Formation Behavior of Phosphoric Acid-Based Chemical Conversion Films Containing Alkaline Earth Metals on Magnesium Alloy∗1

Akinori Nakamura1,*2, Satoshi Oue2, Hiroki Koga1,3 and Hiroaki Nakano2

1Department of Materials Process Engineering, Kyushu University, Fukuoka 819–0395, Japan
2Department of Materials Science & Engineering, Kyushu University, Fukuoka 819–0395, Japan
3Fukuoka Industrial Technology Center, Mechanics Electronics Research Institute, Fukuoka 807–0831, Japan

The phosphating of Mg alloy was performed in unagitated solutions containing 1 g·dm⁻³ of Mg, Ca, Sr, and Ba as alkaline earth metals (M) and 50 g·dm⁻³ of H₃PO₄ of pH 3 at 40°C for 3 min. The structure and formation behavior of the phosphate films were investigated. The X-ray diffraction patterns of phosphate films broadened irrespective of the type of alkaline earth metal, which was a characteristic of an amorphous structure. XPS analysis revealed that the valence of P in the phosphate films was pentavalent. The pH in the vicinity of the Mg alloy during phosphating was measured, and the cross section of phosphate coating, the pH in the vicinity of Mg alloys

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1. Introduction

Because Mg alloys are lightweight yet strong, they have been applied for the parts of portable electronic devices, medical related science, automobile, and aircraft industries.1,2 However, the standard electrode potential (E⁰) of Mg is −2.36 V (vs. NHE), which is significantly less noble than other metals. As a result, its corrosion resistance is inferior. Therefore, anticorrosion coatings are generally applied to Mg alloys. In contrast, phosphating is performed to provide wear resistance, lubricating ability, electrical insulation, and decorativeness to metallic materials. Phosphating has been widely used for pre-paint surface preparation because of good adhesion between the phosphated and paint films.3) During the phosphating of Mg alloys, an alkaline earth metal, such as Ca, is employed as an additive.4–10) The phosphate films containing alkaline earth metals are reported to show an excellent corrosion resistance and adhesion with paint films. However, there are many ambiguities with respect to the structure and formation mechanism of the films. Therefore, in this study, Mg, Ca, Sr, and Ba among the alkaline earth metals were added to the solution for phosphating, and the structure and formation mechanism of the films were investigated. The analysis of the film structure was performed using X-ray diffraction (XRD) analysis, XPS analysis, and differential thermogravimetric analysis. To investigate the formation mechanism of phosphate coating, the pH in the vicinity of Mg alloys during phosphating was measured, and the cross section of phosphate films formed in succession using two types of phosphate solutions was analyzed.

Table 1 Chemical pre-treatment conditions for the phosphate coating for Mg alloy.

<table>
<thead>
<tr>
<th>Process</th>
<th>Conditions</th>
</tr>
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<tbody>
<tr>
<td>Degreasing</td>
<td>200 g·dm⁻³ NaOH, 80°C, 5 min</td>
</tr>
<tr>
<td>Pickling</td>
<td>Phosphoric acid-based solution, pH3, 40°C, 1 min</td>
</tr>
<tr>
<td>Desmutting</td>
<td>200 g·dm⁻³ NaOH, 80°C, 5 min</td>
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</tbody>
</table>

Table 2 Phosphate coating conditions for Mg alloy.

<table>
<thead>
<tr>
<th>Bath composition</th>
<th>Operating conditions</th>
<th>Coating conditions</th>
</tr>
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<tbody>
<tr>
<td>H₃(PO₄)₂</td>
<td>Temperature</td>
<td>40°C</td>
</tr>
<tr>
<td>Mg(NO₃)₂·6H₂O</td>
<td>Immersion time</td>
<td>5 min</td>
</tr>
<tr>
<td>Ca(NO₃)₂·4H₂O</td>
<td>pH</td>
<td>3</td>
</tr>
<tr>
<td>Str(NO₃)₁₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ba(NO₃)₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.89 g·dm⁻³</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10.55 g·dm⁻³</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.42 g·dm⁻³</td>
<td></td>
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<tr>
<td>1.9 g·dm⁻³</td>
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</table>

∗1This Paper was Originally Published in Japanese in J. Japan Inst. Met. Mater. 80 (2016) 684–690.
∗2Graduate Student, Kyushu University. Present address: JFE Steel Corporation, Fukuayama 721–8510, Japan
(0.025 mol·dm\(^{-3}\)), Sr(NO\(_3\))\(_2\) 2.416 g·dm\(^{-3}\) (0.011 mol·dm\(^{-3}\)), and Ba(NO\(_3\))\(_2\) 1.9 g·dm\(^{-3}\) (0.0073 mol·dm\(^{-3}\)). The pH was adjusted to 3.0 using NaOH, and phosphating was performed for 3 min of immersion time in an unagitated solution at 40°C.

The phosphate films were exfoliated with a scraper, and the structure was analyzed via XRD (Cu-K\(_\alpha\), tube voltage of 40 kV, tube current of 30 mA). The exfoliated 10 mg phosphate films were examined via differential thermogravimetric analysis (TG-DTA). The chemical bonding state of the phosphate films was investigated using XPS. To elucidate the formation behavior of phosphate films, the phosphating was first performed in a solution containing Ca(NO\(_3\))\(_2\), following which, it was performed in a solution containing Sr(NO\(_3\))\(_2\).

The cross section of the phosphate films was examined via EDX line analysis.

An Sb microelectrode\(^{11}\) was manufactured to investigate the pH change because of hydrogen evolution in the vicinity of Mg alloy substrate during phosphating. The Sb microelectrode was fixed at a distance of 0.1 mm from the Mg alloy, and the potential of Sb electrode was measured during phosphating. The distance between the capillary of the reference electrode and the Sb microelectrode was approximately 2 mm, and the distance between the capillary of the reference electrode and the Mg alloy was identical to that between the Sb microelectrode and the Mg alloy. Using the pH–potential calibration curve that was constructed in advance, we determined the pH near the Mg alloy during the phosphating.

To investigate the effect of alkaline earth metal on the dissociation reaction of phosphoric acid, pH titration curves were measured by dripping 0.1 mol·dm\(^{-3}\) of NaOH at a speed of 2×10\(^{-3}\) dm\(^3\)·min\(^{-1}\) into the 0.12 dm\(^3\) solution containing both 0.01 mol·dm\(^{-3}\) alkaline earth metal and 0.01 mol·dm\(^{-3}\) phosphoric acid. Because the pH in the vicinity of Mg alloy was found to be 10.4 to 12.0 during phosphating via an Sb microelectrode, the pH titration curves were measured to approximately pH 12, and the precipitations that occurred in the solution were analyzed via XRD. The precipitates that occurred during the pH titration curves measurement were collected using a centrifuge tube, and were separated from the supernatant liquid via centrifugal separation. Subsequently, each rinsing and centrifugal separation cycle was repeated 4 times, and the precipitates were dried at 80°C for 24 h (except for the addition of Mg: 48 h). The obtained powder sample was analyzed using XRD.

### 3. Results and Discussion

#### 3.1 Structure of phosphate films

Figure 1 shows the XRD patterns of phosphate films obtained from the solution containing Mg, Ca, Sr, and Ba as alkaline earth metals. In all the phosphate films, multiple peaks were observed. However, these resulted from the metallic Mg, which mixed from the Mg alloy substrate during the exfoliation of phosphate films. Except for the peaks resulting from the metallic Mg, the diffraction patterns of all the phosphate films broadened regardless of the type of alkaline earth metal, characterizing the films as amorphous structures.

Figure 2 shows the heat and mass variation using differential thermogravimetric analysis of phosphate films obtained from the solution containing Sr. In the heat variation curve, an endothermic peak at approximately 100°C and two exothermic peaks around 500°C were observed. In contrast, the mass variation revealed that the mass of phosphate films decreased with increasing temperature and remained constant above 200°C. The inclination of curve of decrease in mass changed somewhat at approximately 100°C to show an endothermic peak. Because the mass of phosphate films was 10 mg before the experiment, the ratio of decrease in mass was 25% above 200°C. The phosphate films obtained from the solutions containing Mg, Ca, and Ba as alkaline earth metals showed almost the same trend as that shown in Fig. 2. In contrast, the heat and mass variations of ammonium magnesium phosphate (Mg\(_2\)NH\(_4\)PO\(_4\)·6H\(_2\)O) determined using differential thermogravimetric analysis has been reported. According to the
the endothermic peaks were present at 90°C and 230°C. At these temperatures, the decrease in mass occurred in two steps, indicating that MgNH₄PO₄·6H₂O changes to Mg₂P₂O₇ via MgNH₄PO₄·H₂O. In addition, the exothermic peak is reported to be present at 600°C, which corresponds to the crystallization of Mg₂P₂O₇. In this study, the endothermic peak at approximately 100°C seems to result from the desorption of crystallization water, and the exothermic peaks at approximately 500°C possibly correspond to the crystallization of phosphate films. Therefore, XRD analysis was performed after heating the phosphate films at 200 and 600°C. However, there was no clear difference in XRD spectra between the before heating, shown in Fig. 1, and the after heating. This shows that the details of endothermic and exothermic peaks obtained via differential thermogravimetric analysis in this study are unknown.

XPS analysis was performed to elucidate the chemical bonding state of phosphate films obtained in this study. Figure 3 shows the XPS spectra of phosphate films obtained from the solutions containing Ca, Sr, and Ba as alkaline earth metals. In all the phosphate films obtained from the solutions containing Ca, Sr, and Ba, the peak position of the P spectrum was almost constant inside the phosphate films after Ar sputtering except for the outermost surface. In all the phosphate films, the binding energy of the peak in the P spectrum was in the range of 136.9–137.4 eV. The binding energy of the P₂p orbital of Na₂HPO₄ is reported to be 137 eV. This indicates that P of the phosphate films obtained in this study is present in a five-valence state. The peak at 136.9 to 137.4 eV in XPS spectra shown in Fig. 3 broadened, showing the possibility of mixing of a multi chemical bonding state.

3.2 Formation behavior of phosphate films

Figure 4 shows the pH change with time in the vicinity of Mg alloy during the phosphating in solutions containing Mg, Ca, Sr and Ba. In all the solutions containing Mg, Ca, Sr, and Ba, pH changed significantly due to a large quantity of hydrogen evolution accompanied by the dissolution of Mg alloy during the initial stage of phosphating. However, the region of stable pH was observed with increasing time. During the initial stage of phosphating, pH does not seem to be accurately measured because of the adhesion of hydrogen to the Sb microelectrode and capillary as a reference electrode. Therefore, the value in the region of stable pH after the fixed time was measured. The stable pH values in the vicinity of Mg alloy during the phosphating in solutions containing Mg, Ca, Sr and Ba were 10.4, 11.4, 10.7, 12.0, respectively. These values were similarly high regardless of the type of alkaline earth metal.

Figure 5 shows the pH titration curves measured for the solutions containing each 0.01 mol·dm⁻³ of alkaline earth metal and phosphoric acid titrated with 0.1 mol·dm⁻³ NaOH. In the solution only containing phosphoric acid, the increase in pH stagnated at three regions of pH 2 to 3, 6 to 7 and 10.5 to 11.5. This is attributed to three steps of dissociation reactions described by eqs. (1)–(3)

\[
\begin{align*}
H₃PO₄ & \rightleftharpoons H₂PO₄⁻ + H⁺ \quad K_1 = 7.5 \times 10^{-3} \\
H₂PO₄⁻ & \rightleftharpoons HPO₄²⁻ + H⁺ \quad K_2 = 6.2 \times 10^{-8} \\
HPO₄²⁻ & \rightleftharpoons PO₄³⁻ + H⁺ \quad K_3 = 2.2 \times 10^{-13}
\end{align*}
\]

The ratio of activity of H₃PO₄ and H₂PO₄⁻ in eq. (1) is 1:1 at pH 2.12. Similarly, the ratio of activity of H₂PO₄⁻ and HPO₄²⁻ in eq. (2) is 1:1 at pH 7.21. The ratio of activity of HPO₄²⁻ and PO₄³⁻ in eq. (3) is 1:1 at pH 12.66. These pH values were almost identical with those at which the increase in pH stagnated, as shown in Fig. 5. In solutions containing an alkaline earth metal, the increase in pH stagnated at three pH regions as well as in solution only containing phosphoric acid. The
The precipitate began to form above pH 6, and the formation amount of precipitate increased significantly above pH 10.5. The precipitate above pH 6 is caused by the formation of hydrogen phosphate salt [MHPO₄, M: alkaline earth metal] containing alkaline earth metal due to dissociation of phosphoric acid to second stage. However, the precipitate above pH 10.5 is caused by the formation of phosphate [M₃(PO₄)₂] containing alkaline earth metal due to dissociation of phosphoric acid to third stage. As shown in Fig. 4, the pH in the vicinity of Mg alloy during the phosphating was lowest in the solution containing Mg, and was second lowest in the solution containing Sr. The stagnation of increase in pH at the lowest pH in the solution containing Mg is attributed to the formation of Mg₃(PO₄)₂ at the lowest pH. The second moderate increase in pH in the solution containing Sr seems to be caused by the formation of Sr₃(PO₄)₂ at lower pH next to Mg.

The structures of precipitates that occurred in solutions during the measurement of pH titration curves that are shown in Fig. 5 were investigated via the XRD analysis. Figure 6 shows the XRD patterns of precipitates that occurred in solutions containing Mg, Ca, Sr, and Ba. Prior to the XRD analysis, the precipitates were dried for 24 h at 80°C. Because the precipitate obtained from the solution containing Mg showed no peak in the XRD pattern, the precipitate containing Mg was dried for 48 h at 80°C. By evaluating the crystallinity of the precipitates from the XRD pattern, the crystallinity was highest for the precipitates obtained from the solution containing Mg. Table 3 shows the result of the XRD pattern obtained using the XRD analysis software of JADE. All the precipitates that occurred in solutions containing Mg, Ca, Sr, and Ba were found to be phosphate [M₃(PO₄)₂] containing alkaline earth metals. The phosphate including OH radical was observed in solutions containing Mg, Ca, and Sr, and apatite [Ca₅(PO₄)₃(OH)] was detected in the solution.
containing Ca. From the XRD analysis of precipitates, the significant increase in precipitates above pH 10.5 in the pH titration curve shown in Fig. 5 was demonstrated to be attributed to the formation of phosphate $[\text{M}_3(\text{PO}_4)_2]$ due to the dissociation of phosphoric acid to third stage.

To investigate the formation behavior of phosphate films, the phosphating was first performed in a solution containing Ca, and it was subsequently performed in another solution containing Sr. The cross section was analyzed using EDX and backscattered electron image. The result is shown in Fig. 7. The backscattered electron image (a) revealed that cracks occurred in phosphate films. The Ca content in phosphate films increased from the Mg alloy substrate toward the top of the films. On the contrary, the Sr content in phosphate films decreased from the Mg alloy substrate toward the top of the films. That is, the phosphate films containing Sr formed first and were concentrated on the upper area of the films, and the films containing Ba formed later and were concentrated at lower area. From the results shown in Figs. 7 and 8, during phosphating, it was found that new phosphate films were formed at the interface between the Mg alloy substrate and phosphate film, and the former phosphate films were boosted up toward the upper area of the films.

During phosphating, during the dissolution of Mg alloy substrate accompanied by hydrogen evolution, phosphoric acid dissociates to third stage, and $\text{PO}_4^{3-}$ ions are formed on Mg alloy. These $\text{PO}_4^{3-}$ ions diffuse from Mg alloy substrate to the top of phosphate films. In contrast, alkaline earth metal ions in solution diffuse in phosphate films from the solution to the Mg alloy substrate. Comparing the diffusion rates of $\text{PO}_4^{3-}$ ions in phosphate films with those of alkaline earth metal ions, the phosphate films seem to be formed at the upper area of films in the case of higher diffusion rate of $\text{PO}_4^{3-}$ ions, whereas the phosphate films are formed at the interface between the Mg alloy substrate and the phosphate films in the case of higher diffusion rate of earth metal ions. In this study, phosphate films containing an alkaline earth metal are formed at the interface between the Mg alloy substrate and the phosphate films. This indicates that the diffusion rate of alkaline earth metal ions in phosphate films is higher than that of the $\text{PO}_4^{3-}$ ions. As determined from the pH change with time in the vicinity of Mg alloy during phosphating (Fig. 4), the dissolution of Mg alloy continues even after the formation of phosphate films. This is because H$_2$O migrates in phosphate films and always contacts the Mg alloy. In the case of defect-free phosphate films, the diffusion of $\text{PO}_4^{3-}$ and alkaline earth metal ions in phosphate films seems to occur extremely slow at room temperature. However, the cracks are reported to be present in phosphate films, and the diffusion of $\text{PO}_4^{3-}$ and alkaline earth metal ions in phosphate films seems to occur.

### Table 3
Precipitates analyzed via the X-ray diffraction (XRD) patterns shown in Fig. 6.

<table>
<thead>
<tr>
<th>Alkaline earth metals</th>
<th>Precipitates</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>$\text{Mg}_6(\text{PO}_4)_2$, $\text{Mg}_3(\text{PO}_4)_2(\text{H}_2\text{O})_8$</td>
</tr>
<tr>
<td>Ca</td>
<td>$\text{Ca}_3(\text{PO}_4)_2$, $\text{Ca}_3(\text{PO}_4)_2(\text{H}_2\text{O})_4$, $\text{Ca}_3(\text{PO}_4)_2(\text{OH})$</td>
</tr>
<tr>
<td>Sr</td>
<td>$\text{Sr}_3(\text{PO}_4)_2$, $\text{Sr}_3(\text{PO}_4)_3(\text{OH})$, $\text{Sr}_3\text{O}_2\text{PO}_4$</td>
</tr>
<tr>
<td>Ba</td>
<td>$\text{Ba}_3(\text{PO}_4)_2$</td>
</tr>
</tbody>
</table>

Fig. 6 XRD patterns of the precipitates that resulted from the solutions containing Mg, Ca, Sr and Ba after measuring the pH titration curves shown in Fig. 5 [(a) Mg, (b) Ca, (c) Sr, (d) Ba]
Fig. 7  Composition profiles in the depth direction of phosphate films. (The phosphate coating was performed first in the solution containing Ca, and successively was performed in the solution containing Sr)

Fig. 8  Composition profiles in the depth direction of phosphate films. (The phosphate coating was performed first in the solution containing Sr, and successively was performed in the solution containing Ba)
through the cracks.

Focusing on the effect of the type of alkaline earth metal on the structure and formation behavior of phosphate films, there was some difference in pH in the vicinity of Mg alloy during phosphating, and the pH was lowest in a solution containing Mg and highest in a solution containing Ba. The thickness of phosphate films is reported to be the largest in a solution containing Mg and the smallest in a solution containing Ba, which corresponds to the pH in the vicinity of Mg alloy during phosphating, i.e., in a solution containing Mg, the phosphate films are formed at a lower pH, and therefore, the thickness appears to increase. In the precipitation that occurred during the measurement of pH titration curve, only Ba$_3$(PO$_4$)$_2$ with the highest crystallinity was formed in a solution containing Ba (Fig. 6, Table 3), which seems to be related to the smallest thickness of phosphate films. The corrosion resistance of phosphate films is reported to be the worst in a solution containing Mg, which is attributed to the formation of cracks because of the increase of phosphate film thickness.

4. Conclusion

The structure and formation behavior of phosphate films of Mg alloy obtained from phosphating solutions containing Mg, Ca, Sr, and Ba as alkaline earth metals were investigated. XRD patterns of all the phosphate films broadened irrespective of the type of alkaline earth metal, which characterizes the films as amorphous structures. XPS analysis revealed that P in phosphate films existed in the five-valence form. The pH in the vicinity of Mg alloy during the phosphating was measured using an Sb microelectrode. The pH of Mg alloy in solutions containing Mg, Ca, Sr, and Ba was 10.4, 11.4, 10.7, 12.0, respectively, indicating that phosphoric acid dissociates to third stage and that phosphate [M$_3$(PO$_4$)$_2$] containing alkaline earth metal (M) is formed during phosphating. The cross section of phosphate films obtained repeatedly from the two types of solution was analyzed. As a result, the new phosphate films were found to be formed at the interface between the Mg alloy substrate and the phosphate film, and the former phosphate films were lifted toward the upper area of the films.

REFERENCES