between 4 and 5 in alkaline bath and the deposition temperature was fixed at 85–90 °C. Plating was done for 2 h at the rate of 10–12 μm/h. This bath provided the Ni–P coating of ~20 μm thick with a high phosphorous content, 10–12% P.

2.2. Heat treatment of Ni–P coatings

Heat treatment of the as-deposited electroless Ni–P coating on steel substrate was carried out in an electric resistance furnace (Matri, MAC 2265 A, India) at three different temperatures viz. 200 °C, 400 °C, 600 °C in air for 2 h, followed by air cooling to room temperature. The effect of intermediate temperature oxidation on the crystallization mechanism and corrosion properties of electroless Ni–P coating was investigated.

2.3. Microstructural and phase characterizations

A Zeiss, Sigma HD (UK) field emission scanning electron microscope (FE-SEM) was used to investigate the cross-sectional morphologies of the electroless Ni–P coatings. Elemental mapping analysis was performed using an Oxford Instruments (X-Max 50,UK) and EDS detector that was attached with FE-SEM. The operating voltage was maintained as 20 kV and the images has been taken at 1024 × 768 pixel frame, ~21 pixel width per frame was selected for analysis.

Phase analysis of the coating was executed by using an X-ray diffractometer (Rigaku, TTRAX III, Japan) with Cu K_α radiation operating at 40 kV and 20 mA in the range of 30–70°. The scanning rate and scanning step for this characterization was fixed at 2°/min and 0.02°, respectively. The average grain size of the coating was calculated using Debye–Scherrer equation, which is given as Eq. (1)

$$D = \frac{K\lambda}{\beta_{1/2}\cos\theta} \tag{1}$$

where $K = 0.9$ is the Scherrer constant, $\beta_{1/2}$ denotes the full width at half maximum of the peak, θ is the Bragg angle and λ represents the wavelength of CuK_α radiation which is 1.54 Å. In addition to that, the microstrain (ε) was calculated using the following Eq. (2).

$$\varepsilon = \frac{\beta_{1/2}}{4\tan\theta} \tag{2}$$

where $\beta_{1/2}$ is the full width half maximum of the peak, θ is the Bragg angle. The texture coefficient of the coatings annealed at 400 °C and 600 °C were calculated from the X-ray diffraction peaks using Eq. (3).

$$TC_{(hkl)} = \frac{I_{(hkl)}}{I_{0(hkl)}}\left\{\frac{1}{n}\sum\frac{I_{(hkl)}}{I_{0(hkl)}}\right\}^{-1} \tag{3}$$

where $I_{(hkl)}$ represents the measured intensity of (hkl) plane, $I_{0(hkl)}$ denotes the standard intensity of the same (hkl) plane obtained from the JCDPS data and n denotes the number of planes considered for calculating the $TC_{(hkl)}$ value.

Micro-Raman spectroscopy was used further to confirm the presence of NiO in the coating. An internal Si-reference ICR crystal target with a laser wavelength of 514 nm was used and the laser was produced using source from Renishaw (Model 3900S, UK) with a charge coupled detector (CCD) from Renishaw, UK

2.4. Differential scanning calorimetry characterization

In order to understand the crystallization behaviour, DSC (TA make, Q20 DSC, USA) was carried out on the peeled-off Ni–P coating. Total 20 mg of the samples were heated from 50 °C to 500 °C at a heating rate of 10 °C/min. Nitrogen gas with a flow rate of 50 ml/min was passed over the sample during the test.

2.5. Corrosion measurements

Corrosion behaviour of as-deposited and annealed coatings at 200 °C, 400 °C, 600 °C were studied using potentiodynamic