Pretreatment Effect on the Properties of Electroless Nano-Crystalline Nickel Phosphorous Coating

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ABSTRACT

The influence of mechanical polishing pre-treatments on steel substrates is investigated in terms of microstructure, deposition rate, adhesion, mechanical and corrosion properties of electroless Ni-P nanocoating with 9-10% wt. of P content. XRD analysis of Ni-P coatings demonstrated the nanocrystalline structure of coating with the grain size of 39 nm. Results showed that pretreatment of substrate can affect the microstructure and modularity of coatings. Coatings with homogeneous surface profile and lower nodule boundaries had higher corrosion resistance. The roughness of the substrate had a direct influence on the surface roughness of the substrate which had a direct influence on the surface roughness of the applied coating. Prog. Color Colorants Coat. 3(2010), 47-57. © Institute for Color Science and Technology.

1. Introduction

The electroless Ni-P coatings as well-known commercial materials has found numerous applications due to excellent properties such as high corrosion resistance, excellent wear resistance, high mechanical properties and solderability. The corrosion properties as well as microstructures of Ni-P coatings are usually affected by their phosphorous content [1-4].

Appropriate surface preparations are essential for the surface conditioning prior to any plating procedure. The anti-corrosion performance of electroless plating Ni-P coatings has been investigated extensively. A concise review of electroless Ni-P coatings and their industrial applications were given by Krishnan [1]. However, available information on the effect of pretreatment on the properties of Ni-P electroless coating is very limited. The corrosion resistance characteristics of electroless Ni-P coating are governed primarily by their phosphorous content and the corresponding structure and mechanical states. Microporosity, roughness and homogeneity, which result from internal stresses within a coating, are...
all strongly impacted by the substrate pretreatment method [2, 5]. C.K. Lee et al. [5] investigated the effect of pretreatment of substrate together with electrochemical properties of Ni-P deposited on carbon fiber reinforced plastic (CFRP) composites. Their studies showed phosphorous content, thickness, wear corrosion and microstructural properties of the electroless Ni-P coatings were strongly correlated with the pre-polishing condition of the substrate.

Liu et al. [6] demonstrated that Ni deposition initiated on the phase or grain boundaries. Fine substrate microstructure provided a large amount of nucleation sites, promoting the nucleation and growth processes of the electroless Ni plating and hence leading to a lower surface roughness on the Mg alloys.

The presence of additives in the electroless bath can affect the adhesion, internal stress and roughness of Ni-P coatings. According to Chen [7] addition of saccharin to the Ni-P bath restrained the coalescence of the islands within the nodules of Ni-Cu-P and consequently decreased the intrinsic stress of the coating as a result the brightness and hardness of the deposit increase. Despite the above criteria, available information on the effect of pretreatment of the substrate, especially metallic substrates, on the properties of electroless Ni-P coatings are very limited.

In this work, the influence of mechanical polishing pre-treatments on steel substrates has been investigated in terms of microstructure, deposition rate, adhesion, electrochemical and corrosion properties of electroless Ni-P coatings with 9-10 % wt. of P content. Corrosion properties of electroless Ni-P coatings were evaluated in 3.5 % wt. of NaCl solution. The surface morphology of coatings after corrosion tests has been evaluated by scanning electron microscopy (SEM).

2. Experimental

2.1. Materials and surface preparation

The deposition was performed on API-5L X65 steel substrates (30×25×15 mm) with the composition considering weight percent (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 surface of substrate was carefully polished with various SiC emery papers (grades #400, #600, #800 and #1200). All the specimens were subjected to the following pre-treatment and plating procedure:

- Ultrasonic cleaning in acetone.
- Cleaning in 20 Vol.% of H₂SO₄ at room temperature (R.T.) for 30 s.
- Cleaning in 5 Vol.% of H₂SO₄ at R.T. for 30 s.
- Electrocleaning in a solution containing 75 g/l sodium hydroxide (NaOH), 25 g/l sodium sulfate (Na₂SO₄), 75g/l sodium carbonate (Na₂CO₃), at R.T. for 20 min. The current density applied was 10 mA/cm² according to ASTM G1.
- Between each of the above mentioned steps the specimen was rinsed by immersion in distilled water at R.T. for 30 s.

2.2. Coating application

After pretreatment, the substrates were dipped into commercial electroless nickel bath (SLOTONIP 70 A from Schlotter) with sodium hypophosphite as reducing agent for 2 hours. Temperature changed within 88-93°C and pH of 4.6 during coating process. This bath provided NiP deposits with a high phosphorous content, 9-10 % P.

2.3. Surface characterization

The surface roughness of all samples prior and post coating application was measured by means of a stylus profilometer. The standard roughness estimation parameter, namely Rₐ was used to describe the surface roughness. The surface morphology and element composition of the coatings were characterized by SEM (CAMSCAN MV2300) equipped with an X-ray energy dispersive spectrometer (EDS). Surface hardness of the coating was determined using a Vickers micro-hardness tester (AMSLER D-6700) with a load of 100 g for a period of 20 s. The microhardness of the specimens was the average of five experimental runs. Coating thickness was determined by observation of cross section of the specimen via SEM. For the thickness determination, specimens were cut in the cross section to expose the surface contours, mounted in a plastic mold, polished following standard metallurgical procedure, etched in 2 % Nital solution, and dried before being subjected to SEM examination. Philip's Xpert pro type X-ray diffractometer (XRD) with a cobalt target was used for determining the microstructure of coatings.

2.4. Adhesion test

Quench test was used to determine the adhesion of
electroless Ni-P coatings. In this test, specimens were heated at 300±10°C for 1 hour then quenched at room temperature in water. The appearance of blisters or peeling taken as the evidence of inadequate adhesion [5,8].

2.5. Electrochemical testing

Electrochemical behaviors of coatings were examined using potentiodynamic polarization technique at room temperature. A potentiostat (EG & G Model 273A) equipped with analytical software was used. All potentials were referred to the Ag/AgCl electrode, using platinum foil as the counter electrode. The potentiodynamic polarization curves were acquired by scanning from -400mV vs. Ag/AgCl under open circuit potential (OCP) to +400mV vs. Ag/AgCl at a scan rate of 1mVs⁻¹. Surface morphology of the specimens after electrochemical test was analyzed by SEM.

3. Results and discussion

3.1. Morphology and component of electroless Ni-P coating

It is well-known that the microstructure of as-deposited electroless Ni-P films varies with the phosphorous content in the film [9-10]. The composition of the electroless Ni-P deposits has been evaluated by energy dispersive spectroscopy (EDS) (Table 1). It is evident that the pretreatment conditions have no significant effect on the phosphorous content of the coatings.

Thickness of deposited Ni-P coatings was found to be 26±2 μm which is shown in Figure 1. The X-Ray diffraction pattern of electroless Ni-P coating obtained from different pretreatment conditions is shown in Figure 2. Measurements carried out according to Debye-Sherrer equation revealed that the coatings have a nanocrystalline structure. The grain size of the coatings is about 39 nm. Such results were obtained by Elsner and Revez [11-12].

<table>
<thead>
<tr>
<th>Table 1: Composition of coating deposited onto different mechanical grinding condition of substrate.</th>
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<tbody>
<tr>
<td><strong>Grinding condition</strong></td>
</tr>
<tr>
<td>------------------------</td>
</tr>
<tr>
<td>Ni</td>
</tr>
<tr>
<td>P</td>
</tr>
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**Figure 1**: SEM micrograph from the cross section of coated sample after polishing with # 400 emery paper.
Figure 2: The X-ray diffraction patterns of electroless Ni-P deposit on API-5L-X65 steel.

Figure 3: The X-ray diffraction patterns of electroless Ni-P deposit on API-5L-X65 steel.

Figure 3 (a) and (b) shows the adhesion test result of samples coated after polishing with #400 and #1200 emery papers. Results show that the adhesion of electroless Ni-P coatings on substrates polished with # 1200 emery paper (Figure (3a)) is insufficient as compared with that of the substrates polished with # 400 emery paper (Figure (3b)). In these samples peeling of coating was appeared after the quench test. The adhesion between electroless nickel and substrate depends essentially on a mechanical bond. Deposition into micro-crevices results in a keying action so that the preparation of the substrate can have substantial effect on adhesion. According to the literatures the adhesive strength increases with increasing surface roughness [13]. So for samples polished with # 1200 emery paper, the adhesion between coating and substrate was inadequate which can
be due to a smooth interface between coating and specimen substrate that can decrease mechanical interlocking between them [1].

Figure 4 shows the roughness of the samples before and after coating. As it can be seen roughness of the substrate decreases with increasing grinding grades. The surface roughness of electroless Ni-P coatings is decreased as surface roughness of the substrate decreases, thereby supporting the observations made by Lu and zangari [14]. This Figure indicates that the changes of surface roughness values after plating is higher for # 100 grade polishing. This behavior can be due to the higher surface roughness of substrate before plating so nucleation site for electrode potion and the nodules are larger in this condition.

The lowest surface roughness among different conditions is related to #1200 grade polishing condition. This is perhaps due to both fine microstructure and leveling ability of electroless plating. During the leveling process more nickel is deposited onto the recessed areas than the protruding areas because the recessed areas are in close proximity to the grains or phase boundaries, where the three dimensional crystallites are mainly initiated. This leveling effect reduces the roughness and the total area of the surface during coating [6, 15].

Figure 5 presents the SEM images of the coating samples. These SEM images demonstrate that nodule size is small, the boundary smears and nodule roughness decreases when surface roughness of the substrate is decreased. These phenomena can be ascribed to "nodule coalescence" [16]. In principle, surface modification of substrate using mechanical polishing can promote instantaneous formation of small and numerous nuclei, which favors the spread of early islands and their merging into a more smooth film. So with decreasing surface roughness, nucleation density increases while nodulation minimizes.

![Figure 4](image.png)

**Figure 4:** Surface roughness (Ra) of the substrate prior and post coating application, obtained after mechanical polishing with various grades of emery paper.
Figure 5: Surface morphology of electroless Ni-P coatings deposited under various polishing conditions of the substrate: (a) # 100, (b) # 400, (c) # 800, (d) # 1200 emery paper.
Figure 6 presents the relationship between the average Vickers micro-hardness HV and various polishing conditions of the substrate. The micro-hardness of electroless Ni-P coatings changes slightly, when the surface roughness of the substrate varies. Rougher surfaces have larger nodule boundaries. These can induce internal stresses in the coating and decrease hardness as can be seen in the specimen coated after grinding with # 100 emery paper. Rougher surfaces are chemically more active and adhesion of the coating on them is much better [6-7]. It is believed that the interfacial mechanical interlocking effect plays an important role in improving adhesion strength and mechanical properties of coatings. Nevertheless various substrate roughnesses influence the coating performance [5-6].

Figure 7 shows the potentiodynamic polarization curves obtained for the electroless Ni-P coating in 3.5 wt. % NaCl solution. Table 2 lists the corrosion potential $E_{corr}$ and corrosion current density $i_{corr}$ of the coatings. Among the electroless Ni-P coatings, the resistance of the specimens polished with #400 emery paper prior to coating have the highest corrosion resistance.
Table 2: Electrochemical data obtained from potentiodynamic polarization curves of electroless Ni-P coatings deposited under various polishing conditions for the substrate.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>E (mV vs. Ag/AgCl)</th>
<th>(i_{corr}) (µA)</th>
</tr>
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<tbody>
<tr>
<td>substrate</td>
<td>-650.7</td>
<td>2.344</td>
</tr>
<tr>
<td>#100</td>
<td>-382.8</td>
<td>0.707</td>
</tr>
<tr>
<td>#400</td>
<td>-330.6</td>
<td>0.416</td>
</tr>
<tr>
<td>#800</td>
<td>-345.6</td>
<td>0.436</td>
</tr>
<tr>
<td>#1200</td>
<td>-350.8</td>
<td>0.467</td>
</tr>
</tbody>
</table>

Figure 7: Potentiodynamic polarization curves of electroless Ni-P coatings deposited at various polishing conditions of substrate in 3.5 wt. % NaCl solution.

After grinding the substrate with #400 grade emery paper a more homogeneous surface profile is formed. Under this condition, there are less surface defects such as nodule boundaries or grooves, dislocations and kink sites, so it can promote greater corrosion resistance of the electroless Ni-P coating.

It is evident from literature reports on electroless Ni-P coatings that preferential dissolution of nickel occurs at open circuit potential, leading to the enrichment of phosphorous on the surface layer.

The enriched phosphorous surface reacts with water to form a layer of adsorbed hypophosphite anions (\(H_2PO_2^-\)). This layer in turn will block the supply of water to the electrode surface, thereby preventing the hydration of nickel which is considered to be the first step to form either soluble \(Ni^{2+}\) species or a passive nickel film [8].

Figure 8 presents SEM images of electroless Ni-P coatings deposited using various polishing conditions of the substrate after potentiodynamic polarization test. Corrosion along the nodule boundaries especially in specimens which were polished with high grade emery paper (> #400) is inevitable. The nodule boundaries were the weak sites of electroless Ni-P coatings. \(Cl^-\) was a kind of strong adsorbing anion which would preferentially adsorb at the nodule boundaries. Then the dynamic balance of \(Ni↔ Ni^{2+}+2e\) would be broken and the soluble \(NiCl_2\) (\(Ni^{2+}+2Cl^- ↔ NiCl_2\)) would be produced. In another word the corrosion of Ni-P coatings initiated from the nodule boundaries. Blocked
corrosion cells were formed under the corrosion products. This corrosion path can grow in the light of autocatalytic reaction and can penetrate the coating quickly [18]. Electroless Ni-P coating obtained by grinding the substrate with #400 emery paper resulted in a very homogenous surface profile and less nodule boundaries, dislocations, kink sites and other surface defects. These characteristics can also account for the high corrosion resistance of the electroless Ni-P coating deposited under this polishing condition.

![Surface morphology of electroless Ni-P coatings deposited under various polishing conditions of substrate after polarization test: (a) # 200, (b) # 400, (c) # 800, (d) # 1200.](image)

**Figure 8:** Surface morphology of electroless Ni-P coatings deposited under various polishing conditions of substrate after polarization test: (a) # 200, (b) # 400, (c) # 800, (d) # 1200.
4. Conclusion
Roughness of substrate affects the nodularity and roughness of the deposit, so roughness of deposit increases with increasing in substrate roughness. Moreover, coating with lower surface defects such as nodule boundaries and kinks have higher corrosion resistance. In addition, adhesion of electroless Ni-P coating to the substrate increases with increasing the surface roughness due to decreasing the mechanical interlocking between deposit and substrate. Furthermore, maximum hardness is achieved by the lower nodularity of deposits.
5. References


