Influence of Phosphate Concentration on Plasma Electrolytic Oxidation of AZ80 Magnesium Alloy in Alkaline Aluminate Solution

Santosh Prasad Sah, Yoshitaka Aoki and Hiroki Habazaki

Graduate School of Engineering, Hokkaido University, Sapporo 060-8628, Japan

Plasma electrolytic oxidation of AZ80 magnesium alloy in alkaline aluminate electrolytes develops MgAl2O4-based highly crystalline oxide coatings with the morphology changing largely with phosphate concentration in electrolyte. The thickness of the coatings increases with phosphate concentration from 5 μm in phosphate-free electrolyte to ~70 μm in the electrolyte containing 0.1 mol·dm⁻³ phosphate after anodizing for 900 s. The formation of the latter thick coating is associated with intense sparking during anodizing. The thick coatings formed in the electrolytes containing 0.075 and 0.1 mol·dm⁻³ phosphate are highly cracked. In contrast, the coating formed in the electrolyte containing 0.05 mol·dm⁻³ phosphate is relatively uniform, showing the highest corrosion protection in 0.5 mol·dm⁻³ NaCl solution. The coatings consist of two layers, comprising an outer thick layer with high concentration of aluminum and an inner thin magnesium-rich layer.

1. Introduction

Magnesium and its alloys have several advantageous properties, including low density, high specific strength, high thermal conductivity, good electromagnetic shielding characteristics, high damping characteristics, good machinability and easy recyclability, which make them attractive for many industrial applications. However, the wide industrial applications are limited due to their high susceptibility to corrosion. For protection of magnesium alloys from corrosion, surface treatments, forming protective coating layers on the alloy surface, become essential. Chemical conversion coatings and anodizing are the most widely used processes with the latter generally providing thicker and more protective layers. In these processes, the electrolytes containing toxic chromate and fluoride have been often used to form protective coatings, but a coating process, free from chromate and fluoride, must be used recently from environmental point of view.

The behavior of anodic film formation on magnesium is dependent upon the formation voltage, current density, electrolyte and the substrate alloy. Huber showed the relationship between the formation voltage and the characteristics of anodic films formed on magnesium in 1 mol·dm⁻³ NaOH. A very thin film is formed at below 3 V, while a thick anodic film is developed with simultaneous oxygen evolution between 3 and 20 V. A thin protective film is produced again above 20 V. Sparking due to dielectric breakdown occurs above 50 V. Similar filming behavior has been found in alkaline aluminate and phosphate electrolytes and various fluoride-containing electrolytes.

Plasma electrolytic oxidation (PEO) has recently attracted attention to form ceramic-like coatings on aluminum, magnesium and titanium for corrosion and wear resistance. Spark micro-discharge in PEO process modifies the structure, composition and morphology of the oxide layer; a thick, highly crystalline and melt-quenched high temperature oxide coating is formed by this process. Although the oxide is exposed locally and instantaneously at extremely high temperatures (10³–10⁴ K), the metal substrate should be kept at low temperatures, not causing mechanical damage. Thus, PEO is a promising technique to form a thick protective coating on light metals.

There are a number of studies on PEO coatings of magnesium alloys for corrosion protection. The composition, thickness and morphology of the PEO coatings are dependent upon various parameters including electrolyte composition, current density, applied voltage and current wave form. Pulsed DC or AC mode of anodizing is generally used, instead of simple DC anodizing, due to wider possibility of controlling the PEO process. Since electrolyte species are usually highly incorporated into the PEO coating, probably due to plasma-assisted thermo-chemical reactions, the electrolyte composition markedly influences the coating composition.

Aluminium is a beneficial element in enhancing the passivity of magnesium. Khaselev et al. anodized magnesium alloys in alkaline electrolytes containing aluminate spinel phase under continuous sparking. PEO coatings were developed on AM60 magnesium alloy in alkaline aluminate-phosphate electrolytes containing different concentrations of aluminate, and improved corrosion protection of the coatings by increasing aluminate concentration was reported. Since magnesium phosphate is insoluble in aqueous solutions, it is likely that the concentration of phosphate also influences the protective nature of the coatings. Thus, PEO coatings have been developed in this study in alkaline 0.15 mol·dm⁻³ aluminate electrolytes containing different concentration of Na₃PO₄. The results have demonstrated the importance of phosphate concentration on the formation of protective coatings by PEO in alkaline aluminate solution. There is an appropriate phosphate concentration to develop a relatively uniform PEO coating.

2. Experimental

AZ80 magnesium alloy specimens of ~1 mm thickness were cut from an extruded commercial bar. The specimens were wet ground through successive grades of silicon carbide.
The electrolytes used were 0.15 mol dm\(^{-3}\) K\(_2\)Al\(_2\)O\(_4\) + 0.01 mol dm\(^{-3}\) KOH solutions with varied concentrations of Na\(_3\)PO\(_4\) (Table 1). The PEO coating was carried out by applying a rectangular current wave of 600 A m\(^{-2}\) at a frequency of 100 Hz for 900 s using a Takasago, AA/X2 power supply. During the coating, voltage transient was monitored and recorded on PC. In addition, photo-intensity of sparking was recorded by Advantest TQ8215 optical power meter with a TQ82014 silicon photo-diode sensor. Influence of Phosphate Concentration on Plasma Electrolytic Oxidation of AZ80 Magnesium Alloy in Alkaline Aluminate Solution 95. The thickness of the coating was measured by eddy current thickness meter (Kett, LH-300C). Average thickness of the coatings was measured from ten readings on a coating thickness meter (Kett, LH-300C). The protective nature of the coatings against corrosion was evaluated by potentiodynamic polarization in 0.5 mol dm\(^{-3}\) NaCl aqueous solution at ~293 K at a sweep rate of 1 mV s\(^{-1}\).

### Table 1 Composition and conductivity of the electrolytes used.

<table>
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<tr>
<th>Composition of electrolyte (mol dm(^{-3}))</th>
<th>Conductivity (S m(^{-1}))</th>
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<tr>
<td>K(_2)Al(_2)O(_4)</td>
<td>NaOH</td>
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<td>0.015</td>
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Fig. 1 Changes in (a,c) peak voltage and (b,d) photo-intensity during anodizing of AZ80 magnesium alloy at a rectangular AC current of 600 A m\(^{-2}\) (100 Hz) in 0.15 mol dm\(^{-3}\) K\(_2\)Al\(_2\)O\(_4\) + 0.01 mol dm\(^{-3}\) KOH electrolytes with different concentrations of Na\(_3\)PO\(_4\).
known that the voltage of dielectric breakdown changes linearly with logarithm of the conductivity of electrolyte. Thus, similar breakdown voltage should be associated with the fact that the conductivity of the electrolyte does not change largely with phosphate concentration (Table 1). The photointensity increases with anodizing time up to 230 s in the electrolytes containing 0.05 and 0.075 mol dm\(^{-3}\) Na\(_3\)PO\(_4\), while the increase in the photo-intensity is further delayed in the phosphate-free electrolyte. However, the final photo-intensity at 900 s is similar in the electrolytes except that containing 0.1 mol dm\(^{-3}\) Na\(_3\)PO\(_4\). Despite the high photo-intensity in the electrolyte containing 0.1 mol dm\(^{-3}\) Na\(_3\)PO\(_4\) throughout the anodizing time, the anodic peak voltage is lowest between 40 s and 600 s. In this period, the voltage decreases with increasing phosphate concentration, except for the phosphate-free electrolyte. At 900 s the anodic peak voltage becomes \(\sim 400\) V in all the electrolytes. Thus, there is no clear correlation between the photo-intensity and anodic peak voltage.

The coatings formed by anodizing for 900 s thicken with an increase in phosphate concentration (Fig. 2). The coating formed in the phosphate-free electrolyte is only 6 \(\mu\)m thick, while the coating formed in the electrolyte containing 0.1 mol dm\(^{-3}\) Na\(_3\)PO\(_4\) becomes as thick as \(\sim 70\) \(\mu\)m. The formation of the thick coating in the latter electrolyte should be associated with the intense sparking, since the sparking induces development of film materials in PEO process.\(^{32,33}\)

### 3.2 Phases in the PEO coatings

The PEO coating developed in each electrolyte is highly crystalline, as is clearly seen in the XRD patterns shown in Fig. 3. The detected phases are MgAl\(_2\)O\(_4\) and MgO, with the former being a major component. Weak diffraction peaks of Mg\(_2\)(PO\(_4\))\(_2\) are also detected in the coating formed in the electrolyte containing 0.1 mol dm\(^{-3}\) Na\(_3\)PO\(_4\). In this specimen, no substrate peaks are detected in the XRD pattern, in agreement with formation of the thick coating. Aluminum to form MgAl\(_2\)O\(_4\) should be derived mainly from electrolyte, since MgO is a major phase in the coatings formed on AZ91 and AM60 magnesium alloys in aluminate-free alkaline solutions.\(^{13,23,34}\)

### 3.3 Morphology and composition of the PEO coatings

The surface morphologies of the coatings change significantly with the concentration of phosphate (Fig. 4). In the low magnification images, the formation of relatively uniform coatings is evident in the electrolytes free from phosphate (Fig. 4(a)) and containing 0.05 mol dm\(^{-3}\) Na\(_3\)PO\(_4\) (Fig. 4(b)). In contrast, the coatings are highly cracked when they are formed in the electrolytes containing higher concentrations of phosphate (0.075 and 0.1 mol dm\(^{-3}\) Na\(_3\)PO\(_4\)) (Figs. 4(c), 4(d)). The cracks are developed even if the coating thickness was reduced to \(\sim 10\) \(\mu\)m by shorter anodizing time. A characteristic feature of PEO coatings that is the formation of many discharge pores is disclosed in the high magnification images. The pore sizes are in the range of 0.8–2.0 \(\mu\)m in the electrolytes containing 0–0.05 mol dm\(^{-3}\) Na\(_3\)PO\(_4\), while the pore size as large as \(\sim 7\) \(\mu\)m is developed in the electrolytes containing 0.075 and 0.1 mol dm\(^{-3}\) Na\(_3\)PO\(_4\). In the latter two electrolytes the pores of 0.2–2.0 \(\mu\)m are also present. The large discharge pores should be developed as a consequence of intense sparking. The intense sparking in the electrolyte containing 0.1 mol dm\(^{-3}\) Na\(_3\)PO\(_4\) induces the development of thick coating and formation of large discharge pores.

Cross-sectional observations (Fig. 5) reveal the thickening of the coatings with phosphate concentration. In the coating...
developed in the phosphate-free electrolyte, high density of pores is present in the coating, but thickness is relatively uniform. The thickness becomes approximately twice when 0.05 mol dm⁻³ Na₃PO₄ is added in the electrolyte. This coating is also highly porous, but the porosity appears to be slightly lower than that formed in the phosphate-free electrolyte. The thickness is also relatively uniform. In contrast, the coatings do not cover uniformly the substrate when the electrolytes containing 0.075 and 0.1 mol dm⁻³ Na₃PO₄ are used (Figs. 5(c), 5(d)). There are several regions where no coating material covers the substrate, probably associated mainly with cracking in the coatings.

The compositions of the coatings have been examined by EDS elemental mapping of the cross-sections (Figs. 6–8). The coatings consist of two layers. The major part of the coatings is composed of an aluminum-rich oxide layer, in which MgAl₂O₄ is a main phase. A thin inner layer, less than 1 μm thick, developed in all the electrolytes, is deficient of aluminum. Thus, MgO may be a main component in this inner layer. From the comparison of the magnesium and aluminum maps in each coating, it is obvious that the composition is not uniform in the outer main layer of the coatings. Phosphorus species are incorporated into the coating formed in the phosphate-containing electrolytes, and they are enriched approximately in the inner half of the coatings.

EDS point analysis revealed that phosphorus was contained in the inner magnesium-rich layer, and the content increased from ~3 at% in 0.05 mol dm⁻³ Na₃PO₄ to ~14 at% in 0.1 mol dm⁻³ Na₃PO₄. Aluminum (~10 at%) was also contained in the inner layer. Compared with the inner layer, the phosphorus content in the outer layer was low. The phosphorus content in the outer layer was as low as ~3 at% even when the coating was formed in the electrolyte containing 0.1 mol dm⁻³ Na₃PO₄. The aluminum content in the outer main layer of the coatings (23–32 at%) is comparable or even higher than the magnesium content in this layer (18–32 at%).

### 3.4 Corrosion protection of the PEO coatings

Corrosion protection of the PEO coatings, examined by anodic potentiodynamic polarization in 0.5 mol dm⁻³ NaCl solution (Fig. 10), reflects the morphology of the coatings shown in Figs. 4 and 5. The lowest anodic current density is obtained for the coating formed in the electrolyte containing 0.05 mol dm⁻³ Na₃PO₄. This coated specimen shows the anodic current density of 1 mA m⁻² or less up to ~1.4 V vs Ag/AgCl. Then, the current density increases an order of magnitude at about ~1.37 V vs Ag/AgCl, probably local breakdown of the coating through the pores. The specimens with highly cracked coatings formed in the electrolytes containing higher phosphate concentrations revealed higher anodic current density. Further higher anodic current density is obtained for the specimen coated in the phosphate-free electrolyte, due to the thin coating with high porosity density.
Fig. 5 Scanning electron micrographs of cross-sections of the PEO coatings formed by anodizing of AZ80 magnesium alloy at a rectangular AC current of 600 A m\(^{-2}\) (100 Hz) in 0.15 mol dm\(^{-3}\) \(K_2Al_2O_4\) + 0.01 mol dm\(^{-3}\) KOH electrolytes with (a) 0 mol dm\(^{-3}\), (b) 0.05 mol dm\(^{-3}\), (c) 0.075 mol dm\(^{-3}\) and (d) 0.1 mol dm\(^{-3}\) \(Na_3PO_4\) for 900 s.

Fig. 6 Scanning electron micrograph and X-ray images of magnesium, aluminum and oxygen of a cross-section of the PEO coating formed by anodizing of AZ80 magnesium alloy at a rectangular AC current of 600 A m\(^{-2}\) (100 Hz) in 0.15 mol dm\(^{-3}\) \(K_2Al_2O_4\) + 0.01 mol dm\(^{-3}\) KOH electrolyte for 900 s.
4. Discussion

Findings disclose the significant influence of phosphate concentration on thickness and morphology of the PEO coatings formed in alkaline aluminate electrolyte. The coating thickens with phosphate concentration. Since the electric charge passed during coating is the same in all the electrolytes, the increase in phosphate concentration enhances the efficiency of coating formation. Magnesium phosphate is insoluble in alkaline solution, promoting the coating formation. In addition, intense sparking in the electrolyte containing 0.1 mol dm\(^{-3}\) Na\(_3\)PO\(_4\) induces thick coating, since the development of coating material in PEO process is associated with sparking.\(^6,32,33\) The enhancement of occurrence of sparking by addition of phosphate was also reported recently.\(^{35}\) The peak voltage increases more rapidly in the electrolyte containing 0.1 mol dm\(^{-3}\) Na\(_3\)PO\(_4\) during initial anodizing (Fig. 1(a)), indicating the increased field strength in the barrier layer that supports the electric field and/or suppressed dissolution magnesium species. In general, phosphate incorporation into anodic oxide increases the field strength in growing barrier-type anodic oxide films. It is likely that the field strength in the inner barrier layer of the present oxide films is increased in the electrolytes with higher phosphate concentrations, leading to the more intense sparking.

A main part of the coating developed contains high concentration of aluminum species, as shown in Figs. 6–9. From XRD patterns (Fig. 3), aluminum should be present in MgAl\(_2\)O\(_4\) spinel phase. It is known that aluminum species are incorporated into the anodic films formed on magnesium and its alloys in aluminate electrolytes.\(^{27,28}\) Verdier et al. formed PEO coatings on AM60 magnesium alloy in mixed solutions of KOH, KF, Na\(_2\)HPO\(_4\) and different concentrations of
aluminate.\textsuperscript{23) XRD patterns revealed that no MgAl$_2$O$_4$ peaks are detected in the coating formed in the aluminate-free electrolyte. The content of MgAl$_2$O$_4$ increased with the concentration of aluminate. In this context, aluminum species should be incorporated mainly from electrolyte into the present coatings, although aluminum derived from substrate may also contribute to the formation of MgAl$_2$O$_4$. Phosphate ions are also incorporated into the coatings, particularly in the inner part of the coatings. Their content in coating increases with the concentration of phosphate in electrolyte. Higher concentration of phosphorus species in the inner part of PEO coatings was also found when Ti-15V-3Al-3Cr-3Sn alloy was anodized in the similar electrolyte.\textsuperscript{36) The incorporation of phosphate in anodic oxide films on magnesium is known,\textsuperscript{37–41) but the enrichment in the inner part of the present coating is the subject of further study.

Beneath the main coating layer containing the high concentration of aluminum, a thin magnesium-rich layer, less than 1 µm thick, is developed (Figs. 6–8). The layer is compact and apparently pore-free. Since the aluminum content in this layer is relatively low, this layer seems to be formed without influence of dielectric breakdown of coating. Thus, the development of the outer main coating layer is associated with dielectric breakdown; new coating material is developed mainly near the coating/metal interface with electrolyte penetrating through a short-circuit path.\textsuperscript{32,42,43) The inner thin layer may be formed due to usual ionic transport in anodic oxide under the high electric field. This is
consistent with the estimation that an anodic film of ~600 nm thickness is formed, since the formation ratio of anodic films on magnesium alloys is 1.3–1.5 nm V⁻¹.⁴⁴)

In chloride-containing solutions, the coating formed in the electrolyte containing 0.05 mol⋅dm⁻³ phosphate showed the highest corrosion protection. This fact is in agreement with the morphology of the coatings (Figs. 4 and 5). The coatings formed in the electrolyte containing higher phosphate concentrations contain high density of cracks, such that corrosive solution penetrates readily into the substrate surface through the cracks. The coatings formed in the electrolytes free from phosphate and containing 0.05 mol⋅dm⁻³ phosphate are crack-free or crack-less and the substrate surface is covered entirely with the coatings of uniform thickness. However, the former coating is as high as ~5 μm and has relatively high density of pores, showing relatively poor corrosion protectiveness. Thus, the relatively uniform coating of ~15 μm thickness, formed in the electrolyte containing 0.05 mol⋅dm⁻³ phosphate reveals the highest protective properties. However, this coating also contains high porosity, such that long-term stability for corrosion was not sufficiently high. Thus, further study is necessary to reduce the porosity of the PEO coating. Recently, it has been reported that highly dense PEO coatings can be developed by adjusting current wave forms in PEO coating of aluminum alloys.⁴⁵) The importance of negative charge density has been pointed out. Further modification of anodizing parameters in a suitable composition of electrolyte in PEO coating of magnesium alloys may lead to the development of coatings with long-term stability against corrosion.

5. Conclusions

1) Plasma electrolytic oxidation of AZ80 magnesium alloy in alkaline aluminate electrolytes containing different concentrations of phosphate produces two-layered coatings, comprising an outer main layer with relatively high content of aluminum, and a thin inner magnesium-rich layer. MgAl₂O₄ is a major phase in the outer layer. Phosphorus species are present in the coating, particularly in the inner part of the coating.

2) The thickness of the coatings increases with the concentration of phosphate in electrolyte. The coating formed in the electrolyte containing 0.1 mol⋅dm⁻³ Na₃PO₄ is as thick as ~70 μm.

3) The coatings of uniform thickness are developed in the electrolytes containing up to 0.05 mol⋅dm⁻³ phosphate. Further increase in the phosphate concentration results in the formation of highly cracked coatings.

4) The coating of uniform thickness, formed in the electrolyte containing 0.05 mol⋅dm⁻³ Na₃PO₄ reveals the highest corrosion protective nature in 0.5 mol⋅dm⁻³ NaCl solution.

Acknowledgments

The present work was supported in part by Grant-in-Aids for Scientific Research (A) No. 19206077 from the Japan Society for the Promotion of Science as well as by the Global COE Program (Project No. B01: Catalysis as the Basis for Innovation in Materials Science) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

REFERENCES

23) S. Verdiere, M. Boinet, S. Maximovitch and F. Daland: Corros. Sci. 47