

The Characteristic Study of Plasma Electrolytic Oxidation in AZ31B Magnesium Alloy

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and Yeon-Jae Jung***

Abstract – In this study low voltage Plasma Electrolytic Oxidation (PEO) was utilized to eliminate high voltage PEO drawbacks such as high cost, dimensional deformation and porosity. Low voltage PEO produces a thin coating which causes low corrosion resistance. In order to solve such problem, 0.1~0.6M pyrophosphates were added in a bath containing 1.4M NaOH, and 0.35M Na₂SiO₃. 70 V PEO was conducted at 25°C for 3 minutes. Chemical composition, morphology and corrosion resistance of the anodized coating were analyzed. The anodized film was composed of MgO, Mg₂SiO₄, and Mg₂O₇P₂. The morphology of film showed appropriately dense structure and low porosity in the anodized layers. It is found that low voltage Plasma Electrolytic Oxidation in cooperation with phosphating treatment can provide a good corrosion protection for the AZ31B magnesium alloy.

Keywords: Magnesium, AZ31B, Plasma electrolytic oxidation, Pyrophosphate, Low voltage

1. Introduction

Magnesium alloys are commonly utilized as lightweight materials having significantly good physico-chemical properties such as relatively high specific strength, electromagnetic shielding, vibration damping ability and dimensional stability. Due to their higher specific strength, outstanding castability and excellent mechanical properties, magnesium alloys are used in a wide range of industries such as the automotive, aerospace and communication industries in order to meet the demands for environmental protection and energy saving requirements. However, magnesium-based alloys are susceptible to galvanic corrosion, and thus the widespread applications are severely limited [1-9].

Fortunately, a series of surface modification techniques, such as electrochemical coating, chemical conversion coatings, hydride coating, anodizing, gas-phase deposition, laser surface alloying and polymer coating have been developed to improve the corrosion resistance of magnesium alloys over the last few decades [10]. Among these techniques, plasma electrolytic oxidation (PEO) is a well-known technique for its ability to obtain high quality ceramic anodized coatings with perfect corrosion resistance, high hardness and good adhesion to substrates [11-14]. AZ31B magnesium alloy is hardly oxidized by conventional anodizing techniques because of its compact and dense surface, as compared with the case of cast materials (ex AZ91D). The plasma electrolytic oxidation seems to be

more appropriate for AZ31B magnesium alloy than for AZ91D alloy because the former alloy has denser surface. Although the remarkable progress has been made on the synthesis of the PEO coatings, very few researches on the effects of the compositions and microstructures of substrates on the formation and properties of the PEO coatings in cooperation with phosphating treatment are done, as existing reports on only anodized magnesium alloys pay more attention on developing optimization procedures for electrical parameters and electrolyte compositions [15, 16]. Plasma electrolytic oxidation has been applied to many magnesium products to improve their corrosion resistance. Generally, high voltage is applied in PEO process. However, such high voltage operation results in high cost and several other practical problems such as burning on edges of products because of high local current convergence as well as electric shock in working field. Moreover, the resultant anodized coatings generally consist of porous layer exhibiting low corrosion resistance. As a consequence, it is essential to find a solution for these drawbacks, which can be applicable in industrial field [17-18].

In this work low PEO method was employed with constant low voltage as driving force for anodized film growth. However, low voltage PEO films have insufficient thickness for satisfactory corrosion resistance. In order to overcome this problem, pyrophosphate was added to electrolytic bath, and its effect on the corrosion resistance of the oxidized film was investigated for the PEO coatings in cooperation with phosphating treatment.

2. Experimental

AZ31B magnesium alloys used as anode in this

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experiment were provided by POSCO (Korea). Specimens with a size of 50×50×0.8 mm were cut from AZ31B wrought sheet. Surface roughness was adjusted by mechanically polishing using SiC paper #1,000. A schematic diagram of the experiment equipment setup is shown in Fig. 1. Cooling device was installed to prevent the solution from heating. Cathode was a graphite plate.

The PEO processes were carried out in pyrophosphate bath applying 70V DC of power source at 25 °C. Table 1 lists chemical composition of the bath and operating conditions.

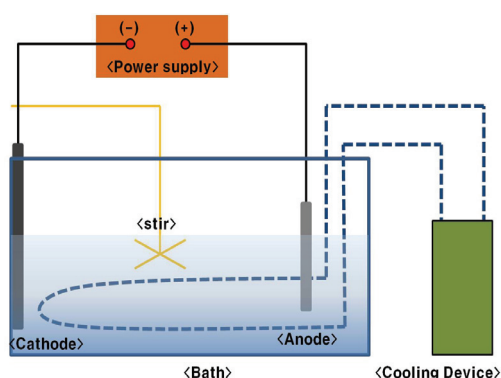


Fig. 1. Schematic diagram of experiment equipment setup

Table 1. Composition of the anodizing bath and operating conditions for PEO process of AZ31D Mg alloy

Bath composition	Operating conditions
Sodium Hydroxide 1.4M	Temperature : 25 °C
Sodium Silicate 0.35M	Voltage : 70V
Potassium Pyrophosphate 0.1 ~ 0.6M	Time : 3min

The crystallinity and phase of the coatings were identified by using a Rigaku D/MAX-2200H (Japan) X-Ray diffraction equipment. Surface morphology and thickness of the oxidized film were investigated using a scanning electron microscopy (SEM, Hitachi, S-4200, Japan). The atomic ratio of oxidized film was determined by Energy Dispersive X-ray Spectroscopy (EDS, Hitachi, S-4200, Japan). Surface roughness was observed by Optical Surface Measurement (INNOWEP, OPTPTOP, Germany). The corrosion resistance of the oxidized film was measured by Electrochemistry Analysis Equipment (AMERREK PAR, VERSASTATE4) in 3.5% NaCl solution.

2.1 Main title and author affiliation

The font size of the title and the authors is bold 16 pt and 12 pt, respectively. And the authors' affiliation should appear in the lower left corner of the first page as a footnote.

2.2 Abstract and keywords

Before the body of the abstract and the keywords, the

terms ‘**Abstract -**’ and ‘**Keywords:**’ should come in bold 11 pts, respectively. Abstract should be limited to 50~200 words and keywords are usually composed of about five terms or phrases in alphabetical order, separated by commas.

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Full-length papers generally, for example, consist of introduction, nomenclature, if any, main parts of the body, conclusions. The font sizes of the section headings are bold 11 pts and those of the subsection headings bold 10 pts, respectively.

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Citations must be numbered consecutively in square brackets [1]. The sentence punctuation should be put after the brackets [2]. Multiple references [2, 3] are each numbered with separate brackets [1-3]. In sentences, refer simply to the reference number, as in [3]. Do not use ‘Ref. [3]’ or ‘reference [3]’ except at the beginning of a sentence. The list of references should be arranged in the order of citation in text, not in alphabetical order. The photographs, names, the vitae and the research interests of the authors should be given at the end of the paper.

3. Results and Discussion

Fig. 2 shows the X-ray diffraction patterns taken from the surfaces on AZ31B PEO-treated at different pyrophosphate concentrations. The phases of the anodized films were mainly composed of MgO, Mg₂SiO₄, and Mg₂O₇P₂ with no amorphous phases.

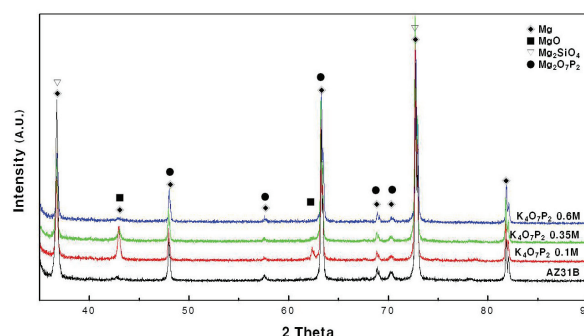
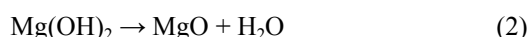


Fig. 2. XRD patterns of AZ31B Mg alloy PEO-treated in the baths containing 0.1~0.6M Potassium Pyrophosphate.

The following mechanism was proposed for formation of anodized film [19] as follows:

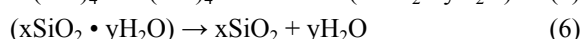
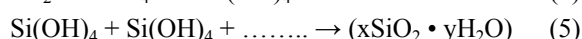
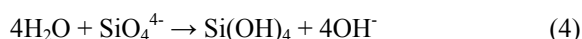


Dehydration of Mg(OH)₂:



The MgO can form via the formation of magnesium hydroxide (Reaction (1)) and its subsequent dehydration (Reaction (2)). MgO can also form via PEO process

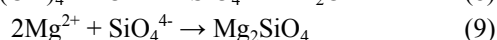
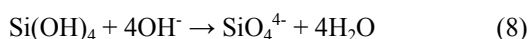
Na_2SiO_3 existed as Si(OH)_4 in alkaline solution which reacts at electrode surface due to the plasma heat effect [20, 21]:



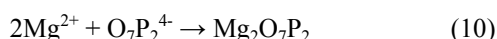
Then, MgO and SiO_2 react to form Mg_2SiO_4 that melts and solidifies during plasma spark discharge stage according to the following reaction:



On the other hand, Mg_2SiO_4 can form as Reactions (8) and (9). Si(OH)_4 transforms SiO_4^{4-} ion with dehydration by plasma heat and combined with magnesium ion to generate Mg_2SiO_4 by electrochemical reaction [21]:



Besides, $\text{O}_7\text{P}_2^{4-}$ ion and magnesium ion combine to produce $\text{Mg}_2\text{O}_7\text{P}_2$:



A small amount of $\text{Mg}_2\text{O}_7\text{P}_2$ was formed after addition of pyrophosphate. Comparatively, P content of chemical conversion coatings of AZ31B alloy with an alkaline phosphate-permanganate solution was only 0.52 weight percent [22]. The amount of MgO in the XRD patterns decreases by increasing pyrophosphate concentration. Element contents (atomic %) determined by EDS analysis are in consistent with pyrophosphate concentration, as shown in Figs. 3-1 and 3-2. Phosphorus content in the anodized films was increased in pyrophosphate concentration. However, the oxidized film had low phosphorus contents because of evaporating the pyrophosphate component. Pyrophosphate easily evaporates in the PEO process of which the plasma temperature was in the range of 1000 to 1500°C and can also easily reach to 2000°C, because of its rather low boiling temperature of 1500°C. As shown in Fig. 2, main component of the PEO films is MgO.

Fig. 4 shows SEM micrographs of surface and cross-section of the PEO-treated AZ31B alloy with different pyrophosphate concentrations. Interface between the oxidized film and the Mg substrate operated at 0.1M of a

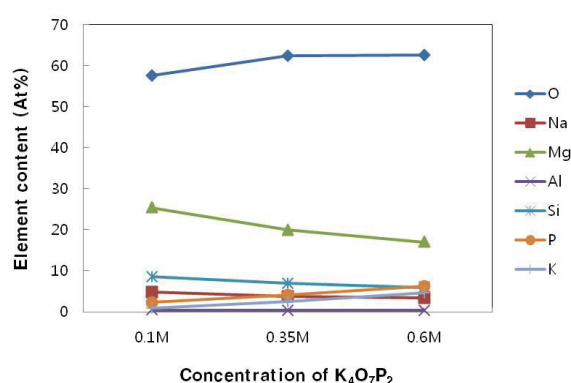


Fig. 3-1. EDS of AZ31B Mg alloy PEO-treated in the baths containing 0.1~0.6M Potassium Pyrophosphate.

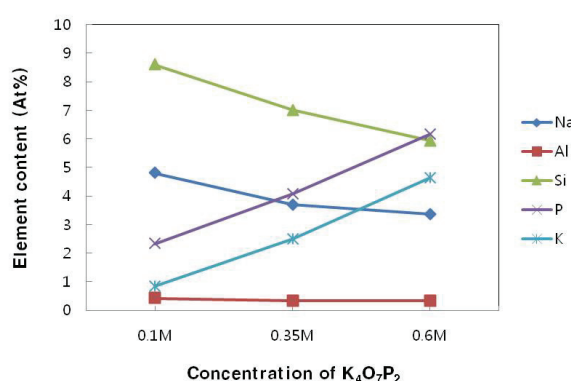


Fig. 3-2. EDS of PEO-treated AZ31B Mg alloy [enlarged the portions of elements with low contents].

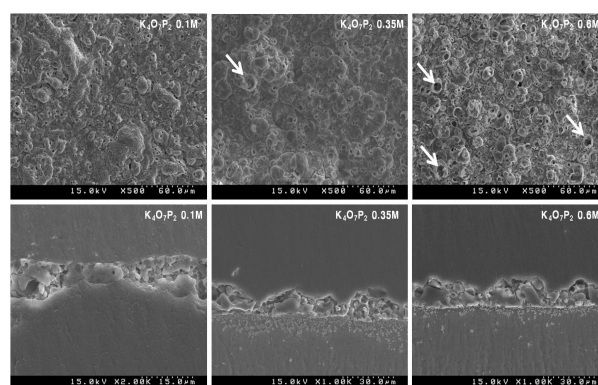


Fig. 4. SEM images of AZ31B Mg alloy PEO-treated in the baths containing 0.1~0.6M Potassium Pyrophosphate.

pyrophosphate concentration was greatly different from those operated at other concentrations. The cross-sectional view in the case of 0.1M of pyrophosphate concentration exhibited rougher interface between the oxide film and Mg alloy substrate than in the case of other pyrophosphate concentrations. However, the surface morphology is quite different from the case of such interface morphology. From the corrosion-resistant point of view, the anodized film PEO-operated with 0.1M of the pyrophosphate concentration was the most satisfactory because thick

oxide film covered completely with the magnesium substrate. While plasma formed an intense ridge of rough surface, which addition of pyrophosphate decreased the surface roughness and led to the growth of a smooth and compact anodized film. The cross-sectional SEM images showed rough surface on the anodized film because plasmas were focused on the ridge of rough surface. The oxidized film at the arrow point in each SEM image had bigger pores than at surroundings. Those small pores were formed by pyrophosphate evaporation or oxygen bubbling, whereas bigger pores were formed by micro-arcing between the electrolytic bath and the substrate [23].

The cross-sectional images reveal lots of vacant sites around large particles in the cases of AZ31B alloy anodized in the baths of 0.35 and 0.4M of pyrophosphate concentrations. As observed earlier by XRD pattern and EDS analysis, MgO content decreased with increasing of pyrophosphate concentration. Therefore, those vacant sites might be due to a reduced amount of MgO and pyrophosphate evaporation by plasma heating effect.

Fig. 5 shows the thickness of anodized film as a function of pyrophosphate concentration. All the anodized films have almost the same thickness of 11 μm.

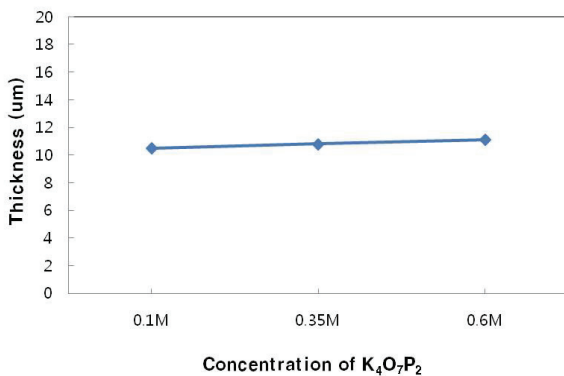


Fig. 5. Thickness of AZ31B Mg alloy PEO-treated in the baths containing 0.1~0.6M Potassium Pyrophosphate.

Thickness (d) can be calculated by following Eq. [24]:

$$\text{Thickness, } d = qM / zrF\rho, \quad (11)$$

Where:

M: Molecular weight, r: Roughness factor, ρ: Density of presumed homogeneous oxide, q: The charge, z: The number of electrons.

The above equation can be simplified as:

$$M/\rho = VM, \text{ molecular volume [cm}^3/\text{mole]} \quad (12)$$

Therefore, the anodized film has been greatly influenced by its molecular volume.

The crystal structure of Mg₂O₇P₂ is monoclinic with

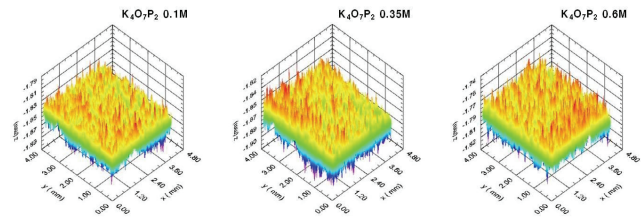


Fig. 6. Surface roughness images of AZ31B Mg alloy PEO-treated in the baths containing 0.1~0.6M Potassium Pyrophosphate.

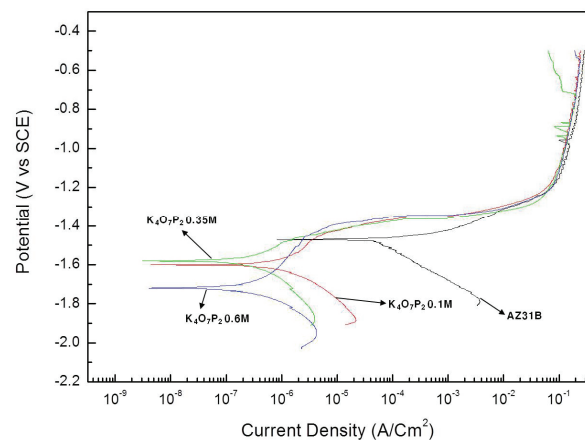


Fig. 7 Potentiodynamic polarization of AZ31B Mg alloy PEO-treated in the baths containing 0.1~0.6M Potassium Pyrophosphate.

$a=7.189\text{\AA}$ $b=18.309\text{\AA}$, $c=7.665\text{\AA}$ and $\alpha=92.360^\circ$. Structure of MgO is Halite (Cubic) with $a=4.212\text{\AA}$. The crystal size has no effect on thickness as compared with phases of Mg₂O₇P₂ and MgO.

Fig. 6 demonstrates the oxidation surface roughness as a function of pyrophosphate concentration. Surface roughness (Ra) is one of the important factors for guidance of the anodizing process. For 0.1, 0.35 and 0.6 M of pyrophosphate concentration, Ra were 4.601, 4.606 μm and 4.471 μm, respectively. Low voltage PEO coating seems to have little effect on surface roughness. The surface roughness as shown in Fig. 6 is consistent with surface smoothness, that is the anodized film for 0.1M of pyrophosphate has smoother surface.

Fig. 7 is potentiodynamic polarization graphs in 3.5 % NaCl solution of AZ31B alloy anodized in baths containing 0.1~0.6M of pyrophosphate.

Table 2 indicates corrosion potentials, corrosion current densities and polarization resistances for 0.1~0.6M potassium pyrophosphate baths.

Polarization resistance (R_p) defined by Stern-Geary equation [25]:

$$R_p = \frac{\beta a \times \beta c}{2.303 I_{corr} (\beta a + \beta c)} \quad (13)$$

Table 2. Corrosion resistance of Potentiodynamic test of AZ31B Mg alloy PEO-treated in the baths containing 0.1~0.6M Potassium Pyrophosphate.

	E_{corr} (V vs. SCE)	I_{corr} (A/cm ²)	R (Ω .cm ²)
AZ31B	-1.472	-44.113×10^{-6}	285.57
0.1M K ₄ O ₇ P ₂	-1.601	-2.937×10^{-6}	29.97×10^3
0.35M K ₄ O ₇ P ₂	-1.580	-830.835×10^{-9}	98.51×10^3
0.6M K ₄ O ₇ P ₂	-1.719	-695.097×10^{-9}	101.55×10^3

where R_p is the polarization (charge transfer) resistance, β_a and β_c are Tafel slopes of anodic and cathodic parts in the Tafel plot, respectively, and I_{corr} is the corrosion current density.

From a point of view of corrosion rate, polarization resistance is increased with increasing pyrophosphate concentration. It was found that the addition of pyrophosphate was very effective method for corrosion resistance. It is confirmed that decrease in amount of MgO as indicated in XRD patterns reduces the density of the anodized film structure. Corrosion resistance of the oxidized film was affected by film thickness and density of structure [26]. In other words, amount of MgO is closely related to corrosion resistance. The phase Mg₂O₇P₂ formed by anodizing AZ31B Mg alloys in pyrophosphate baths seems to hinder chlorine ion from pitting the surface of film. Chlorine ion tends to strongly combine with magnesium ion due to large electronegativity gap. On the other hand, phosphorus ion tends to weakly combine with chlorine ion because of little electro-negativity gap. However, phosphorus-chlorine compound may be formed when Mg₂O₇P₂ meets chlorine ion or gas. As a consequence, phosphorus compound increased corrosion resistance.

4. Conclusions

In this study, the effect of pyrophosphate addition in an anodizing bath was investigated to prevent poor corrosion resistance from low thickness induced by low PEO operation. The addition of pyrophosphate component in the anodizing bath had a characteristic effect of forming low amounts of Mg₂O₇P₂ as well as interruptive formation of MgO due to evaporation. The pyrophosphate provides a smooth interface between Mg substrate and anodized film generated by plasma on the rough surface. Corrosion resistance increased by the addition of pyrophosphate, despite of low density of its film structure by suppressing the formation of MgO.

Acknowledgements

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