Preparation of electroless Ni–P composite coatings containing nano-scattered alumina in presence of polymeric surfactant

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Received 17 April 2012; accepted 28 May 2012
Available online 27 September 2012

Abstract Ni–P electroless coating was applied on low carbon steel with the incorporation of different amounts of nano Al₂O₃ powder (ranging from 3 g/l to 30 g/l) in electroless bath. Corrosion properties and microstructures of the coating were studied. The dispersion stability of alumina colloidal particles stabilized by polymeric (non-ionic) surfactants in an electroless bath was also investigated. The surface morphology and the relevant structure were evaluated by scanning electron microscopy (SEM) and X-ray diffraction (XRD). Corrosion behavior of the coated steel was evaluated by electrochemical impedance spectroscopy (EIS) and polarization techniques. The results showed that increasing alumina concentration not only changed the surface morphology, but also promoted the corrosion resistance. Addition of surfactants has an indirect effect on the amount of the incorporated particles. Meanwhile, in the presence of surfactant, corrosion resistance of Ni–P coating containing even a small quantity of alumina was improved since a stabilized bath was obtained.

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1. Introduction

Since the invention of electroless plating technology by Brenner and Riddell in 1946 [1], electroless nickel coatings have been used in many industrial fields owing to their unique properties which classified into three types of coatings; low phosphorous (1–3 wt% P), medium phosphorous (4–7 wt% P) and high phosphorous (> 7 wt% P). Only electroless Ni–high P coating is effective in offering an excellent protection whereas electroless Ni–low P and Ni–medium P coatings are not recommended for severe corrosive environment [2]. Embedding particles in high phosphorous electroless deposited
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Newly developed Ni–P composite coatings with particles like Al2O3 [3–8], SiC [9–12], diamond [13], SiO2 [14] and Si3N4 [15] have shown to improve corrosion and abrasion properties. However, limited investigations have been conducted to study electroless composite coating with nano-sized alumina particles. Most of investigations have been focused on micro-sized alumina co-deposition. Hamdy et al. [16] investigated the corrosion behavior of Ni–P–Al2O3 composite coating in which the nano-sized alumina added to electroless bath ranging from 25 to 100 g/l. Their investigation also showed that the co-deposition of alumina up to 75 g/l in Ni–P coating bath improved the corrosion resistance of steel substrate in 3.5% NaCl solution. However the agglomeration of the nano-sized particles in coating was not studied.

Maintaining dispersion stability for the nano-sized particles throughout the electroless bath is one of the most important parameters for improving the related properties. To obtain the high performance of coatings such as corrosion and wear resistance, high dispersion of particles in the electroless bath is needed. Therefore, selecting the appropriate type of surfactant plays an important role in preventing the nano-sized particles to be agglomerated. Surfactants enhance the stability of a suspension by increasing the wettability and the surface charge of suspended particles. In addition, they improve the electrostatic adsorption of suspended particles on the cathode surface by increasing their net positive charge [17]. Hazan et al. [18,19] studied the dispersion stabilization of colloidal alumina by comb-polyelectrolyte surfactant in electroless bath which showed that the dispersion stabilization not only changes the particle dispersion in the coatings but also has strong influence on the co-deposition efficiency.

According to previous investigations on corrosion properties, the wide range of alumina particles (25–100 g/l) were studied but they could not prevent the agglomeration of particles in the coating [17]. Therefore, the present work aims to study the formation of electroless Ni–P coatings with lower amounts of nano-sized alumina particles ranging from 3 g/l to 30 g/l in the presence of polyethylene glycol (PEG) surfactant with the concentration from 0.3 to 1 g/l. It is worthy to note that in past researches, the effects of polymeric surfactant on the coating deposition properties and the agglomeration phenomena have not been widely studied.

2. Experimental details

Low carbon steel plates with surface area of 30 × 30 mm² have been used as the substrate material for preparation of electroless nickel composite coating. The chemical composition of carbon steel is shown in Table 1.

Each specimen was abraded to 400 grit finish with SiC paper, degreased in acetone, washed with distilled water and dried in air. Then, the specimens were subjected to ultrasonic cleaning in acetone and degreased in alkaline solution at 70 °C for 8 min. All specimens were etched in 10% aqueous H2SO4 solution for 5 s and then rinsed with deionized water and acetone prior to plating. Alumina nano-sized particles with the particle size of approximately 70 nm were used as reinforcement for composite coating. A commercial electroless nickel bath (SLOTONI-P 70A from Schluter) was used to provide Ni–P deposit coating with high phosphorous content (9–11 wt%). Before electroless plating, different concentrations of nano-sized Al2O3 particles (ranging from 3 to 30 g/l) and polymeric surfactant (0–1 g/l) were added to 100 ml bath, then stirred by magnetic stirrer for 20 min and ultrasonic mixer for 10 min. The mixture was added to 11 bath for electroless plating at 90 °C with stirring rate of 100 rpm and pH = 4.5.

The surface morphology and cross-sectional views of electroless Ni–P coating co-deposited by different concentrations of alumina and surfactants were studied by SEM (model Cam Scan MV230). Energy dispersive X-ray spectroscopy (EDS) was used to determine the point analyses of Al, Ni and P in the coating. Further structural assessment was carried out by X-ray diffraction (XRD, Philips, X’pert, the Netherlands), using Cu-Kα radiation in 40 kV, scanning in the 2θ = 10–120° range. The corrosion behavior of the samples in 3.5% NaCl solution at ambient temperature was also investigated using potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) technique. A saturated calomel electrode was used as the reference electrode whereas the coated sample (with exposed surface area of 1 cm²) and platinum plate utilized as working and counter electrode respectively. The charge transfer resistance (Rct) and double layer capacitance (Cdl) were determined from the corresponding Nyquist plots by fitting the data using Zview software. DC polarization tests for specimens immersed in aerated 3.5% NaCl solution were made at a scan rate of 2 mV/s for the applied potential ranging from –1.2 VSCE to 0.6 VSCE. Ecorr was determined using EG&G galvanostat/potentiostat model 270A. In the polarization tests, the open circuit potential (OCP) of steel in 3.5% NaCl solution was measured when the potential remained constant with time.

3. Results and discussion

3.1. Characteristics of the deposits

Fig. 1 shows the surface morphology and cross-section of the specimens prepared by different amounts of alumina. It can be observed that the agglomeration occurred despite good dispersion of particles throughout the coatings. The lack of defects in interface of coating in Fig. 1 suggests that good adherence is obtained. Fig. 1a allows comparison between a surface morphology of nickel–phosphorous coating and Ni–P/Al2O3 coatings at different concentrations of Al2O3 (Fig. 1b–f). The variation in surface morphology of these coatings suggests a definite dependence on the particle contents. In the case of Ni–P (Fig. 1a), some nodular structures are distributed uniformly in the composite coating. The appearance of cauliflower-like nodules, which is typical of amorphous material, was observed in earlier studies for electroless Ni–high P coating [20]. Such nodular structures becoming very small in size which was not visible in low magnification were also observed at Ni–P coatings with higher concentrations of Al2O3 (Fig. 1b–f). Moreover, the

<table>
<thead>
<tr>
<th>Elements</th>
<th>C</th>
<th>P</th>
<th>S</th>
<th>N</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt%</td>
<td>0.17</td>
<td>0.04</td>
<td>0.04</td>
<td>0.08</td>
<td>Remaining</td>
</tr>
</tbody>
</table>
particles were trapped in nodular boundaries and cause the particles to be agglomerated. It can be stated that the presence of particles in nodular boundaries affects on nodules growth accordingly. In spite of decreasing the size of nodules, the incorporation of particles increased significantly when the concentrations of Al2O3 were increased.

In order to prevent particles agglomeration, polymeric surfactant (PEG 1500), was added to the coating bath. Fig. 2 presents the surface morphology of the specimens prepared by 3 g/l alumina in the bath with different concentrations of surfactant (PEG1500). The nodular structure of the composite coating did not change significantly compared to Ni–P–3g/lAl2O3 while the incorporation of particles increased specifically in Fig. 2b. It can be inferred that the particles surrounded by surfactants, obtained the opportunity to be incorporated. Addition of surfactant more than 0.3 g/l in bath decreased the incorporation amount (Fig. 2c and d). The percent of particles kept their size was governed to those agglomerated. It can be stated that the surfactant prevents agglomeration by surrounding the particles. The steric repulsion existing between the particles surrounded by the PEG molecules is known to be responsible for this event.

The average elemental compositions including Al, Ni and P wt% obtained from EDS are shown in Table 2. Adding the nano-sized alumina particles decreased the amount of P compared to Ni–P coating. The amounts of P were increased by increasing the alumina content. This trend was continued by addition of surfactant in a given amount of alumina (3 g/l).

According to the XRD analyses (Fig. 3), all the coatings have an amorphous structure. A broad peak at 45° is located in all the EN deposits which are related to the amorphous profile of Ni–P deposits. The amount of Al2O3 in the specimens is too low (less than 5wt%), so that Al2O3 diffraction peaks cannot be seen in their XRD patterns. Fe peaks were detected in coatings in which the coating thickness was less than the diffusion depth of X-ray resulting in observing the substrate’s peak. However, the SEM images of the surface morphology, cross section (Fig. 1) and the elemental composition obtained from EDS (Table 2) clearly confirm the presence of Al2O3 particles in the Ni–P matrix for both mentioned systems.

3.2. Coating deposition rate

Fig. 4 shows increasing concentration of Al2O3 has a significant effect on the deposition rate of the Ni–P/Al2O3 system. The deposition rate for the specimen with no nano-sized particles was measured to be 21μm/h. The addition of Al2O3 to the system decreased the deposition rate. The highest co-deposition rate of 18.5μm/h was obtained from the specimen co-deposited in 3 g/l alumina in EN bath. The deposition rate fell dramatically with the addition of Al2O3 up to the 20 g/l and then followed a steady trend with increasing the concentration of Al2O3 in the bath. It can be concluded that by increasing the Al2O3 particles in the plating bath, some particles may physically adsorb on the catalytic surfaces by which it suppresses available active sites for the deposition process and the overall deposition rate. This explains the fact that at high oxide loads the rate of deposition decreases.

Fig. 5 exhibits the effect of surfactant concentration on the deposition rate of Ni–P–3 g/l Al2O3 composite. For a given amount of Al2O3 (3 g/l), the deposition rate for the specimen with no surfactant was measured to be 18.5μm/h. It can be seen that addition of surfactants to bath causes a decrease in the coating rate. This could be due to the fact that when surfactants are added into the solution, the surfactant particles are more likely to cover the cathode surface that suppress the diffusion of the Ni2+ ions towards the interface results in hindering the co-deposition [21].
3.3. Corrosion resistance of coating

The polarization curves obtained for Ni–P coating co-deposited by different concentrations of Al₂O₃ nano-particles as well as Ni–P coating alone, in 3.5% sodium chloride solution, are shown in Fig. 6. The corrosion potential ($E_{corr}$), corrosion current density ($I_{corr}$) and polarization resistance ($R_p$) calculated using Tafel extrapolation method are given in Table 3. Among the electroless Ni–P coatings co-deposited by different ratios of Al₂O₃ particles, the coating prepared by 20 g/l alumina revealed the lowest $I_{corr}$. There was no passive area for a coating co-deposited by 3 g/l Al₂O₃ in bath, similar to Ni–P coating. However, the passive areas were appeared for the other coatings. Higher the ratio of particles, cause the broader the passive areas. Hence, it can be inferred that the addition of particles promoted the corrosion resistance due to the formation of more passive areas.

<table>
<thead>
<tr>
<th>Coating</th>
<th>Deposit composition (wt%)</th>
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</thead>
<tbody>
<tr>
<td>Electroless Ni–P</td>
<td>Ni</td>
</tr>
<tr>
<td>Electroless Ni–P+3 g/l Al₂O₃</td>
<td>92.42</td>
</tr>
<tr>
<td>Electroless Ni–P+5 g/l Al₂O₃</td>
<td>89.03</td>
</tr>
<tr>
<td>Electroless Ni–P+10 g/l Al₂O₃</td>
<td>88.64</td>
</tr>
<tr>
<td>Electroless Ni–P+20 g/l Al₂O₃</td>
<td>86.68</td>
</tr>
<tr>
<td>Electroless Ni–P+30 g/l Al₂O₃</td>
<td>85.95</td>
</tr>
<tr>
<td>Electroless Ni–P+3 g/l Al₂O₃+1 g/l PEG 1500</td>
<td>87.52</td>
</tr>
<tr>
<td>Electroless Ni–P+3 g/l Al₂O₃+0.5 g/l PEG 1500</td>
<td>84.96</td>
</tr>
<tr>
<td>Electroless Ni–P+3 g/l Al₂O₃+0.3 g/l PEG 1500</td>
<td>85.86</td>
</tr>
</tbody>
</table>

Fig. 2  Surface morphology of Ni–P/3 g/l Al₂O₃ composite coatings plated from the baths with different concentration of PEG 1500: (a) free from surfactant, (b) 0.3 g/l, (c) 0.5 g/l and (d) 1 g/l.
Fig. 7 shows the Nyquist plots obtained for Ni–P coating co-deposited by different concentrations of nano-sized Al₂O₃ as well as electroless Ni–P coatings in 3.5% sodium chloride solution. Plots for all coatings were exhibited a single semicircle in the frequency range of 10 kHz–0.01 Hz. However, the obtained semicircles considerably differ in their size which is an indicative of different corrosion resistances. Occurrence of a single semicircle indicates that the corrosion process of electroless Ni–P coatings involves a single time constant. Hence, it is evident that Ni–P coating with sodium chloride
solution interface exhibits charge transfer behavior. This is in agreement with Balaraju et al. [23], Zeller III [24], Lo et al. [22] and Van der Kouwe [25] works, which they reported a single time constant for their prepared coatings. An equivalent electrical circuit model (Fig. 8) which consists of solution resistance ($R_s$), double layer capacitance ($C_{dl}$) and charge transfer resistance ($R_{ct}$) were utilized to determine the corrosion kinetic parameters for the coatings. Lo et al. [22] and Balaraju et al. [23] have also used a similar model to study the electrochemical impedance behavior of the electroless Ni–P coatings in 3.5% NaCl solution. $R_{ct}$ and $C_{dl}$ values were obtained from the equivalent circuit and impedance data using Zview software are compiled in Table 3. The results obtained from electrochemical impedance studies also indicate a similar trend in the corrosion resistance that was observed by potentiodynamic polarization studies. The $C_{dl}$ values are related to the porosity of the coatings. Hence based on the $C_{dl}$ values it can be inferred that electroless Ni–P co-deposited by high amount of $Al_2O_3$ particles, is relatively less porous compared to those co-deposited by lower amount. However, the addition of nano-particles decreases the porosity relatively in uniform trend.

Co-deposition in 3 g/l $Al_2O_3$ bath showed that $R_{ct}$ is less than that of Ni–P coating. It seems that decreasing the P content adversely affects corrosion resistance. The high corrosion resistance of Ni–P coating is due to the formation of protective layer of metallic nickel and nickel phosphide phase that acts as a barrier to oxygen diffusion on the metal surface [18]. Generally, the corrosion resistance of Ni–P coatings is

<table>
<thead>
<tr>
<th>Sample no</th>
<th>$E_{corr}$ (V)</th>
<th>$I_{corr}$ (A)</th>
<th>$R_{ct}$ ($\Omega$) from impedance</th>
<th>$C_{dl}$ (pF)</th>
<th>$R_p$ ($\Omega$) from polarization</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni–P–3 g/l $Al_2O_3$</td>
<td>−0.23</td>
<td>$7.7 \times 10^{-6}$</td>
<td>69,00</td>
<td>77.7</td>
<td>5040.242</td>
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<tr>
<td>Ni–P–5 g/l $Al_2O_3$</td>
<td>−0.24</td>
<td>$6.3 \times 10^{-6}$</td>
<td>18,638</td>
<td>62.4</td>
<td>11,138.5</td>
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<tr>
<td>Ni–P–10 g/l $Al_2O_3$</td>
<td>−0.25</td>
<td>$3.98 \times 10^{-6}$</td>
<td>20,000</td>
<td>62.3</td>
<td>13,960.53</td>
</tr>
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<td>Ni–P–20 g/l $Al_2O_3$</td>
<td>−0.23</td>
<td>$1.99 \times 10^{-6}$</td>
<td>34,314</td>
<td>31.2</td>
<td>27,941.72</td>
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<tr>
<td>Ni–P–30 g/l $Al_2O_3$</td>
<td>−0.27</td>
<td>$3.98 \times 10^{-6}$</td>
<td>21,238</td>
<td>33.9</td>
<td>9858.833</td>
</tr>
</tbody>
</table>

Fig. 6 Potentiodynamic polarization curves of Ni–P coating specimens with different amount of alumina: 3 g/l, 5 g/l, 10 g/l, 20 g/l and 30 g/l after immersion in 3.5% NaCl solution.

Fig. 7 Nyquist plots of Ni–P composite coatings and Ni–P coating with different amounts of alumina 3 g/l, 5 g/l, 10 g/l, 20 g/l and 30 g/l in the bath after immersion in 3.5% NaCl solution.

Fig. 8 Equivalent circuit where $C_{dl}$: double layer capacitance, $R_s$: solution resistance, and $R_{ct}$: charge transfer resistance.
improved with increasing P content [19]. Mukherjee et al. [26] reported that high phosphorus amorphous Ni–P coatings have very high corrosion resistance. In the present study, a similar trend was observed since all the coatings had an amorphous structure (Fig. 3). The amount of P in specimen co-deposited by Al₂O₃ decreased compared to that of the Al₂O₃ free specimen (Table 2). Because the P content increased in the other specimens, \( R_{ct} \) went up. Meanwhile, this could be attributed to both synergistic effect of addition of Al₂O₃ particles as reinforcement in Ni–P coating matrix and decreasing the coatings porosity too. Higher the Al₂O₃ incorporation, the higher \( R_{ct} \) will be. This trend was not observed in the specimen co-deposited by 30 g/l Alumina in the bath. This may be attributed to the fact that the synergistic effect of alumina as a reinforcement may not overcome the reduction in P content.

Fig. 9 Potentiodynamic polarization curves of Ni–P composite coatings and Ni–P–3 g/l Al₂O₃ with different amounts of surfactant: 0.3 g/l, 0.5 g/l and 1 g/l.

Because the addition of 3 g/l nano-sized alumina in the bath did not increase the corrosion resistance of the coating compared to that of Ni–P electroless coating, the effect of adding the polymeric surfactant in the bath was also studied. According to Fig. 9, the addition of surfactant in small amount even 0.3 g/l creates a passive area in the related curves. Increasing the surfactants more than 0.3 g/l increased the current. Fig. 10 presents the impedance results of the coatings produced in a bath of Ni–P–3 g/l Al₂O₃ with different concentrations of surfactant. From EIS method and the results obtained from simulation from equivalent circuit (Table 4), it was concluded that presence of surfactant in different ratios increases the \( R_e \) of steel substrate in 3.5% NaCl compared to that of Ni–P–3 g/l Al₂O₃ coating significantly. This may be due to the fact that surfactant adsorbs to alumina particle surfaces and prevents agglomeration.

In order to indicate the effects of particle size and addition of surfactant on corrosion properties, it is interesting to note that the polarization resistance of coating codeposited by 3 g/l nano-sized alumina in presence of optimum concentration of surfactant has been obtained in this work even higher than that of coating codeposited by 6 g/l micro-sized alumina studied by Balaraju et al. [3]. Although surfactants prevent agglomeration, the presence of surfactant more than the optimum amount, decelerate the trapping of alumina in the coating. Moreover, a better corrosion resistance may be due to the enrichment of phosphorus on the coating sample, a condition, which is not favored in electroless Ni–P–3 g/l Al₂O₃ coating according to Table 2. Based on \( C_d \) results, the porosity of coating decreased considerably which implies that the corrosion resistance of coated sample was increased.

Fig. 10 Nyquist plots of Ni–P composite coatings and Ni–P–3 g/l Al₂O₃ with different amounts of surfactant: 0.3 g/l, 0.5 g/l and 1 g/l.

4. Conclusion

The codepositions of nano-sized alumina ranging from 3 g/l to 30 g/l in the bath were investigated. The effect of addition of non-ionic surfactant to bath including 3 g/l nano-sized alumina was also studied. The results showed that:

- Even at high codeposition densities, the particles are still well dispersed in the coatings but the agglomeration occurred.
- Increasing the particle concentrations interfere with the electroless Ni–P precipitation. The particles occupied the active sites needed for precipitation of Ni–P electroless coating. Hence, the addition of alumina concentration affects the coating rate deposition inversely.
- Based on EIS and polarization results, the addition of small amounts of alumina nano-sized (3 g/l) to Ni–P electroless coating bath did not improve polarization resistance compared to that of Ni–P coating, however, the addition of higher concentration of alumina improved the corrosion resistance significantly.

### Table 4

<table>
<thead>
<tr>
<th>Sample no</th>
<th>( E_{corr} ) (V)</th>
<th>( I_{corr} ) (A)</th>
<th>( R_p ) (Ω) from polarization</th>
<th>( C_d ) (µF)</th>
<th>( R_e ) (Ω) from impedance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni–P–3 g/l Al₂O₃</td>
<td>−0.23</td>
<td>( 7.7 \times 10^{-6} )</td>
<td>5040.242</td>
<td>77.7</td>
<td>6900</td>
</tr>
<tr>
<td>Ni–P–3 g/l Al₂O₃+0.3 g/l PEG1500</td>
<td>−0.12</td>
<td>( 1.13 \times 10^{-5} )</td>
<td>33,925.32</td>
<td>27</td>
<td>51,041</td>
</tr>
<tr>
<td>Ni–P–3 g/l Al₂O₃+0.5 g/l PEG1500</td>
<td>−0.41</td>
<td>( 4.48 \times 10^{-6} )</td>
<td>32,681.215</td>
<td>26.8</td>
<td>31,731</td>
</tr>
<tr>
<td>Ni–P–3 g/l Al₂O₃+1 g/l PEG1500</td>
<td>−0.7</td>
<td>( 2.51 \times 10^{-5} )</td>
<td>31,731.95</td>
<td>25</td>
<td>16,137</td>
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</table>
● The corrosion resistance of the specimen in presence of surfactant codeposited by 3 g/l alumina was increased even more than that of the specimen codeposited by 20 g/l alumina free from surfactant.

References