Characterization of calcium-modified zinc phosphate conversion coatings and their influences on corrosion resistance of AZ31 alloy

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Two kinds of phosphate conversion coatings, including zinc phosphate coating and zinc–calcium phosphate coating, were prepared on the surface of AZ31 alloy in phosphate baths. The morphologies of these coatings were observed using scanning electron microscopy. Their chemical compositions and structures were characterized using energy-dispersive X-ray spectrum, X-ray photoelectron spectroscopy and X-ray diffraction. The corrosion resistance of the coatings was evaluated by potentiodynamic polarization technique. The results show that the flowerlike Zn–Ca phosphate conversion coatings are mainly composed of hopeite (Zn3(PO4)2·4H2O). They have a quite different morphology from the dry-riverbed-like Zn phosphate coatings that consist of MgO, MgF2, Zn or ZnO and hopeite. Both of the zinc and zinc–calcium phosphate coatings can remarkably reduce the corrosion current density of the substrates. The Zn–Ca coating exhibits better corrosion resistance than the Zn coating. Introduction of calcium into the phosphate baths leads to the full crystallinity of the Zn–Ca coating.

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1. Introduction

Magnesium alloys are the lightest metals developed for structural applications such as aerospace and automobile industries [1]. Their applications are currently still not as popular as aluminum alloys because of their poor corrosion resistance [1,2]. To improve their corrosion resistance, one of the most effective approaches is to prepare a coating that can protect the substrates by providing a non-reactive barrier between the metal and its environment. These so-called surface modifications include anodic oxidation [3], electro-less plating [4] and chemical conversion coating [5–11]. Among these approaches, the chemical conversion coatings such as chrome conversion coating [5] have been widely used due to their lower cost and easier operation. However, one of the major components (Cr6+) is detrimental to the environment. It is therefore necessary to find a substitute process with Cr6-free. The phosphate conversion coatings demonstrate a promising application and are considered to be environmentally friendly [12,13].

The phosphate coatings on steels are categorized into five kinds [13]: zinc system coating [14], zinc calcium system, manganese system [15], manganese iron system and iron system coating [16]. However, not all of these coatings are suitable for magnesium alloys. Till now, zinc [17], stannate and manganese [11–13,18] as well as molybdate/phosphate composite conversion coating [19] were reported to be suitable for magnesium alloys. Niu et al. [20] investigated the zinc phosphate coating on AZ91D alloy. They found that the obtained coat has a typical phosphate microstructure, and consists of Zn3(PO4)2·4H2O, Zn, AlPO4 and MgZn2(PO4)2. However, Kouisini [21], Li [22] and Zeng [23] suggested that a well-crystallized zinc phosphate layer, which was formed in phosphating solutions, predominantly consists of hopeite (Zn3(PO4)2·4H2O). Han et al. [24] obtained a phosphate film with Mn11(PO4)12 on the AZ31D alloy in a bath containing phosphate and manganese. All these coatings can more or less improve the corrosion resistance of magnesium alloys.

The introduction of calcium into the phosphate conversion baths results in a microstructural refinement of coatings and consequently an improvement of corrosion resistance [25]. It was reported that the introduction of calcium ions into a Mn-containing phosphate bath can modify the quality of the phosphate conversion coatings on magnesium alloys [25]. A Zn–Ca phosphate conversion coating with homogeneous fine grains on the surface of magnesium alloy AZ31 was successfully prepared in our previous study, which exhibits very good corrosion resistance [23]. However, the beneficial effects of the introduction of calcium on the coatings are not yet well understood. More investigations on this novel zinc–calcium phosphate coating are needed. Therefore, the present work explores the influence of the introduced calcium on the zinc phosphate conversion coatings.
through a comparison between zinc phosphate coating and Zn–Ca coating.

2. Experimental

The materials used were an extruded AZ31 sheet (nominal chemical composition: 3 wt.% Al, 1 wt.% Zn and Mg, Bal.). The plates were machined into samples with a size of 35 mm × 50 mm × 2 mm. These samples were ground with 800 grit SiC papers to ensure the same surface roughness.

Two types of phosphate baths designated as Bath 1 and Bath 2 were used (Table 1). In Bath 1, zinc ions in the form of zinc nitrate were added to favor the formation of a crystalline film of insoluble zinc phosphate (hopeite). Fluoride ions were added as an activation agent [21]. The pH value of the bath was adjusted to approximately 2.5 with phosphoric acid. The samples were treated in Bath 1 at 55 °C for 20 min. In Bath 2, calcium ions in the form of calcium nitrate were added. The processing parameters were the same as that in Bath 1.

The surface morphologies of the coatings were observed by means of scanning electron microscopy (SEM, JSM-64660LV) equipped with energy-dispersive X-ray spectroscopy (EDS). The chemical compositions were analyzed with EDS. The chemical composition of the conversion film was probed using X-ray photoelectron spectroscopy (XPS, ESCAL AB250) with Al Kα radiation (1487 eV) at a power of 300 W and a vacuum degree of 1.0 × 10⁻⁵ Pa. Data was taken after 30 s of ion etching. The data were analyzed with Xpspeak 41 software. In addition, the phosphate coatings were analyzed using X-ray diffraction (XRD) with a Cu target.

The corrosion rates of coatings in 3.5 wt.% NaCl solutions were evaluated at room temperature. The corrosion tests were performed on a potentiostat (EG & G 273) using a classical three electrode cell: platinum as counter electrode, saturated calomel electrode (SCE) as reference electrode, and the sample with an exposed area of 2.84 cm² as working electrode. The scan rate and scan voltage range were ±300 mV, respectively. The polarization curves were recorded after 5 min immersion in the solutions.

3. Results

3.1. Microstructure and composition

Fig. 1 designates that the microstructure of the substrate AZ31 is characterized by α-Mg and AlMnSi phases, which were identified with EDS and will be shown later. No [5] phases observed indicate that AlMnSi rather than Mg₅₋₇Al₁₋₃ phases seem to form preferentially. This case results from the much lower Al content in the AZ31 alloys.

The surface morphologies of Zn and Zn–Ca coatings are shown in Fig. 2a and b, respectively. The morphologies between these two kinds of coatings are quite different. Zn coating has two typical structures: a dry-riverbed-like or network-like morphology (Fig. 2b), which is different from that of the Zn coating. The thickness of the Zn–Ca coatings exhibited in Fig. 2c is approximately 10 μm.

The chemical compositions of these two coatings are shown in Table 2. The film of the Zn coating (Spectrum 1 in Fig. 2a) is composed of the elements: F, O, Mg and a trace of P, indicating the possible existence of MgF₂ and MgO. The white particles in the coating (Spectrum 2 in Fig. 2a) enrich with O and Zn elements, and additionally contain a small quantity of P element, implying the possible existence of crystals Zn, ZnO and the hopeite (Zn₃(PO₄)₂·4H₂O). In contrast to the Zn coating, magnesium and fluoride are not identified in the Zn–Ca coatings. Moreover, the Zn–Ca coating has a much higher content of phosphor. The composition analysis of Spectrum 3 demonstrates that the Zn–Ca coating mainly contains the hopeite crystals and possibly a trace of Ca₃(PO₄)₂.

3.2. XRD analysis

Typical XRD patterns for these two phosphate coatings and the substrate are shown in Fig. 3. The peaks of the substrate correspond to the α-Mg phase. There exists no large difference in diffraction peaks between the substrate and the Zn-coating. The latter reveals the additional weak diffraction peaks corresponding to crystal zinc and hopeite. In the Zn–Ca coating, the tetra-hydrated zinc phosphate (hopeite) is identified [9]. This result confirms that the Zn–Ca conversion coating mainly contains the hopeite crystals.

3.3. XPS analysis

The XPS results of the phosphate conversion coatings are displayed in Fig. 4. The Zn coating predominantly contains Mg, O, P, F, C and Zn elements. The Zn–Ca coating includes Ca, O, P, C, and Zn elements. The results are in good agreement with that obtained by EDS analysis. The high content of carbon detected in the film is due to the adventitious hydrocarbons from the environment, which is common for the XPS results.

The spectra of P, Zn, Ca, Mg and O are further analyzed to discuss the detailed structure of the Zn and Zn–Ca coatings. Fig. 5 shows the high resolution spectra of the major alloying elements in the Zn coating. The high resolution spectrum of P 2p₁/₂ can be divided into two peaks: one at 132.9 eV and another at 133.8 eV (Fig. 5a), which
correspond to PO$_4^{3-}$ and HPO$_4^{2-}$, respectively. This result proves that the conversion film contains the compounds of PO$_4^{3-}$ and HPO$_4^{2-}$. Fig. 5b illustrates that the high-resolution spectrum of Zn2p has two peaks:

\[2\text{Zn} + \text{H}_2\text{O} \rightarrow \text{Zn(OH)}_2 \downarrow + \text{H}_2\]  \hspace{1cm} (1)

\[\text{Zn(OH)}_2 \rightarrow \text{ZnO} + \text{H}_2\text{O}\]  \hspace{1cm} (2)

Both of the high-resolution spectra of Mg 1s (Fig. 5c) and O1s (Fig. 5d) display only one peak, which corresponds to magnesium.

Table 2
Chemical compositions of the coating in different positions (wt.%).

<table>
<thead>
<tr>
<th>Locations</th>
<th>O</th>
<th>F</th>
<th>Mg</th>
<th>P</th>
<th>Zn</th>
<th>Ca</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spectrum 1</td>
<td>26.13</td>
<td>57.68</td>
<td>13.56</td>
<td>2.63</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Spectrum 2</td>
<td>49.80</td>
<td>–</td>
<td>–</td>
<td>1.48</td>
<td>48.73</td>
<td>–</td>
</tr>
<tr>
<td>Spectrum 3</td>
<td>39.79</td>
<td>–</td>
<td>–</td>
<td>15.15</td>
<td>44.52</td>
<td>0.54</td>
</tr>
</tbody>
</table>
fluoride MgF₂ and MgO, respectively. The intensity of Mg 1s and O1s peaks is high owing to the existence of MgF₂ and MgO although they are not detected by XRD.

In the formation of MgF₂, an oxidation reaction occurs as follows:

$$\text{Mg} + 2\text{H}_2\text{O} \rightarrow \text{Mg(OH)}_2 + \text{H}_2\uparrow.$$  \(\text{(3)}\)

Since Mg(OH)₂ is not stable in an acidic solution, further reactions should occur as follows:

$$\text{Mg(OH)}_2 + 2\text{HF} \rightarrow \text{MgF}_2 + 2\text{H}_2\text{O}$$  \(\text{(4)}\)

$$\text{Mg(OH)}_2 \rightarrow \text{MgO} + \text{H}_2\text{O}.$$  \(\text{(5)}\)

The overall reaction occurs as follows [26]:

$$2\text{Mg} + 2\text{H}_2\text{O} + 2\text{F}^- \rightarrow \text{MgO} + \text{MgF}_2 + \text{H}_2\uparrow.$$  \(\text{(6)}\)

In summary, based on the aforementioned analyses of EDS, XRD and XPS, it could be concluded that the Zn coating is mainly composed of four components: Zn or ZnO, MgO, MgF₂ and hopeite.

Similar to the Zn-coating, the high-resolution spectra of P 2p₃/₂, Zn 2p, Ca 2p and O 1s of the Zn–Ca coating are also further analyzed and discussed (Fig. 6). Apparently, the spectra shown in Fig. 6a and b are analogous to that shown in Fig. 5a and b, respectively. The high-resolution spectrum of Ca 2p can be split into two peaks as a result of spin orbit splitting: Ca 2p₃/₂ and Ca 2p₁/₂ (Fig. 6c). Ca 2p₃/₂ is the satellite peak and Ca 2p₁/₂ is the energy peak. The Ca 2p₃/₂ peaks at 347.8 and 346.9 eV can be attributed to calcium hydrogen phosphate hydrate CaHPO₄·2H₂O and tricalcium phosphate Ca₃(PO₄)₂, respectively, which are coincident with the analysis of P2p. The high-resolution spectrum of O 1s can be divided into three peaks: first at 530.0 eV, second at 531.2 eV and third at 532.1 eV (Fig. 6d). These three peaks correspond to ZnO, Zn₃(PO₄)₂·4H₂O and Ca₃(PO₄)₂, respectively. In summary, the Zn–Ca coating mainly contains Zn₃(PO₄)₂·4H₂O with a small quantity of Zn/ZnO, CaHPO₄·2H₂O and Ca₃(PO₄)₂.

3.4. Corrosion resistance

Fig. 7 presents the polarization curves of the AZ31 alloy with and without the phosphate conversion coatings in 3.5 wt.% NaCl solution. The interesting data are listed in Table 3. The free corrosion potential increases from −1.527 for the substrate to about −1.49 V for the AZ31 alloy with phosphate coatings. The corrosion current densities (i_corr) of the substrate, the Zn coating and the Zn–Ca coating are 242.9 μA/cm², 41.8 μA/cm² and 11.5 μA/cm², respectively (Table 3). This result indicates that the coatings can remarkably reduce the corrosion current density. In comparison with the Zn coating, the Zn–Ca coating improves the corrosion resistance of the AZ31 alloy more effectively. It should be mentioned that the assessment of the corrosion resistance is very preliminary only.

4. Discussion

The microstructural characteristic of conversion coatings depends on the bath components and their compositions. The Zn–Ca coating is denser and has much fewer cracks than the Zn coatings. The difference in their surface morphologies is ascribed to the
introduction of calcium ions, which leads to the crystallizing of the phosphate conversion coating.

Both the components and morphology of the present Zn–Ca coating are different from that reported in the previous literatures [25,27]. Song [27] prepared a conversion film in the bath that contained Ca(NO₃)₂ 25 g/l, NH₄H₂PO₄ 25 g/l at a pH value of 3.0. The chemical components of the conversion film include calcium hydrogen phosphate dihydrate CaHPO₄·2H₂O, tricalcium phosphate Ca₃(PO₄)₂ and magnesium phosphate Mg₃(PO₄)₂. The conversion film consists of a large number of leaf-like particles and exhibits a lamellar structure. Liu found that the coating on the surface of AZ91D has a dry-riverbed-like morphology without any crystalline particles which were fabricated in the bath of manganate, phosphate, fluoride and Ca(NO₃)₂ [25]. Therefore, even for the Zn–Ca coatings, the difference in the chemical compositions of the baths results in the large discrepancy in their morphology, structure and constituents.

The hydrogen evolvement can occur at the β phase (Mg₁₇Al₁₂) in AM60 and AZ91D alloys because the β phase is regarded as the microcathode [12,20]. The present substrate alloy is the AZ31 alloy. There exists no β phase besides some AlMnSi particles in this alloy, which were identified by EDS (Fig. 8a and b). After this alloy was immersed into the acidic solution with pH = 2.5 (solution in Bath 2) for 5 s, it started to corrode quickly. The AlMnSi particles with a higher potential act as the cathode, and the α-Mg with a lower potential as the anode [1]:

Anode reaction:

\[
\text{Mg} \rightarrow \text{Mg}^{2+} + 2e^-.
\]  

(7)

Hydrogen is given out from AlMnSi microcathode,

\[
\text{H}_2\text{O} \rightarrow \text{OH}^- + \text{H}^+
\]  

(8)

\[
2\text{H}^+ + 2e^- \rightarrow \text{H}_2.
\]  

(9)

Table 3

<table>
<thead>
<tr>
<th>Sample</th>
<th>(E_{corr}(V))</th>
<th>(i_{corr}(\muA/cm^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>AZ31 substrate</td>
<td>−1.527</td>
<td>242.9</td>
</tr>
<tr>
<td>Zn coating</td>
<td>−1.494</td>
<td>41.8</td>
</tr>
<tr>
<td>Zn–Ca coating</td>
<td>−1.498</td>
<td>11.5</td>
</tr>
</tbody>
</table>

Fig. 6. XPS spectra for the Zn–Ca coating, (a) P 2pₓ/₂, (b) Zn 2p, (c) Ca 2p, and (d) O 1s.

Fig. 7. Polarization curves for the coatings and the AZ31 alloy.
The microcathode reaction (Eq. (8)) results in an increase of the pH value in the local area near the AlMnSi particles, which facilitates the precipitation of insoluble phosphates Mg$_3$(PO$_4$)$_2$, Ca$_3$(PO$_4$)$_2$ and MgF$_2$. Figure 8.

(a) Surface morphologies of the alloy after immersion for 5 s in Bath 2, (b) AlMnSi particles, and (c) precipitate of magnesium phosphate.

Table 4
Solubility product constant of some compounds (298.15 K) [28].

<table>
<thead>
<tr>
<th>Compounds</th>
<th>$K_{sp}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca(OH)$_2$</td>
<td>$5.5 \times 10^{-6}$</td>
</tr>
<tr>
<td>CaHPO$_4$</td>
<td>$1.0 \times 10^{-7}$</td>
</tr>
<tr>
<td>Ca$_3$(PO$_4$)$_2$</td>
<td>$2.0 \times 10^{-20}$</td>
</tr>
<tr>
<td>MgF$_2$</td>
<td>$5.1 \times 10^{-11}$</td>
</tr>
<tr>
<td>Mg(OH)$_2$</td>
<td>$5.6 \times 10^{-12}$</td>
</tr>
<tr>
<td>Mg$_3$(PO$_4$)$_2$</td>
<td>$1.5 \times 10^{-16}$</td>
</tr>
<tr>
<td>Mg$_2$(PO$_4$)$_3$</td>
<td>$1.0 \times 10^{-25}$</td>
</tr>
<tr>
<td>Mg$_3$(PO$_4$)$_2$</td>
<td>$1.0 \times 10^{-29}$</td>
</tr>
<tr>
<td>Zn(OH)$_2$</td>
<td>$5.6 \times 10^{-12}$</td>
</tr>
<tr>
<td>Zn$_3$(PO$_4$)$_2$</td>
<td>$5.1 \times 10^{-11}$</td>
</tr>
<tr>
<td>Zn$_2$(PO$_4$)$_2$</td>
<td>$9.0 \times 10^{-13}$</td>
</tr>
</tbody>
</table>

Figure 9.

(a) Surface morphologies of the alloy after immersion for 15 s in Bath 2; nuclei formation of (b) zinc and calcium phosphate, and (c) zinc phosphate.

The microcathode reaction (Eq. (8)) results in an increase of the pH value in the local area near the AlMnSi particles, which facilitates the precipitation of insoluble phosphates Mg$_3$(PO$_4$)$_2$, Ca$_3$(PO$_4$)$_2$ and MgF$_2$.

Table 5
Thermodynamics data for calcium phosphate and zinc phosphate at 298.15 K. $\Delta H$ is the enthalpy change, $\Delta S$ is the entropy change, and $T$ is the absolute temperature.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>$\Delta H$ (kJ/mol)</th>
<th>$\Delta S$ (J/K mol)</th>
<th>$T \Delta S$ (kJ/mol)</th>
<th>$\Delta G$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca$_3$(PO$_4$)$_2$</td>
<td>62.49</td>
<td>839.3</td>
<td>250.2</td>
<td>$-187.71$</td>
</tr>
<tr>
<td>Zn$_3$(PO$_4$)$_2$</td>
<td>116.97</td>
<td>1017.3</td>
<td>303.3</td>
<td>$-186.33$</td>
</tr>
</tbody>
</table>
Zn₃(PO₄)₂ (Table 4) [12,20]. Due to the large amount of released magnesium ions, the compound Mg₃(PO₄)₂ precipitates preferentially (Fig. 8c) in advance of Ca₃(PO₄)₂ and Zn₃(PO₄)₂, although the latter has a lower solubility product constant. After immersion in Bath 2 for 15 s, more severe attacks occur on the surface (Fig. 9a). The compounds Ca₃(PO₄)₂ and Zn₃(PO₄)₂ are formed (Fig. 9b and c). Table 5 lists the related thermodynamic data [28]. Change in Gibbs free energy, ΔG of the phosphates Ca₃(PO₄)₂ and Zn₃(PO₄)₂ is −187.71 kJ/mol and −186.33 kJ/mol, respectively. These two values are really close, indicating that both calcium phosphate and zinc phosphate can simultaneously precipitate on the surface:

\[
\text{Ca}^{2+} + \text{HPO}_4^{2-} \rightarrow \text{CaHPO}_4
\]

(11)

\[
3\text{CaHPO}_4 \rightarrow \text{Ca}_3(\text{PO}_4)_2 + \text{H}_3\text{PO}_4.
\]

(12)

The precipitates Ca₃(PO₄)₂ and Zn₃(PO₄)₂ have nearly identical formulations, calcium and zinc being both octahedrally coordinated, it
is possible to exchange calcium with zinc ions and thus lead to the formation of zinc hydrogen phosphate Zn(HPO₄)₂·3H₂O, hopeite Zn₃(PO₄)₂·4H₂O and scholzite CaZn₂(PO₄)₂·2H₂O [29]. Zinc doped hopeite is formed by the following mechanisms:

\[
3\text{CaHPO}_4 + 2\text{H}_2\text{O} \rightarrow \text{CaZn}_2(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O} + \text{H}_3\text{PO}_4.
\]  

(13)

Phosphoric acid is consuming during phosphating and therefore the balance in the above equation is shifted to the right.

\[
3\text{Zn}^{2+} + 2\text{H}_2\text{PO}_4^- + 2\text{H}^+ + 4\text{H}_2\text{O} + 6\text{e}^- \rightarrow \text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O} + 3\text{H}_2\text{O}.
\]  

(14)

Zn₃(PO₄)₂·4H₂O is therefore the main ingredient of the Zn–Ca coating. After the phosphate film is formed, it further acts as the microcathode. During the phosphating process in the areas of microcathode, Zn²⁺ ions become zinc by absorbing the electrons and deposits on the surface [20]:

\[
\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn}.
\]  

(15)

Consequently, zinc was detected by XRD in both Zn and Zn–Ca coatings.

The growth of few nuclei of calcium phosphate and zinc phosphate leads to the formation of flower-like phosphates after immersion for 30 s (Fig. 10a). About one third of the film is covered by these flower-like phosphates after immersion for 1.5 min (Fig. 10b). After immersion for 5 min, the film is completely covered by these flower-like phosphates (Fig. 10c). The surface morphology has no obvious variation with further increasing the immersion time from 10 to 30 min (Fig. 10d–f). The formed phosphates are considered as the hopeite after immersion for more than 20 min, because EDS analysis shows that the Zn–Ca coating contains no magnesium and calcium (Table 6).

Based on the previous discussion, a model is proposed to explain the formation of the Zn–Ca coating (Fig. 11). The formation of the Zn–Ca coating follows four steps: (1) dissolution of magnesium and evolution of hydrogen (Fig. 10a), (2) nuclei formation of magnesium phosphate (Fig. 10b), (3) nuclei formation of calcium phosphate and zinc phosphate (Fig. 10c) and (4) growth of the crystalline zinc phosphate (Fig. 10d).

### 5. Conclusions

1. The Zn–Ca coating has a flower-like morphology, which is different from the Zn coating with a dry-riverbed-like morphology. The Zn–Ca coating is denser with almost no cracks than the Zn coatings.
2. The Zn coating contains Zn, ZnO, Mg, MgF₂ and Zn₃(PO₄)₂·4H₂O. The Zn–Ca coating is mainly composed of Zn₃(PO₄)₂·4H₂O, and a small quantity of ZnO, Ca₃(PO₄)₂ and CaHPO₄.
3. The formation of the Zn–Ca coating follows four steps: (1) dissolution of magnesium and evolution of hydrogen, (2) nuclei formation of magnesium phosphate, (3) nuclei formation of calcium phosphate and zinc phosphate and (4) growth of the crystalline zinc phosphate.
4. Both Zn coating and Zn–Ca coating are corrosion resistant than the substrate alloy. In comparison with the former, the latter Zn–Ca coating can reduce the corrosion current density more significantly.

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### References