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An investigation on effects of heat treatment on corrosion properties of Ni–P electroless nano-coatings

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ABSTRACT

Electroless Ni–P coatings are recognized for their excellent properties. In the present investigation electroless Ni–P nano-crystalline coatings were prepared. X-ray diffraction technique (XRD), scanning electron microscopy (SEM), potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) were utilized to study prior and post-deposition vacuum heat treatment effects on corrosion resistance together with the physical properties of the applied coatings.

X-ray diffraction (XRD) results indicated that the As-plated had nano-crystalline structure. Heat treatment of the coatings produced a mixture of polycrystalline phases. The highest micro-hardness was achieved for the samples annealed at 600 °C for 15 min due to the formation of an inter-diffusional layer at the substrate/coating interface.

Lower corrosion current density values were obtained for the coatings heat treated at 400 °C for 1 h. EIS results showed that proper heat treatments also enhanced the corrosion resistance, which was attributed to the coatings' structure improvement.

1. Introduction

Since the invention of electroless plating technology in 1946 by A. Brenner and G. Riddell, electroless nickel (EN) coatings have been actively and widely studied [1,2].

Nano-crystalline Ni–P alloys show a high degree of hardness, wear resistance, low friction coefficient, non-magnetic behavior and high electro-catalytic activity. Today such Ni–P alloys are widely used in the electronic industry as under-layer in thin film memory disks and in a broad range of other evolving technological applications. It is generally accepted that only nano-crystalline alloys – irrespective of the way of production – show high corrosion resistance. Indeed, electrodeposited Ni–P alloys with crystalline structure (6–11 at.% P) showed anodic dissolution in 0.1 M NaCl. On nano-crystalline samples (17–28 at.% P) a current arrest was found instead [3–5].

To explain high corrosion resistance of Ni–P electroless coatings different models have been proposed, but the issue is still under discussion: a protective nickel phosphate film, the barrier action of hypophosphites (called "chemical passivity"), the presence of phosphides, a stable P-rich amorphous phase or the phosphorus enrichment of the interface alloy-solution were proposed. Note that such phosphorus enrichment at the interface was reported by some of the authors to explain the outstanding corrosion resistance of Fe70Cr10P13C7 amorphous alloys [5].

Electroless Ni–P alloys are thermodynamically unstable and eventually form stable structures of face-centered cubic (fcc) Ni crystal and body-centered tetragonal (bct) nickel phosphide (Ni_3P) compounds. Different results have been reported regarding the microstructures in the As-deposited condition and the stable phases after heat treatments. For low P and medium P alloys, nickel crystal precipitated firstly and Ni_3P followed; however, Ni_3P and (or) Ni_xP_y compounds such as Ni_2P, Ni_5P_2, $Ni_{12}P_5$, and Ni_7P_3 occur firstly in high P alloys [6–8].

In general, the hardness of the electroless Ni–P coatings can be improved by appropriate heat treatment, which can be attributed to fine Ni crystallites and hard inter-metallic Ni_3P particles precipitated during crystallization of the amorphous phase [8–10].

The main reasons for heat treatment are: (1) to eliminate any hydrogen embrittlement in the basic metal, (2) to increase deposit hardness or abrasion resistance, (3) to increase deposit adhesion in the case of certain substrate and (4) to increase temporary corrosion resistance or tarnish resistance [11].

The crystallization and phase transformation behavior of electroless-plated Ni–P deposits during thermal processing has also been the subject of various investigations; it has been shown that different alloy compositions and heat treatment conditions could affect both the corrosion resistance and crystallization behavior of the deposit [8].

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The aim of this work is to study the post-deposition heat treatment effects and corrosion behavior of electroless deposited nanocrystalline Ni–P alloys. The temperature dependence of the coating structures and compositions were also evaluated and discussed.

2. Experimental procedures

2.1. Deposition of electroless Ni–P coating

The deposition was performed on API-5L X65 steel substrates ($30 \times 25 \times 15$ mm) with a composition of (Fe: base, Mn: 1.42, Si: 0.199, Cu: 0.144, Mo: 0.132, C: 0.061, Nb: 0.0538, Al: 0.0417, Sn: 0.0167, Ti: 0.0142, Cr: 0.0126, P: 0.01). The substrate surface was carefully polished with SiC emery papers (from grades #100 to #400). All the specimens were subjected to the following pre-treatment and plating procedure:

1. Ultrasonic cleaning in acetone.
2. Rinsing by immersion in distilled water at room temperature (RT) for 2 min.
3. Cleaning in 20 vol.% H_2SO_4 at RT for 30 s.
4. Rinsing by immersion in distilled water at RT for 2 min.
5. Cleaning in 5 vol.% H_2SO_4 at RT for 30 s.
6. Rinsing by immersion in distilled water at RT for 2 min.
7. Electrocleaning in solution containing 75 g/l sodium hydroxide (NaOH), 25 g/l sodium sulfate (Na_2SO_4), 75 g/l sodium carbonate (Na_2CO_3), at room temperature for 20 min. The current density applied was 10 mA/cm^2 in accordance to ASTM G1.
8. Rinsing by immersion in distilled water at RT for 30 s.

For deposition, the substrates were dipped into commercial electroless nickel bath (SLOTONIP 70A from Schlotter) with sodium hypophosphite as reducing agent for 2 h. This bath provided Ni–P deposits with a medium phosphorous content, 9–10% P. Temperature changed within 88–93 °C and pH changed within 4.5–4.7 range, during coating process.

2.2. Heat treatment and hardness measurement of Ni–P coatings

In order to study the film properties, coated samples were thermally treated in a vacuum environment. The coatings were isothermally heat treated at different conditions that gave maximum hardness, i.e. 200 °C (for 2 h), 400 °C (for 1 h), 600 °C (for 15 min). During heating process, the total pressure in the chamber was maintained below 1 mbar. Then the samples were allowed to cool down, for at least 15 min in the high vacuum environment prior to their exposure to the atmosphere.

The hardness of coatings was measured using an (AMSLER D-6700) Vickers diamond indenter at a load of 100 g for a loading time of 20 s. The average of five repeated measurements is reported.

2.3. Morphology and microstructure of Ni–P coatings

The morphology and microstructure of the coatings were studied using scanning electron microscopy SEM, (CAMSCAN MV2300). X-ray diffraction (XRD) patterns were obtained using Philip's Xpert pro type X-ray diffractometer with a cobalt target and an incident beam mono-chromator (λ = 1.7889 Å).

2.4. Electrochemical measurements

Corrosion behavior of As-plated and heat treated electroless Ni–P coatings was studied by using potentiodynamic polarization test and electrochemical impedance spectroscopy (EIS) in 3.5 wt.% NaCl solution. The tests were carried out in a standard three-electrode cell using an EG&G potentiostat/galvanostat, model 273A. Platinum plate and Ag/AgCl electrode were used as counter and reference electrodes, respectively. Potentiodynamic polarization test was carried out by sweeping the potential at a scan rate of 1 mV s^{-1} within the range of ±400 mV vs. open circuit potential (OCP). The EIS tests were undertaken using a Solartron Model SI 1255 HF Frequency Response Analyzer (FRA) coupled to a Princeton Applied Research (PAR) Model 273A potentiostat/galvanostat. The EIS measurements were obtained at (OCP) in a frequency range of 0.01 Hz–100 kHz with an applied AC signal of 5 mV (rms) using EIS software model 398. The equivalent circuit simulation program (ZView2) was used for data analysis, synthesis of the equivalent circuit and fitting of the experimental data.

3. Results and discussion

3.1. Micrograph and structure

Fig. 1 shows the SEM images of the surface morphologies of Ni–P coatings before and after vacuum heat treatment at different conditions. As it can be seen heat treatment at different temperatures has not had any significant effect on morphology of the coatings.

Fig. 2 shows the cross section image with line scan analysis of Ni–P coating heat treated at 600 °C (for 15 min) which shows the formation of an inter-diffusional layer and its elemental distribution that affects the coating properties.

Atoms under low temperature heat treatment (below 400 °C) can have short-range movement which is called structural relaxation such as annihilation of point defects and dislocations within grains and grain boundary zones rather than long range diffusion [4]. The higher the temperature is, the greater the atomic vibration energy is. As the temperature of the metal increases, more vacancies are present and more thermal energy is available, and so the diffusion rate is higher at higher temperatures [11].

Hence, production of an inter-diffusional layer, formed as a result of inter-diffusion of nickel and phosphorous from the coating to the substrate and iron in the reverse direction from the substrate will develop upon heating at 600 °C.

3.2. XRD analyses of Ni–P coatings

Fig. 3 shows XRD patterns of As-deposited and heat treated Ni–P coatings. The results show that both the phase composition and phase transformation behavior of the electroless Ni–P deposits depended on the heating temperatures.

There was no significant change in XRD patterns observed for the samples treated at 200 °C and only a single broad amorphous profile was found, indicating that no phase transition took place at this temperature. When the heat treatment temperature was increased to 400 °C, new XRD peaks corresponding to crystalline fcc Ni and Ni_xP_y appeared, indicating that the second phase precipitation was initiated. At this temperature, the diffraction peaks corresponding to the metastable Ni_8P_3, fcc nickel and stable Ni_3P phases in the XRD profile can be seen. At 600 °C the fcc Ni and Ni_3P peaks intensities increased with the heat treatment temperature. Therefore, the Ni_8P_3 metastable phase was decomposed completely at this temperature. Similar behavior has also been observed by Huangs et al. [12].

Regarding the intensities of fcc nickel diffraction peaks, they are increased and the full width at half maximum (FWHM) became narrower with increasing the heat treatment temperature to 600 °C. In the case of As-plated condition, using FWHM of 6.4676° and Scherrer equation, the grain size was estimated as1.5 nm.