The Effect of accelerator types on the phosphate Zn-%12Ni electrodeposited coating

Fazel Baniasadi¹, Hafez Alizadeh², Amir Hanaei³, Armita Shahbazkhan⁴, Naghi Parvini Ahmadi², Amirhossein Pakseresht³

¹: Corresponding Author at: Department of Materials Science and Engineering, Virginia Tech, USA. E-mail: fbasadi@vt.edu

2: Department of Materials Engineering, Sahand University of Technology, Tabriz, Iran.

3: School of Metallurgy and Materials Engineering, College of Engineering, University of Tehran, Tehran, Iran.

4: Materials Science and Engineering Department, Sharif University of Technology, Iran.

5: Center of Ceramic Coatings, Department of Ceramics, Materials and Energy Research Center, Karaj, Iran.

Abstract

The aim of this study is to investigate the effect of nitrate and nitrite on the weight, morphology and electrochemical properties of phosphated Zn-%12Ni electrodeposited coatings. In order to investigate phase structure and surface morphology of samples, X-ray diffraction and scanning electron microscopy were employed. In order to measure corrosion resistance behavior of the coats, Potentiostat/Galvanostat test was used. The results showed that nitrite accelerator reduces coating weight and surface porosity simultaneously obtaining by phosphating solution. Furthermore, coatings which were obtained by the nitrite accelerator had a higher corrosion resistance than that of the nitrate accelerator.

Keywords: phosphate coating, nitrate, nitrite, Zn-Ni coating, porosity.

1. Introduction

As the matter of steel corrosion protection, Zinc electrodeposits have been vastly engaged[1]. These days, corrosion resistance of conventional Zn coatings is not sufficient because of the permanent industry requires (especially automotive) to reduce coating thickness and to increase corrosion resistance of which at the same time. Therefore, extensive
attempts have recently been made to develop highly corrosion resistant coatings on the steels and as a result, the conventional Zn coatings are being replaced by Zn alloys [2-4]. zinc-nickel, zinc-iron and zinc-cobalt are the most widely utilized alloys for coating, even though zinc-manganese, appeared to have an excellent corrosion resistance, is not commercially available [5].

It has been stated in several studies that corrosion resistance of electrodeposited Zn–Ni alloy coatings within a certain composition range (9–15 wt. %) can be significantly higher (5 to 6 times) than that of pure zinc [5-15].

The useful lifetime of Zn and Zn alloy electrodeposits can be further increased by the formation of a passive film on their surface [16-21]. Chromate and phosphate films are common additional surface treatments used for various applications in different industrial fields [22-30]. An excellent anticorrosive behavior of chromate films is well known; however, the toxicity of Cr (VI) compounds restricts application of this technology[31].

Phosphating is one of the most applicable processes carried out as a final surface treatment[22]. Phosphate coatings, because of their low cost, high phosphating rate, very high corrosion resistance, high wear resistance, and good lubricant and cohesion properties, have important role in automotive industry[32].

Short phosphating time is relatively an advantage for its application in industry. However, without any accelerator in the bath, phosphating process would terminate in about 40 min. Therefore, Such accelerators like nitride, nitrate and chlorate[32], should be added to zinc phosphating bath for accelerating and modifying the coating formation [33-37].

In the acidic bath, nitrate and nitrite react with hydrogen ions. The nitrate reduction is[33]:

\[ NO_3^- + 2H^+ + 2e^- \rightarrow NO_2^- + H_2O \]  \hspace{1cm} (1)

Nitrate in the bath and that produced by reaction (1) also has a reduction reaction like below:

\[ NO_2^- + 2H^+ + 2e^- \rightarrow N_2 + O_2 + H_2O \]  \hspace{1cm} (2)
On the ground that these two reactions consume H\(^+\) rapidly, the local pH increase at the metal-solution interface can increase and facilitate the precipitation of insoluble phosphate quickly.

In the present study two phosphating baths were used for investigation of zinc nitrate and nitrite accelerator effects on the morphology and electrochemical properties of phosphate coating.

2. Experimental

For phosphate coating, cylindrical steel samples with 10mm diameter and 10mm thickness were used. The compositions of the samples are listed in Table 1. For surface preparation, the samples were grinded with sandpaper No 240-1000 first. Mechanical preparation was done to achieve uniform and suitable surface, after that, in order to remove pollutions, oil, and corrosion products, degreasing by 60 g/l NaOH at 60-70°C temperature for 20 minutes, and acid cleaning in 30% HCl solution for 1 minute at ambient temperature were carried out. In order to Zn-12Ni coating formation on samples, a bath with chemical composition and working condition as shown in table 2 was used.

In this research two phosphating bath were used. Components and the operating conditions of phosphating baths are shown in Table 3. In general, phosphate coatings are porous. These porosities can be reduced by Chromic acid or its salts as a final treatment. Hence, an aqueous solution with 0.015% chromic acid was used. After phosphating, samples were immerged in the mentioned solution for 15 seconds at room temperature. Figure 1 shows schematic of phosphating process steps. For phase structure studying, X-ray diffraction (XRD) were performed with a D8 advance diffractometer (Brokers) for Cu radiation (Cu\(k_\alpha\)=1.54Å). The step-scan mode was 2–theta from 10° to 60° with a step size of 0.033°.
The surface morphology of samples was investigated with CAMSCAN2300 Scanning electron microscopy (SEM). Coating weight as a main factor in determining the phosphate coating quality was measured for bath parameters and operating conditions standardization. The weight of phosphate coating was determined by weighing the phosphate samples before and after stripping in 25 g/l chromic acid solution for 2 minutes at 50°C temperature. Coating weight was calculated applying the following equation[33]:

\[
\text{Coating weight (g/cm}^2) = \frac{W_f - W_i}{\text{coated area (cm}^2)} \times 10000
\]  

(3)

In which \(W_f\), \(W_i\) are sample weights after phosphating and stripping in chromic acid, respectively.

The corrosion behavior of phosphated coatings was investigated in a 3.5% NaCl solution at 25 °C. In this regard, a standard three electrode system with a Pt counter electrode, a saturated KCl reference electrode and a sample with the area of 0.785 cm\(^2\) as working electrode was used. Samples were introduced into cell system and allowed to reach open-circuit potential equilibrium (OCP) before electrochemical polarization measurements which took 1800s. Electrochemical polarization measurements were performed under potentiodynamic conditions; BEHPAJOOH BHP2063+ potentiostat/galvanostat with a potential scan rate of 0.001 V s\(^{-1}\). After reaching to OCP, Samples were polarized between ±300 mV around OCP. The corrosion current densities (\(i_{corr}\)) were determined by using the following equation:

\[
i_{corr} = \frac{b_a b_c}{2.303 R_p (b_a + b_c)}
\]  

(4)

In which \(i_{corr}\) is the corrosion current density (A/cm\(^2\)), \(b_a\) and \(b_c\) are the anodic and cathodic Tafel slope (V/decad), respectively, and \(R_p\) is the polarization resistance (Ω).
As the corrosion reactions are initiated at the coating–substrate interface, the reduction of phosphate films with reduced porosity is appreciated. Determination of porosity is an important task in controlling the quality of phosphate films. This parameter could be estimated by applying electrochemical measurements and by determining oxidation and reduction rates on the sample surface. By considering the phosphate coatings as electrochemically inert coats at low anodic over potentials, the porosity of coatings was calculated by using the following equation[25]:

\[
F(\%) = \left( \frac{R_{p,m}}{R_p} \right) 10^{\frac{-\Delta E_{corr}}{b_a}} \times 100
\]  

(5)

Where \( F \) is the phosphate coating porosity (%), \( R_{p,m} \) is the polarization resistance of the bare Zn–Ni (\( \Omega \)), \( R_p \) is the polarization resistance of the phosphated Zn–Ni electrodeposits (\( \Omega \)), \( \Delta E_{corr} \) is the difference in \( E_{corr} \) of Zn–Ni electrode with and without phosphate layers (V), and \( b_a \) is the anodic Tafel slope of the bare Zn–Ni electrodeposits (V/dcad).

3. Result and discussion

3.1. Composition and surface morphology

X-ray diffraction patterns of the phosphate samples obtained by two phosphating solutions are shown in figure 2. According to these patterns, phosphate coating contains hopeite (\( Zn_3(PO_4)_{2.4}H_2O \)) and substrate (\( Ni_5Zn_{21} \)). Hopeite structure has a high adherence and corrosion resistance on the surface.

SEM images of the both phosphate coatings and Zn-Ni substrate without phosphate are shown in figure 3. It can be observed that after phosphate coating, flower structure is formed on the surface. Hopeite structure is look like flowers[38, 39], so this phase is hopeite. Moreover, the XRD results are in agreement with SEM results.
By comparing both phosphate coatings, produced by both solution, It can be perceived that phosphate coating resulted by second solution had finer grains than that of first one. The reason of fine grain size in the second coating is attributed to the presence of nitrite. Nitrite leads to increase in the reaction and the nucleation rate and eventually, causes decrease in grain size of zinc phosphate. As the grain size decreases, flower structure with fine grains are formed (reactions 1, 2).

Principally, the structure of inorganic phosphate coatings depends on their weight. Normally, light-weight phosphate coatings (0.2–1.4 g.m$^{-2}$) have an amorphous structure, while middle-weight (1.4–7.5 g.m$^{-2}$) as well as a heavy-weight (7.5–30 g.m$^{-2}$) phosphate film demonstrates a crystalline structure\[40\].

3.2. Coating weight

Coating weights 7.095 and 11.086 g/m$^2$ were obtained for the second and first phosphating solution at 50°C and 10 minute immersion in solution, respectively. Therefore, phosphate coatings produced by both solutions have a crystalline structure. It was probed from the values of weights that phosphate coating produced by second solution has lower weight than that obtained from the first solution. This weight difference is due to nitrite presence in the second phosphating solution. Nitrite increases the rate of phosphate reaction and decreases the amount of coating on the surface. By increasing the reaction rate, relatively uniform coating is formed on the surface. When surface is covered by coating, increase in the weight is not significant. This is one of the conversion coating characteristics. In the acidic bath, nitrate in the first phosphating solution is reduced firstly. Produced nitrite from nitrate reduction, react with hydrogen. In contrast, in the second phosphating solution nitride is present in the solution and this increases the reaction rate (Equations 1, 2).
3.3. Corrosion behavior in a 3.5% NaCl solution

The corrosion behavior of Zn–Ni electrodeposits with/without phosphate coatings was evaluated by open-circuit (corrosion) potential (Ecorr) monitoring and polarization measurements, carried out in a 3.5% NaCl solution. The values of $i_{\text{corr}}$ and $R_p$ were determined from polarization measurements. The obtained curves are presented in Fig. 4 and the results are listed in Table 4. It can be seen from this data that the corrosion current density of Zn-Ni samples without phosphate coating is 2.551 µcm$^{-2}$.

The ratio of the corrosion resistance with phosphate coating to without phosphate coating is 9.48 for the first solution and 10.85 for the second one. Phosphate coating decreases the corrosion current density ($i_{\text{corr}}$) and increases corrosion resistance in both solutions. The presence of hopeite structure on the surface as a suitable structure in phosphate coating causes an increase in corrosion resistance of coating. Also, it is noticed that the amount of $i_{\text{corr}}$ for phosphating coating produced by the second solution is lower than that of produced by the first solution, and therefore, corrosion resistance of coating increases. Also it is seen that $i_{\text{corr}}$ for phosphate coating produced by second solution is lower than that of the first one, and eventually, corrosion resistance of this coating is higher (table 4). This behavior of the phosphate coating produced by second solution can be explained by fine grain structure of the coating. Surface of coating had uniform and fine grain structure in the presence of nitrite. Therefore, surface porosity decreased, and hence, the contact between corrosive material and substrate was prevented, resulting in corrosion resistance increase.

3.4 Coating porosity

The porosity was %0.000519 for the second solution and 0.0116 for the first solution at 50°C and 10 minutes immersion in solutions. These measures are lower than %1, showing an excellent quality level of produced coats. The obtained values of the phosphated coating
Porosities are in a good agreement with the results of corrosion behavior of phosphated Zn–Ni alloy in the 3.5% NaCl solution (Table 4). The obtained data indicates that the protective abilities of phosphate coatings on Zn–Ni electrodeposits in the 3.5% NaCl solution depend mainly on their porosities. Generally, it can be concluded that the lower porosity being on the surface, the lower corrosion rate of the substrate and the higher corrosion resistance level would be. Porosity in the coating obtained by the second solution is lower than that of the first solution. The reason of low porosity has to do with the presence of the nitrite. Nitrite causes an increase in the phosphate reaction and production of the insoluble phosphate rates on the surface, resulting in surface porosity decrease.

4. Conclusion

The effects of nitrite and nitrate accelerators on the properties of phosphated Zn-%12Ni electrodeposited coatings were investigated. Hopeite Zn₃(PO₄)₂·4H₂O was dominant structure in the phosphated coating produced by both solutions. The type of accelerator had no effect on the obtained structure. Nitrite accelerator increases the formation rate of insoluble phosphate in comparison with nitrate, resulting in a low weight coating production from nitrate solution. Compared to the coating produced by nitrate solution, the corrosion resistance of the coating obtained by nitrite solution is higher, notwithstanding lower weight value of the coating obtained by nitrite solution. Due to its low porosity value, corrosion resistance of the coating obtained by nitrite solution is high. The protective properties of the phosphated coatings are related principally to their porosities. A low value of porosity is beneficial for the corrosion resistance enhancement, since a phosphate layer acts as a physical barrier against corrosive agents.
References


List of Tables

Table 1: Chemical composition of the steels used for phosphate coatings.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Fe</th>
<th>C</th>
<th>P</th>
<th>S</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>% wt.</td>
<td>base</td>
<td>≥0.17</td>
<td>0.04</td>
<td>0.04</td>
<td>0.009</td>
</tr>
</tbody>
</table>
Table 2: Components and the operating conditions of the bath for Zn-12%Ni coating.

<table>
<thead>
<tr>
<th>Solution</th>
<th>Components</th>
<th>Temperature (°C)</th>
<th>Time (min)</th>
<th>Current Density (A/dm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn-12%Ni</td>
<td>NiCl₂, ZnO, NH₄Cl, Na₃P₂O₇</td>
<td>20</td>
<td>8</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>5.59, 14.35, 160.47, 133.82</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 3: Chemical composition and operating condition of the phosphating baths.

<table>
<thead>
<tr>
<th></th>
<th>ZnO (g/l)</th>
<th>H$_3$PO$_4$(cc/L)</th>
<th>HNO$_3$(cc/L)</th>
<th>NaNO$_3$(g/l)</th>
<th>NaNO$_2$(g/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Solution 1</strong></td>
<td>10</td>
<td>17</td>
<td>6</td>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td><strong>Solution 2</strong></td>
<td>11</td>
<td>18</td>
<td>7</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td><strong>pH</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.1-2.4</td>
</tr>
<tr>
<td><strong>Temperature (°C)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>50±5</td>
</tr>
<tr>
<td><strong>Time (min)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>10</td>
</tr>
</tbody>
</table>
Table 4: The electrochemical parameters (corrosion current $i_{corr}$, polarization resistance $R_p$, the difference of $E_{corr}$ between Zn–Ni electrode with and without phosphate layers $\Delta E_{corr}$, anodic and Cathodic Tafel slope $b_a$, $b_c$) of phosphate Zn–Ni alloy electrodes, measured in a 3.5% NaCl solution.

<table>
<thead>
<tr>
<th>Phosphate coating type</th>
<th>$i_{corr}$ (µA/cm$^2$)</th>
<th>$R_p$ (kΩ).cm$^2$</th>
<th>(-) $E_{corr}$ (mV)</th>
<th>$b_a$ (mV/dcad)</th>
<th>(-) $b_c$ (mV/dcad)</th>
<th>$\Delta E_{corr}$ (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Without</td>
<td>2.551</td>
<td>8.676</td>
<td>688</td>
<td>53.09</td>
<td>1237</td>
<td>-</td>
</tr>
<tr>
<td>1</td>
<td>0.269</td>
<td>89.309</td>
<td>859</td>
<td>67.7</td>
<td>300.7</td>
<td>171</td>
</tr>
<tr>
<td>2</td>
<td>0.2351</td>
<td>87.678</td>
<td>812</td>
<td>56.03</td>
<td>308.5</td>
<td>124</td>
</tr>
</tbody>
</table>
Figure captions

Fig. 1. Flow chart depicting the operating sequence involved in phosphating process.

Fig. 2. XRD patterns of the phosphate films on the Zn–Ni (12%) alloy surface. Coating produced by a) first solution b) second solution.

Fig. 3. Scanning electron micrograph of a) Zn-Ni substrate without phosphating, b) phosphate coating produced by first solution, c) phosphate coating produced by second solution.

Fig. 4. Potentiodynamic polarization curves of the phosphated and non-phosphated Zn–Ni alloy electrodes in a 3.5% NaCl solution at 25±2 °C. Potential scan rate is 0.001 V s⁻¹.
Figure a: X-ray diffraction pattern showing peaks for \( \text{Zn}_4(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O} \) and \( \text{Ni}_5\text{Zn}_{21} \).

Figure b: X-ray diffraction pattern showing peaks for \( \text{Zn}_4(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O} \) and \( \text{Ni}_5\text{Zn}_{21} \).