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AZ31 마그네슘 합금의 플라즈마전해산화 피막 형성에 미치는 수산화 이온 및 규산 이온의 영향

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Effects of Hydroxide and Silicate ions on the Plasma Electrolytic Oxidation of AZ31 Mg Alloy

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Abstract

Formation behavior of PEO (Plasma Electrolytic Oxidation) films on AZ31 Mg alloy was studied in aqueous solutions containing various concentrations of hydroxide ion (OH^-) and silicate ion (SiO_3^{2-}) by voltage-time curves, and corrosion resistance of the PEO film-covered specimen was investigated by immersion test in 0.5 M NaCl solution. From the analyses of the voltage-time curves, it is suggested that two different types of anions are essentially needed for the formation of PEO films on AZ31 Mg alloy: film formation agent and local film breakdown agent. SiO_3^{2-} ion acts only as a film formation agent but OH^- ion acts not only as a film formation agent but also film breakdown agent. The PEO films prepared on AZ31 Mg alloy in alkaline silicate solution showed very good corrosion resistance without any pitting or filiform corrosions up to 480 h of immersion in 0.5 M NaCl.

Keywords: Magnesium; Plasma electrolytic oxidation; corrosion; anodizing

1. Introduction

Mg and its alloys have been of great interest because of their low density of 1.7 g/cm^3, meaning that they are 30% lighter than Al. However, their poor corrosion resistance has limited their wide applications so many researchers have tried to develop surface treatment methods to improve corrosion resistance of AZ31 Mg alloy. One of the surface treatments of Mg alloys for corrosion protection is plasma electrolytic oxidation (PEO) method. The PEO method is special type of anodic oxidation method in which micro discharges are generated by dielectric breakdown of the anodic oxide film under high electric field and thick and hard anodic films are formed[1-11)].

Anodizing and PEO methods utilize not only substrate elements but also chemical components in electrolytes to form the PEO films. From anodic oxidation of solid–solution Mg-0.8 at.% Cu and Mg-1.4 at.% Zn alloys in an alkaline phosphate electrolyte by Abulsain et al.[12)], and they showed that the anodic films are mainly composed of magnesium hydroxide, and contain copper and zinc species from the alloy and phosphorous species from the electrolyte. Another work on anodizing of solid–solution Mg–W alloys disclosed enrichment of tungsten beneath the anodic film[13)]. Shi et al.[14)] reported that

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Table 1. Current forms and conditions for plasma electrolytic oxidation of AZ31 Mg alloy

Current form	Current density [mA/cm^2]	Pulse width [ms]	Pulse frequency [Hz]
DC	10~80	-	-
Pulse current	300	0.3	65

increasing zinc content led to increased corrosion resistance of an anodized single-phase Mg–Zn alloy, while Al played different roles depending on the alloy purity. The presence of Sn in Mg alloy was observed to be helpful in the formation of corrosion resistive PEO films in a fluoride containing electrolyte10).

The composition and corrosion resistance of PEO films on Mg alloys have been known to be largely dependent upon the solution composition and concentration. PEO treatment of Mg alloys have been conducted in many different aqueous electrolytes containing silicates5,6,15-17), fluorides10,11,18), phosphates3,19), borates20) and stannate electrolytes21). Verdier et al.22) reported that all the elements in the electrolytes could be included in the PEO films on AM60 Mg alloy. Some corrosion inhibitors23) or ceramic particles24,25) were added into the PEO electrolyte or surface pretreatment26) to improve the corrosion resistance of PEO films. Sealing of the PEO films to improve their corrosion protective property has been tried by immersion in boiling water11,27), alkaline phosphate and silicate28), stannate29) and E-paint solution30), sol–gel coatings27,28,31) and polymer or organic coatings27,32). Although a number of such works have been conducted to elucidate the effects of electrolyte compositions on the formation of PEO films on Mg alloys, still there is lack of information about the effects of OH^- and SiO_3^{2-} ions in aqueous electrolyte on the formation and corrosion protective properties of PEO film formed on AZ31 Mg alloy.

In this work, PEO films were formed on AZ31 Mg alloy in aqueous solutions containing various concentrations of OH ions in 0 M, 0.2 M and 1 M $Na_2SiO_3^{2-}$ solutions. PEO film formation behavior and corrosion resistance of the PEO film-covered specimen were investigated by voltage-time curves in the aqueous solutions and by immersion test in 0.5 M NaCl solution, respectively. The cross-sectional morphologies of the PEO films were observed by SEM before and after sealing treatment in boiling water and photographs of the specimens during the immersion test in 0.5 M NaCl solution were taken using a digital camera with time up to 31 days.

2. Experimental

AZ31 Mg alloy plates (wt.%, Al 2.94, Zn 0.8, Mn 0.3, Si < 0.1, Fe < 0.005, Cu < 0.05, Ni < 0.005, and Mg balance) were used for this study. The alloy plate of 1 mm thickness was cut into 12.5 × 70 mm size and masked, leaving 10 cm^2 of exposed area, with a masking tape after abrading the specimen surface successively up to #4000 SiC paper with ethanol. The masked specimen was etched for about 10 s in 0.5 M H_2SO_4+0.5 M HNO_3 solution to remove surface scales and contaminants, washed with DI water and then scrubbed with tissue to remove the surface residuals.

The PEO films were formed in various electrolytes at 20±3°C by the application of DC between 10 and 80 mA/cm^2 or pulse current with a peak current density of 300 mA/cm^2, 0.3 ms width and 65 Hz of frequency, as shown in Table 1. The electrolyte of 4000 ml volume was contained in a plastic cell within which Teflon tubes are coiled for cooling by pumping cold water/glycol mixture through them. A platinum mesh was used as the counter electrode and anodic film formation voltage was recorded with time between the specimen and the counter electrode.

The PEO films formed on AZ31 Mg alloy were sealed for 40 min in boiling water, and then used for the observation of cross-sectional morphologies and corrosion test. Corrosion behavior of the sealed PEO films-covered AZ31 Mg samples was investigated by in-situ observation with immersion time in 0.5 M NaCl solution at 20±1°C. Cross-sectional morphologies of the PEO films were observed by SEM and photographs of the specimens during the immersion test in 0.5 M NaCl solution were taken using a digital camera with time up to 31 days.

3. Results and Discussion

Fig. 1 presents voltage-time curves obtained from AZ31 Mg alloy in aqueous alkaline solutions containing various NaOH concentrations from 0.1 M to 1 M. The anodic voltage increased continuously with time in 0.1 M NaOH solution, reaching a steady-state

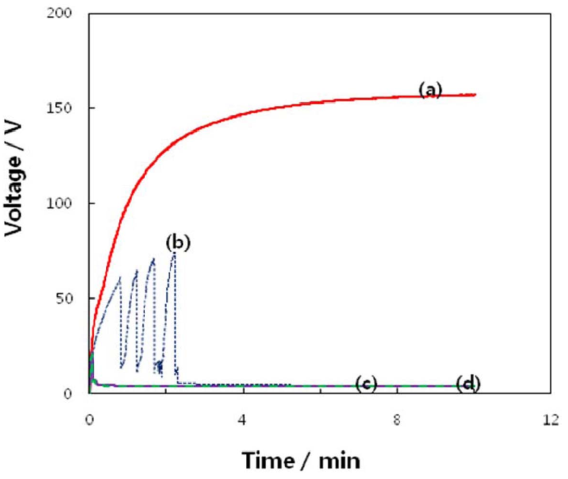

Fig. 1. Voltage-time curves of AZ31 Mg alloy obtained at an anodic current density of 20 mA/cm^2 in aqueous solutions containing various NaOH concentrations of (a) 0.1 M, (b) 0.2 M, (c) 0.5 M, (d) 1 M.

value of about 160 V after about 600 s of anodic oxidation time. In 0.2 M NaOH solution, the anodic voltage increased in the initial stage up to about 60 V but suddenly dropped to about 15 V and then showed three times more rapid increase and drops, finally reaching a very low value of about 4.1 V after about 130 s of anodic oxidation time. The increase and sudden drop of anodic voltage are attributed to the formation and breakdown of surface oxide film, respectively. In 0.5 M and 1 M NaOH solutions (Fig. 1), the anodic voltage showed an instantaneous increase up to about 20 V within 2 s and then reached a very low steady-state value of about 3.9 V. The lowered anodic voltage with increasing NaOH concentration suggests that OH^- ion causes the breakdown of surface oxide films on AZ31 Mg alloy under anodic potential. The reason why OH^- ion breaks the surface film under anodic potential may be attributed to an easy migration of OH^- ion through the surface film from the film surface toward the metal/oxide interface due to its small size, which results in local heating and breakdown of the surface films. Another possible explanation for easy breakdown of the surface films by OH- ion is that OH^- ion dissolves $Al(OH)_3$ on the impurity particles of Al_3Fe which are present inherently in the Mg alloy, thereby resulting in depassivation of the particle surface.

Fig. 2 shows voltage-time curves obtained from AZ31 Mg alloy at various current densities in 0.2 M Na_2SiO_3 solutions containing various NaOH concentrations from 0.1 M to 0.8 M. In 0.2 M Na_2SiO_3 solution, the anodization voltage showed 50~70 V in the initial stage and then lower steady-state values between 10 V and 40 V after 40~75 s of anodic oxidation time. Both the initial and steady-state anodic voltages appeared to be proportional to the applied anodic current density in 0.2 M Na_2SiO_3 solution. The surface products formed in 0.2 M Na_2SiO_3 solution were easily removed from the surface as powders by rubbing the surface with tissue, showing that they are very porous and their

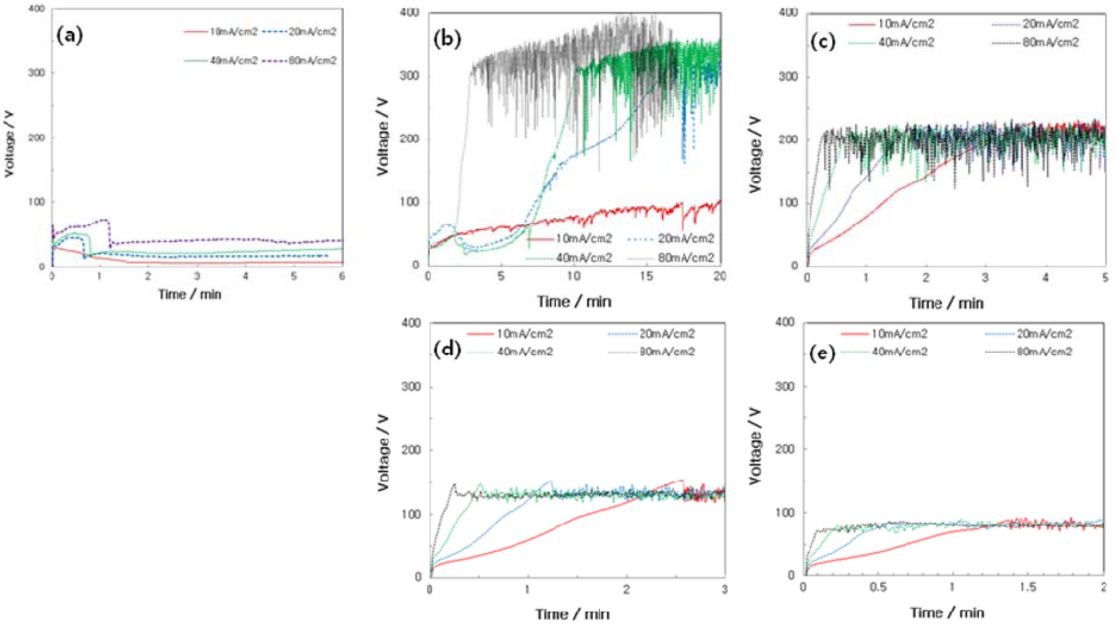

Fig. 2. Voltage-time curves of AZ31 Mg alloy obtained at various applied anodic current densities in 0.2 M Na_2SiO_3 solutions containing various NaOH concentrations of (a) 0 M, (b) 0.1 M, (c) 0.2 M, (d) 0.4 M, (e) 0.8 M.

adhesion with the substrate is poor.

In 0.2 M $Na_2SiO_3 + 0.1$ M NaOH solution, the anodic voltages showed initial low values between 20 and 50 V within several minutes but a sudden and rapid increase of the anodic voltage up to more than 300 V appeared at applied anodic current densities of more than 20 mA/cm^2, followed by large voltage fluctuations with a magnitude of 30~100 V during which micro arcs are generated and PEO films are formed. It should be stressed that the addition of 0.1 M NaOH into 0.2 M Na_2SiO_3 solution makes PEO film formation possible, which implies that the formation of resistive surface films results from the presence of high concentration of OH^- ions together with SiO_3^{2-} ions in aqueous solution.

With increasing NaOH concentration in 0.2 M Na_2SiO_3solution, the magnitudes of PEO film formation voltage and its fluctuations are decreased. The decreased PEO film formation voltage with increasing NaOH concentration in 0.2 M Na_2SiO_3 solution suggests that OH^- ion acts as an oxide film breakdown agent even in the presence of SiO_3^{2-} ions as well as in the absence SiO_3^{2-} ions in aqueous solution in Fig. 1. It is suggested that small size of OH^- ions can migrate through the oxide films by which heat is generated and micro arcs occur.

On the other hand, the slope of anodic voltage-time curves increased with increasing added NaOH concentration in 0.2 M Na_2SiO_3 solution, indicating that OH- ions can help the formation of resistive surface films if $SiO^{-}_{3}{}^{2}$ ions are present in aqueous solution. The formation reactions of surface films on AZ31 Mg alloy in SiO_3^{2-} containing alkaline solution can be written by Eqs. (1) and (2).

$$Mg + OH^- = MgO + H^+ + 2e \quad (1)$$

$$Mg + SiO_3^{2-} = MgO{\cdot}SiO_2 + 2e \quad (2)$$

In order to more clearly understand the effects of OH^- and SiO_3^{2-} ions on the formation of PEO films on AZ31 Mg alloy, anodic voltages-time curves of AZ31 Mg alloy were obtained in 1M Na_2SiO_3 solution containing various NaOH concentrations and the results are illustrated in Fig. 3. In 1 M Na_2SiO_3 solution, the anodic voltage increased up to about 250 V but showed large drops/recoveries and gradually lowered value of around 100~150 V. Micro arcs were generated when the anodic voltage showed small fluctuations around 240 V but no arcing occurred and porous black films with poor adhesion were formed when the anodic voltage is reduced to the low values of about 100~150 V.

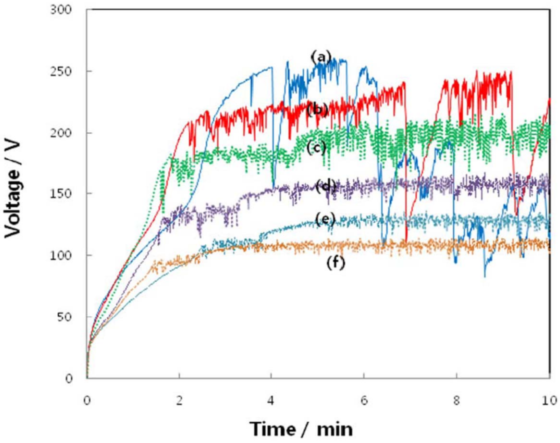

Fig. 3. Voltage-time curves of AZ31 Mg alloy obtained at an applied anodic current density of 20 mA/cm^2 in 1 M Na_2SiO_3 containing various NaOH concentrations of (a) 0 M, (b) 0.1M, (c) 0.2 M, (d) 0.4 M, (e) 0.6 M, (f) 0. 8 M.

In 1 M $Na_2SiO_3 + 0.1$ M NaOH solution, the anodic voltage increased up to about 210 V where micro arcs are generated. The large voltage drops/recoveries were observed in 1 M $Na_2SiO_3 + 0.1$ M NaOH solution as well as in 1 M Na_2SiO_3 solution. In 1 M Na_2SiO_3 solutions containing more than 0.2M NaOH solution, the large voltage drops/recoveries did not occur and the anodic voltage reached steady-state values with fluctuations. The magnitude of the voltage fluctuations appeared to become smaller with increasing OH^- ion concentration in both 0.2 M and 1 M Na_2SiO_3 solutions, suggesting that OH^- ion can help healing of the broken films on AZ31 Mg alloy. On the other hand, the steady-state anodic voltage values decreased with increasing NaOH concentration in both 0.2 M and 1 M Na_2SiO_3 solutions, which represents easier breakdown of the anodic films on AZ31 mg alloy under the presence of high concentration of OH^- ion in 0.2 M and 1 M Na_2SiO_3 solutions.

The dependences of film breakdown voltage on the concentration of NaOH in 0.2 M and 1 M Na_2SiO_3 solutions are shown in linear and semi-logarithmic scales in Fig. 4. The film breakdown voltage decreased exponentially with NaOH concentration, and more rapid decrease was observed in 0.2 M Na_2SiO_3 than in 1 M Na_2SiO_3. Assuming that the surface films formed in 1 M Na_2SiO_3 could have more SiO_2 composition than those in 0.2 M Na_2SiO_3, lower film breakdown voltage in 1 M Na_2SiO_3 than 0.2 M Na_2SiO_3 under low NaOH concentration less than 0.4 M can be

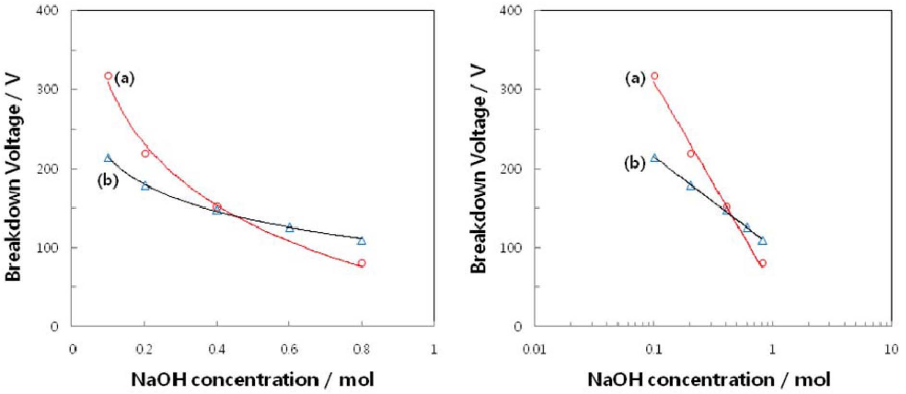

Fig. 4. Plot of the first film breakdown voltage of AZ31 Mg alloy versus added NaOH concentration into (a) 0.2 M Na_2SiO_3 and (b) 1 Na_2SiO_3 solutions.

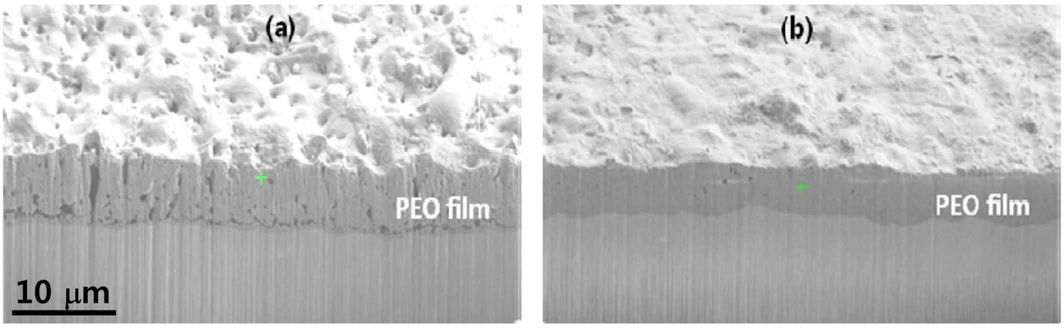

Fig. 5. Typical PEO film morphologies on AZ31 Mg alloy (a) before and (b) after sealing treatment for 40 min in boiling water. The PEO films were formed by application of pulse current in 1 M NaOH + 0.02 M Na_2SiO_3 solution.

attributed to easier breakdown of high SiO_2 containing surface films. On the other hand, slow decrease of film breakdown voltage with OH^- ion concentration in 1 M Na_2SiO_3 than 0.2 M Na_2SiO_3 could be due to the facts that OH^- ion can help the formation of more resistive surface film by adjusting the composition ratio between MgO and SiO_2 and/or attack by OH^- ions is slowed in the presence of high concentration of SiO_3^{2-} ions by competitive adsorption onto the film surface. The effects of the composition ratio between MgO and SiO_2 and competitive adsorption between OH^- ion and SiO_3^{2-} ion on the PEO film formation will be discussed in more detail in a following paper.

Fig. 5 shows typical PEO film morphologies before and after sealing treatment of the PEO films in boiling water. The PEO films contain a number of pores which were formed during micro arcings resulting from the remaining arcing channels and/or incorporation of oxygen bubbles or water vapours. A number of circular shapes of pores and a large through hole were observed in the cross section of the PEO film in Fig. 5(a). Thus, in order to improve corrosion protective property by the PEO films, sealing of the pores and/or cracks are essentially needed. Fig. 5(b) illustrates the PEO film morphology after sealing treatment in boiling water. Most of pores were sealed and a few of pores remain within the PEO films after the sealing treatment. Theses suggest that most of pores in the PEO films are open so that they could be sealed by hydration reaction with boiling water which results in volume expansion of the oxide. The morphological changes and improved corrosion resistance of the PEO films by the sealing treatment have been reported already in a previous paper[11].

Corrosion resistance of PEO-treated AZ31 Mg alloy was investigated by immersion test in 0.5 M NaCl solution after sealing treatment of the PEO films and its result is depicted in Fig. 6. The specimen surface became darken with immersion time in 0.5 M NaCl solution, suggesting the lowered reflectivity of light by the surface film which seems to be due to incorporation of Cl^- ions into the PEO films. Although the surface film became darken within several days, corrosion on the PEO film-

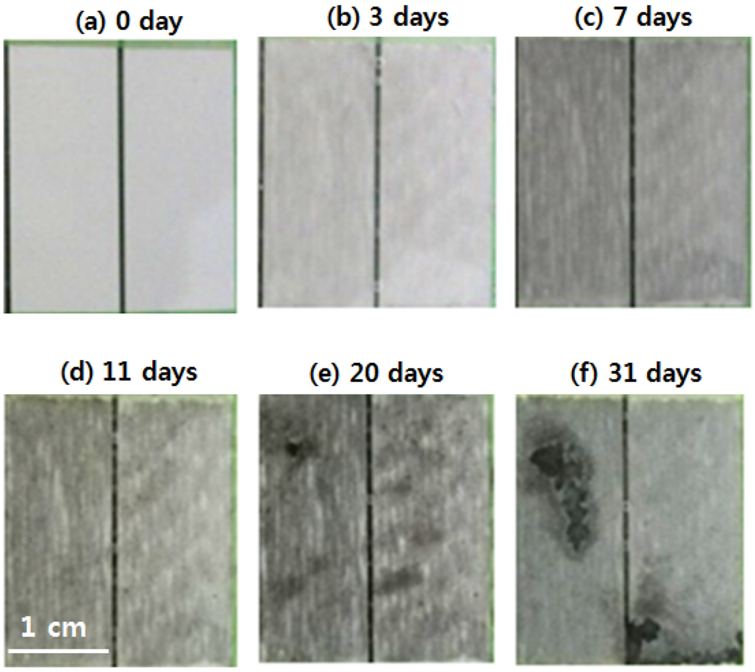

Fig. 6. Photographs of PEO-treated AZ31 Mg alloys with immersion time in 0.5 M NaCl solution after sealing treatment for 40 min in boiling DI water. The PEO films were formed by application of pulse current in 1 M NaOH + 0.02 M Na_2SiO_3 solution.

covered specimen did not occur up to 20 days of immersion (480 h). Thus, it is concluded that the PEO films prepared on AZ31 Mg alloy in alkaline silicate solution can provide very good corrosion resistance without any pitting or filiform corrosions up to 480 h of immersion in 0.5 M NaCl solution although the PEO films are darkened by the incorporation of Cl^- ions. Various anions in electrolyte and alloying elements in Mg alloy could be other important factors affecting the formation and corrosion properties of PEO films and their effects will be studied in the following papers in detail.

4. Conclusions

The formation of PEO films on AZ31 Mg alloy appeared to be critically dependent on the concentrations of not only OH^- ions but also SiO_3^{2-} ions in aqueous solutions. When the solution contains only OH^- ions, anodization voltage of AZ31 Mg alloy did not increase up to the PEO film formation voltages and showed only barrier film formation or local dissolution after film breakdown. When the solution contains OH^- ions together with SiO_3^{2-} ions, the PEO films are readily formed on AZ31 Mg alloy under the application of DC or pulse current. Based on the experimental results, it is suggested that two different types of anions are essentially needed for the formation of PEO films on AZ31 Mg alloy: film formation agent and local film breakdown agent. SiO_3^{2-} ion acts only as a film formation agent but OH^- ion acts not only as a film formation agent but also film breakdown agent. It was found that the PEO films prepared on AZ31 Mg alloy in alkaline silicate solution showed very good corrosion resistance without any pitting or filiform corrosions up to 480 h of immersion in 0.5 M NaCl solution. Based on the experimental results, It is concluded that minimum concentrations of oxide forming anions, such as OH^- and SiO_3^{2-} ions, are necessary for the formation of thick PEO films on AZ31 Mg alloy.

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