Effect of Ca\(^{2+}\) additives on morphology, composition and corrosion resistant of Zn–12\%Ni phosphate coating

Hafez Alizadeh, Amir Hanaei, Amirhosein Pakseresht, Armita Shahbazkhan, Naghi Parvini Ahmadi, Fazel Baniasadi

ARTICLE INFO

Article history:
Received 29 May 2015
Accepted 8 March 2016
Available online 19 April 2016

Keywords:
Ca\(^{2+}\)
Phosphate coating
Zn–Ni alloy
Hopeite

ABSTRACT

The aim of this study is to investigate the effect of phosphate solution with Ca\(^{2+}\) additives on weight, surface morphology and electrochemical behavior of phosphated Zn–Ni film. In order to characterize structure and morphology of surface, X-ray diffraction (XRD) and scanning electron microscopy (SEM) were applied, respectively. Results showed that the main composition in produced coatings was hopeite Zn\(_3\)(PO\(_4\))\(_2\)·4H\(_2\)O, which has high corrosion resistance. On one hand, in the presence of Ca\(^{2+}\) cations in solution, the weight of phosphate coating decreased, but on the other hand surface uniformity and corrosion resistance of the coating increased.

1. Introduction

Zinc electrodeposits are broadly employed as corrosion protection of steels. Nowadays, the corrosion resistance of conventional Zn coatings is not favorable enough on account of permanent requirement of Industry, especially automotive, to reduce coatings thickness and simultaneously to increase corrosion resistance. Accordingly, so many attempts have been recently made to develop a group of coatings with high level of protection on the steels, resulting in the replacement of conventional Zn coatings by Zn alloys [1–5].

Although zinc–manganese has an excellent corrosion resistance, the most widely utilized alloys as the protective coatings on steels are zinc–nickel, zinc–iron and zinc–cobalt. The reason of that is unavailability of commercial zinc–manganese [6–9].
In a certain composition range (9–15 wt.%), corrosion resistance of electrodeposited Zn–Ni alloy coatings is much higher (5–6 times) than that of pure zinc [2,4,5,10–13].

Formation of a passive film on the surface of steels can further increase profitable lifetime of Zn and Zn alloy electrodeposits. Several industrial fields are using additional surface treatments such as chromate and phosphate films on metals for intended applications [14–18].

The application of chromate films has been restricted on the ground of Cr (VI) toxicity, although it has an excellent anticorrosive behavior [19,20].

Hence, one of the most well-known applications, executed as a final surface treatment, is phosphating. Thanks to cost effectiveness, very high corrosion resistance, good phosphatizing rate, wear resistance, lubricant and cohesion properties of phosphate coatings, they have an impressive role in automotive, aerospace and offshore industries [21].

With the passage of time, Ni and Ca components with Zn have been more employed for properties optimization of phosphate coatings and increase in its properties as divalent or multivalent [22].

In this research, two phosphating baths with in each of which Ca²⁺ cation, for phosphating Zn–Ni(12%) coating were used.

### 2. Experimental

For phosphate coating, steel samples as cylindrical with 10 mm diameter and 10 mm height were used (composition of the samples is listed in Table 1). For preparation of surface, samples were grinded with sandpaper No. 240 to 1000, firstly. After mechanical preparation for achieving uniform and suitable surface, it must be cleaned from pollution and oil and corrosion products. Therefore, degreasing was done by 60 g/l NaOH at 60–70°C temperature for 20 min. After that, acid cleaning was carried out in 30% HCl solution for 1 min at room temperature. In order to form Zn–12%Ni coating on samples, a bath with chemical composition and working condition, as shown in Table 2, was used. After that, phosphating was done as the top layer. Hence, the scope of study is the investigation on the top layer. During Zn–12%Ni coating, when deposition process is being done, hydrogen reduction takes place causing pores in surface morphology. When last layer is applied, phosphate coating (Hopeite) deposits on the porosities of the sub-layer.

In this work two phosphating bath were used. Components and the operating conditions of the phosphating bath 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, to do so a solution of 0.015% chromic acid was used. After phosphating and rising, samples were immerged in the mentioned solution for 15 s at ambient temperature. Fig. 1 shows schematic of phosphating process steps.

In order to study the samples structure, X-ray diffraction were performed with a D8 advance diffractometer (Brokers) using CuKα = 1.54 Å. A step-scan mode was used in the 2-theta range from 10° to 60° with a step length of 0.033°.

### 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></td>
<td>0.17</td>
<td>0.04</td>
<td>0.04</td>
<td>0.009</td>
</tr>
<tr>
<td>Base</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Table 2 – Components and the operating conditions bath for Zn–12%Ni coating.

<table>
<thead>
<tr>
<th>Solution</th>
<th>Components (g/l)</th>
<th>Temperature (°C)</th>
<th>Time (min)</th>
<th>Current density (A/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn–12%Ni</td>
<td>NiCl₂ 5.59, ZnO 14.35, NH₄Cl 160.47, Na₃P₂O₇ 133.82</td>
<td>20</td>
<td>8</td>
<td>15</td>
</tr>
</tbody>
</table>

### Table 3 – Chemical composition and operating conditions of the phosphating baths.

<table>
<thead>
<tr>
<th>Solution</th>
<th>ZnO (g/l)</th>
<th>H₃PO₄ (cc/L)</th>
<th>HNO₃ (cc/L)</th>
<th>NaNO₂ (g/l)</th>
<th>Ca(OH)₂ (g/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solution 1</td>
<td>11</td>
<td>19</td>
<td>7</td>
<td>0.8</td>
<td>–</td>
</tr>
<tr>
<td>Solution 2</td>
<td>11</td>
<td>19</td>
<td>7</td>
<td>0.8</td>
<td>3</td>
</tr>
</tbody>
</table>

Fig. 1 – Flow chart depicting the operating sequence involved in phosphating process.
The surface morphology of samples was investigated with CAMSCAN2300 scanning electron microscopy (SEM). Coating weight as a main factor to determine phosphate coating quality was used for standardization the bath parameters and operating conditions. The weight of phosphate coating was determined by measuring the weight of phosphate samples before and after stripping in 25 g/l chromic acid solution for 2 min at 50 °C temperature. Coating weight was calculated using the following equation [21,23]:

Coating weight (g/m²) = \( \frac{w_2 - w_1}{\text{coated area (cm}^2)\times 10,000} \)  

(1)

In which \( w_1 \) and \( w_2 \) are sample weight after phosphating and stripping in acid chromic, respectively.

To investigate the corrosion behavior of phosphate coatings, corrosion test was carried out in a 3.5% NaCl solution at 25 °C, using a standard three electrode system with a Pt counter electrode, a saturated KCL reference electrode, and a sample with an area of 0.785 cm² as working electrode. Samples were introduced into cell system and allowed to reach open-circuit potential equilibrium (OCP) before electrochemical polarization measurements, which took 1800 s. Electrochemical polarization measurements were performed under potentiodynamic conditions using a BHP2063+ with a potential scan rate of 0.001 V s⁻¹. Samples polarized between ±300 mV around OCP after reached to OCP. The corrosion current densities \( (i_{corr}) \) were determined using the following equation:

\[
i_{corr} = \frac{a_b \times b_c}{2.3 \times R_p(b_a + b_c)}
\]

(2)

where \( i_{corr} \) is the corrosion current densities (A/cm²), \( b_a \) and \( b_c \) are the anodic and cathodic Tafel slope respectively (V/dcad) and \( R_p \) is the polarization resistance (Ω).

3. Results and discussion

3.1. Composition and surface morphology

X-ray diffraction of the phosphate samples, obtained by two phosphating solution, is shown in Fig. 2. According to these patterns, phosphate coating content hopeite \( (\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}) \) and substrate content \( \text{Ni}_5 \text{Zn}_{21} \). However, in the coating produced by second solution, due to the presence of the \( \text{Ca}^{2+} \) ion in solution, Zn–Ca phosphate \( (\text{CaZn}_2(\text{PO}_4)_2 \cdot \text{H}_2\text{O}) \) is formed too. Hopeite structure has a high adherence and corrosion resistant on the surface.

SEM images of the both phosphate coating and Zn–Ni substrate without phosphate are shown in Fig. 3. As it is observed,

![Fig. 2 – XRD patterns of the phosphate films on the Zn–Ni(12%) alloy surface. Coating produced by (a) first solution and (b) second solution.](image-url)
after phosphating, flower structure was formed on the surface, and on the ground of hopeite structure, which looks like flowers, so it can be concluded that hopeite has been formed on the surface. Comparing two phosphate coatings produced by two phosphating solutions, it was observed that the number of blade form hopeite produced by solution content Ca$^{2+}$ ion, were more than that of solution without Ca$^{2+}$ ion. The coating formed by solution with Ca$^{2+}$ has CaZn$_2$(PO$_4$)$_2$(H$_2$O) in its structure causing a difference in hopeite shape in coatings with and without Ca$^{2+}$, which can be seen in SEM images, meaning XRD results are in agreement with SEM results.

The structure of inorganic phosphate coatings depends principally 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 [24]. By applying Eq. (1), the weight of phosphate coating with 10 min immersion in solution at 50 °C temperature produced form first and second phosphating solution 7.095 g/m$^2$ and 9.091 g/m$^2$ obtained, respectively. Therefore, the structure of both phosphate coatings are crystalline. Presence of Ca$^{2+}$ ion is the reason of the higher weight of phosphate coating produced by second solution. Ca$^{2+}$ ion leads to number of the phosphate grains increase per unit of surface. By growing grains, the weight of coating increases.

### 3.2. Corrosion behavior in a 3.5% NaCl solution

The corrosion behavior of Zn–Ni electrodeposits without/with the phosphate coatings was evaluated from the open-circuit (corrosion) potential ($E_{corr}$) monitoring and polarization measurements, carried out in a 3.5% NaCl solution. The values of $i_{corr}$ 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 perceived from this data that the corrosion current density of Zn–Ni samples without phosphate coating is 2.551 μ A cm$^{-2}$.

Ratio of the corrosion resistance, $R_p$, with phosphate coating to without phosphate coating is 10.43 for the first solution and 11.69 for the second. Phosphate coating decreased the
corrosion current densities (\(i_{\text{corr}}\)) and increased corrosion resistant in both solutions. In the presence of the hopeite structure on the surface as a suitable structure in phosphate coating, corrosion resistance of coatings was boosted. Also, it was seen that the amount of the \(i_{\text{corr}}\) for phosphate coating produced by second solution is lower than that of first solution. The reason of this phenomenon is attributed to the presence of Ca\(^{2+}\) ions in the solution. Ca\(^{2+}\) ions would cause blade hopeites grow on the surface. Since phosphate coatings are porous coatings, grows of blades cover porosities on the surface. Accordingly, this decrease contact between substrate and corrosive media and subsequently increased the corrosion resistance of coating. SEM images confirm these results.

### 4. Conclusion

Effect of Ca ion on the phosphate Zn–12%Ni coating behavior was investigated. Based on the XRD and SEM investigations, hopeite (\(Zn_3(PO_4)_2\cdot 4H_2O\)), was the Predominant structure of the phosphate coatings produced by solutions with/without Ca\(^{2+}\). In the phosphate coating produced by solution content Ca\(^{2+}\) ions, some Ca–Zn phosphate was formed as well. It was observed that the number of blades of hopeite, produced by solution content Ca\(^{2+}\) ion, are more than that of solution without Ca\(^{2+}\) ion, so those covers the pores more than the coating without Ca\(^{2+}\). Hence, it seemed that porosity more than the coating produced by solution content Ca\(^{2+}\) ion to the coating produced by solution without Ca\(^{2+}\) is decreasing. Phosphate coating produced by solutions with/without Ca\(^{2+}\) had crystalline structure. Ca\(^{2+}\) ion caused increase in the numbers of the blade-shape hopeite, decreasing the contact between corrosive media and coating, and then growth and phosphate coating weight increased in unit surface.

**Conflicts of interest**

The authors declare no conflicts of interest.

**REFERENCES**


