Corrosion Resistance of Phosphate Conversion Coating on AZ31 Magnesium Alloy

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Abstract— Magnesium alloy substrates are currently used in a number of fields including automobile, aerospace components, mobile phones and metal pretreatment before paint application because of their high strength/weight ratio and low density. In this study, a zinc phosphate coating was formed on AZ31 magnesium alloy from phosphating bath containing H3PO4, ZnO, NaNO2, and NaF. The influence of bath temperature and immersion time on the quality of phosphate coating and its appearance was studied. Salt spray and electrochemical measurements were used to examine the corrosion resistance of the phosphate coating. Results from electrochemical tests showed that the phosphate coating has considerable protection against corrosion. Morphology of phosphate film on magnesium alloy was also investigated by scanning electron microscopy (SEM) and X-ray diffraction (XRD). It was found that the protective properties of zinc phosphate coating were dependent on the temperature. In fact, the temperature showed obvious influence on the structure of the phosphate coating crystals. At lower temperature (40 °C and 50 °C) phosphate coating crystals are flower like but at higher temperature (60 °C and 70 °C) both flower and slab like crystals were observed.

Keywords- phosphate coating; magnesium alloy; corrosion resistance

I. INTRODUCTION (Heading 1)

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II. EXPERIMENTALS

A. Phosphating Formulation

AZ31 magnesium alloy samples with specimen size of 30x30x3 mm were used as substrate material. The chemical composition of AZ31 magnesium alloy used in this study is presented in Table 1.

The samples were polished with 400, 1000 and 1200 grit abrasive paper, and then the samples were degreased in 10 wt.% KOH and rinsed in deionized water to remove all the alkali before the zinc phosphate treatment. The composition of the bath is summarized in Table 2. The phosphating treatments were carried out at four different temperatures of 40, 50, 60 and 70 °C during 5 min and for three various immersion times of 3, 5 and 10 min at 60 °C.

B. Structure and Composition Analysis

Morphology was observed by scanning electron microscope (SEM) (Model XL30 Philips). The energy used for analysis was 16 kV. Phase composition of the phosphate coating was analyzed by X-ray diffraction (XRD) (Model X’ Pert MPD) with a diffractometer operating at 40 kV, 40 mA, using CuKα target.

C. Electrochemical Measurements

The corrosion resistance of the phosphate samples was studied by AUTOLAB G12 electrochemical impedance spectroscopy (EIS). The test was done on 1cm2 area of each sample exposed to 3.5wt. %NaCl solution. The electrochemical system, used in this study, includes Ag/AgCl electrode (as reference electrode), platinum electrode (as auxiliary electrode) and phosphate magnesium sample (as working electrode). Measurements were carried out at frequency range and perturbation of 10 kHz–10 mHz and ±10 mV respectively. Using FRA software, the results obtained by EIS were analyzed.
D. Salt Spray Test

According to the ASTM B117 standard, specimens for salt spray test were exposed in the salt spray cabinet (B.AZMA CTS-114) for 24 h.

III. RESULTS AND DISCUSSIONS

A. Effect of Temperature

1) Effect of temperature on the phosphate coating structure

Morphologies of phosphate coatings at different phosphating solution temperature were studied using SEM. Fig. 1 (a, b) shows the surface morphology of the sample immerses in the phosphating solution with the temperature of 40 °C. Some white flowers are observed on the surface but more than half of the substrate is not still covered. There are some cracks on the surface which are caused by internal stresses [20]. Surface morphology of phosphate coating formed at 50 °C is also shown in Fig. 1 (c, d). Phosphate film precipitated on cracks, therefore fewer cracks are observed at 50 °C. Cracks emerged between the depositions because of the dissolution of magnesium in metal matrix [20]. Phosphate coating (Fig. 1 (a, b, c, d)) consists of both flowers and slab like particles. The phase compositions in the coating were analyzed by XRD, and the result was shown in Fig. 2. It is seen that the phase of crystal phosphate coating formed in phosphating solution at 40 and 50 °C mainly consists of hopeite (Zn₄(PO₄)₂·4H₂O) and zinc (Fig. 1 (a, b)). Phosphate coating is formed at 60 °C is compact and complanate. The whole substrate is coated by slab like crystals and no substrate can be seen (Fig 1. (e, f)). It will be proved further by EIS test that because of the least exposed area, the coating formed at 60 °C has the highest corrosion protection property. However, when temperature further increases, some trans cracks [20] appear in the joint of crystal clusters as presented in Fig. 1 (g, h). According to the XRD analysis, the latter coatings are mainly composed of hopeite (Zn₄(PO₄)₂·4H₂O) and no zinc crystal is detected (Fig. 1 (c, d))

The influence mechanism of phosphatization on magnesium alloy could be analyzed by the relative variation of peak intensity of different phases as phosphatization process temperature increased. As shown in Fig. 3, the diffraction intensity variations of (020) plane of hopeite and the (101) plane of magnesium are different with the increase of phosphating bath temperature. It is shown that the plane of magnesium was approximately linearly decreased with the augmentation of temperature till 60 °C and after that there is a slight increase in the intensity of plane of magnesium at 70 °C. It is seen with increase of temperature, the intensity of plane of hopeite increased.

2) Effect of Temperature on the Corrosion Resistance of Phosphate Coating

a) Impedance measurement

The EIS of the phosphate films at different phosphatization temperature during 5 min is shown in Fig. 4. These diagrams are composed of two parts, but one loop can be seen. It can be attributed to the less immersion time in NaCl solution which results in overlapping these two loops. Using electrical model shown in Fig. 5, different parameters including R_p (charge transfer resistance), R_s (solution resistance), R_c (coating resistance), C_dl (double layer capacitance) and C_c (coating capacitance) are calculated (Table 3). R_p and C are the polarization resistance (in which R_p and R_s are included) and capacitance (in which C_dl and C_c are included) respectively [30,31].

Polarization resistance (R_p) can be used to evaluate the corrosion resistance of zinc phosphate films. In comparison with bare magnesium alloy AZ31, zinc phosphate coating formed at 60 °C has the greatest corrosion resistance. Since at 60 °C coating is compact and almost whole substrate is covered (Fig. 1 (e, f)), zinc phosphate coating is propitious to avoid as much as possible reactions at its interface in NaCl solution. The corrosion protection of phosphate coating formed at 40 °C is the least. Because there are some cracks and also substrate is not covered perfectly by zinc phosphate coating, magnesium can dissolve in the media.

It is well known that [31], phase angle (-θ) is a parameter indicating the coating intactness to the substrate. The lowest and the highest intactness can be seen at -θ near to 0 and 90 respectively. With respect to this fact, increase in -θ may show the increase in coating intactness. Variation of theta at 10 kHz films at different phosphatization temperature during 5 min is also shown in Fig. 4. It is observed that samples with phosphate coating shows increasing behavior of phase angle by increasing in temperature till 60 °C (Table 3). It can be attributed to uniformity of phosphate coatings formed at higher temperature. Decreasing of -θ at 70 °C can be caused by loose coating and new cracks.

It can be concluded when the temperature is lower; the heat of the reaction is not enough to drive the reaction. Therefore, the rate of phosphatation is slow, the phosphate layer is thin and its anti-corrosion property is not good. This is why the phosphate coatings formed at 40 and 50 °C could not afford good corrosion resistance. When the reaction temperature is higher, the activation energy of the reaction declines, the rate of phosphatation will be accelerated and the phosphating film will have good corrosion resistance. At very high temperature, the corrosion resistance is decreased, which may be caused by the dissolution of the film by free-acid ion and the film become

### TABLE 1. CHEMICAL COMPOSITION OF THE AZ31 MAGNESIUM ALLOY

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration (g/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>3.109</td>
</tr>
<tr>
<td>Zn</td>
<td>0.914</td>
</tr>
<tr>
<td>Mn</td>
<td>0.307</td>
</tr>
<tr>
<td>Si</td>
<td>0.004</td>
</tr>
<tr>
<td>Fe</td>
<td>0.024</td>
</tr>
<tr>
<td>Na</td>
<td>0.001</td>
</tr>
<tr>
<td>Ca</td>
<td>0.001&lt;</td>
</tr>
<tr>
<td>Mg</td>
<td>Balance</td>
</tr>
</tbody>
</table>

### TABLE 2. THE COMPOSITIONS OF PHOSPHATING BATH

<table>
<thead>
<tr>
<th>Composition</th>
<th>Concentration (g/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>85% Phosphoric acid</td>
<td>17.5</td>
</tr>
<tr>
<td>Zinc oxide</td>
<td>3.2</td>
</tr>
<tr>
<td>Sodium fluoride</td>
<td>1.7</td>
</tr>
<tr>
<td>Organic amine</td>
<td>0.18</td>
</tr>
<tr>
<td>Tartaric acid</td>
<td>2.2</td>
</tr>
<tr>
<td>Sodium nitrate</td>
<td>0.83</td>
</tr>
</tbody>
</table>

### TABLE 3. EFFECT OF TEMPERATURE ON THE PHOSPHATE COATING

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>R_p (kΩ)</th>
<th>C_dl (μF)</th>
<th>C_c (μF)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>60</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

### FIGURES

1) Surface morphology of phosphate coating formed at different temperatures

2) Effect of temperature on the phosphate coating structure

3) Diffraction intensity variations of different phases

4) Impedance measurement of phosphate films

5) Electrical model for the corrosion resistance of phosphate coating.
loose. So it is very important to choose a proper temperature. For 5 min immersion time, the proper temperature is 60 °C.

It can be concluded when the temperature is lower; the heat of the reaction is not enough to drive the reaction. Therefore, the rate of phosphatation is slow, the phosphate layer is thin and its anti-corrosion property is not good. This is why the phosphate coatings formed at 40 and 50 °C could not afford good corrosion resistance. When the reaction temperature is higher, the activation energy of the reaction declines, the rate of phosphatation will be accelerated and the phosphating film will have good corrosion resistance. At very high temperature, the corrosion resistance is decreased, which may be caused by the dissolution of the film by free-acid ion and the film become loose. So it is very important to choose a proper temperature. For 5 min immersion time, the proper temperature is 60 °C.

b) Salt Spray Tests

Figure 6 shows the images of samples with phosphate coating formed at different temperature after salt spray tests. The surface of the specimen with phosphating process temperature of 60 °C looks smoother than others implying its superior corrosion resistance over the rest specimens. These results are in agreement with the data obtained in the electrochemical (EIS) tests.
Figure 2. XRD results of zinc phosphate coatings formed in phosphating bath at various temperature.

Figure 3. The variations of the hopeite and Mg content in the phosphate coating on magnesium alloy AZ31 formed in phosphating baths at different temperature.

B. Effect of Time on Phosphate Coating

Effect of time on the phosphate coating structure formed at 60 °C (the most proper temperature) is studied. The SEM images of phosphate coating formed at different immersion time are shown in Fig 7. After 3 min immersion in phosphating bath many nucleuses were formed on the surface but these clusters of phosphate particles are not large enough to form a compact coating, so corrosive media can easily reach the substrate. After 5 min some flower and slab like particles were covered the surface and this would blocked the access of corrosion media to the surface. This is why the corrosion resistance of phosphate coating formed after 3 min is less than that of formed after 5 min (Fig 8 and Table 5).

Figure 4. EIS of phosphate coating formed in solution at different temperature during 5 min: a) Nyquist plots; b) Bode-phase plots.

Figure 5. Equivalent circuits used to fit EIS measurement for: a) bare sample b,c) samples with phosphate coating.

<table>
<thead>
<tr>
<th>TABLE3. FITTED RESULTS OF EIS PLOTS IN FIGURE 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phosphating temperature/°C</td>
</tr>
<tr>
<td>40</td>
</tr>
<tr>
<td>50</td>
</tr>
<tr>
<td>60</td>
</tr>
<tr>
<td>70</td>
</tr>
</tbody>
</table>
Figure 6. The salt spray test results of the zinc phosphate coatings on magnesium alloy formed in solution at different temperature: a) 40°C, b) 50°C, c) 60°C, d) 70°C.

In Fig. 7 (c), the coating formed after 10 min is loose and several cracks are seen and the corrosion resistance of coating formed after 10 min immersion decrease comparing with coating formed after 5 min (Fig 7 and Table 4), this may be caused by the dissolution of the film by the free-acid ion [24]. As a result, the best phosphating time is 5 min at 60 °C.

**CONCLUSIONS**

In this study, different phosphate coatings were prepared by changing phosphating solution temperature and immersion time. The properties of coatings were investigated by different methods and the results are as following:

- The protective properties of zinc phosphate coating formed on the surface of the magnesium alloy were dependent on the temperature of the phosphating bath.
- When the duration of the immersion in this phosphating bath is 5 min, the optimum temperature of phosphating process is 60 °C.
The temperature has an obvious influence on the structure of the phosphate coating crystals. At lower temperature (40 °C and 50 °C) phosphate coating crystals are flower like but at higher temperature (60 °C and 70 °C) both flower and slab like crystals are observed on the surface.

The coating was formed on the surface is mainly consist of hopeite (Zn3(PO4)2·4H2O).

References