



## Anodic oxidation behavior of AZ31 Mg alloy in aqueous solution containing various NaF concentrations

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### Abstract

This paper deals with anodic oxidation behavior of AZ31 Mg alloy in aqueous solutions containing various NaF concentrations from 0.01 M to 1 M. Three different voltage-time curves and anodic oxide formation behaviors appeared with concentration of NaF in deionized water. When NaF concentration is lower than 0.02 M, the voltage of AZ31 Mg alloy increased linearly and then reached a steady-state value more than 200 V, and large size pits and thin oxide layer were formed. When NaF concentration is between 0.05 M and 0.1 M, the voltage of AZ31 Mg alloy showed large periodic fluctuations of about 30 ~ 50 V around more than 200 V and large number of small particles were observed. If NaF concentration is higher than 0.2 M, PEO films can be formed without visible arcs under solution pH 6.5 ~ 7.5 by F<sup>-</sup> ions without help of OH<sup>-</sup> ions.

*Keywords* : AZ31 Mg alloy; Plasma electrolytic oxidation; Anodic oxidation behavior; NaF.

## 1. Introduction

Magnesium alloys have been of great interest for vehicles and portable equipment because of their high specific strength, good castability and recyclability. Magnesium alloys have been also developed for biomedical applications [1-4]. For such industrial applications, however, their poor corrosion resistance is one of the most difficult obstacles which should be overcome in essence. There are two different methods for improving the corrosion resistance of magnesium alloys. One is to control content

and composition of alloying elements in magnesium alloys to minimize galvanic coupling effect and to form corrosion-resistant layers spontaneously on the surface [5,6]. However, adding and controlling of alloying elements could not provide complete prevention of corrosion damages such as color change and contamination of the surface by corrosion products. The other way to prevent corrosion of magnesium alloys is to form a corrosion-resistant layer by surface treatment methods such as anodic oxide coating, electroplating, ceramic coating or organic coatings.

Anodic oxide coating is one of the most frequently used surface finishing methods for corrosion protection of magnesium alloys.

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PEO (Plasma Electrolytic Oxidation) is one of typical anodic oxide coating methods for valve metals. PEO film formation behaviors of magnesium alloys have been studied by a number of authors [7–11]. During the PEO film formation, dielectric breakdown and healing of the anodic oxide film is essential.  $\text{OH}^-$  ions are known to contribute to the film breakdown which reduces the PEO film formation voltage [12–14]. The PEO film formation voltage was reported to depend on the composition of electrolyte [15–17]. Most of electrolyte used for PEO film formation on magnesium alloys include silicate ions, hydroxide ions and fluoride ions. The effect of NaF concentration on PEO film formation of AZ31 Mg alloy was reported to improve hardness and adhesion in a solution containing high concentrations of  $\text{PO}_4^{3-}$  and  $\text{SiO}_3^{2-}$  and  $\text{OH}^-$  ions [18]. However, at present, the effect of  $\text{F}^-$  ions on PEO film formation on AZ31 Mg alloy, has not been reported in aqueous solution without sufficient concentration of oxide film forming ions of  $\text{PO}_4^{3-}$  and  $\text{SiO}_3^{2-}$  or  $\text{OH}^-$  ions.

In the present work, we studied anodic oxidation behavior of AZ31 Mg alloy in aqueous solutions containing NaF from 0.01 M to 1 M. Voltage–time curves were obtained during the application of a constant current density of  $50 \text{ mA/cm}^2$  and the surface and cross-sectional morphologies of the anodically treated specimens were observed by SEM. The pH of the solutions containing different NaF concentrations was measured and anodic oxidation behavior of AZ31 Mg alloy was discussed in view of the role of

$\text{F}^-$  ions and  $\text{OH}^-$  ions in the formation and dielectric breakdown of anodic oxide films.

## 2. Experimental

AZ31 Mg alloy (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) plate of 1 mm thickness fabricated by POSCO was employed for this work. The plate was cut into  $70\text{mm} \times 11\text{mm}$  size and the sample surface was abraded by #220 SiC paper into 10 mm width and finished using a knife to prepare the fresh surface covered with only air-formed oxide film, as demonstrated in a preceding paper [21]. One part of the sample was masked with a tape and then they were used for the experiments. The anodic oxidation treatment was performed for 2 min at a constant current density of  $50\text{mA/cm}^2$  in aqueous electrolytes containing various NaF concentrations from 0.01 M to 1 M using a DC power supply (Agilent Technologies, N5772A). The electrolyte temperature was kept to be lower than  $25 \text{ }^\circ\text{C}$  by circulating cooling water using a cooling bath. The counter electrode was a STS316 plate with about  $100 \text{ cm}^2$  of surface area. The surface and cross-sectional morphologies of the anodically treated samples were observed using scanning electron microscope (SEM, JSM-6610LV). The solution pH was measured using a pH meter (Mettler Toledo).

## 3. Results and discussion

Fig. 1 shows changes in voltages of

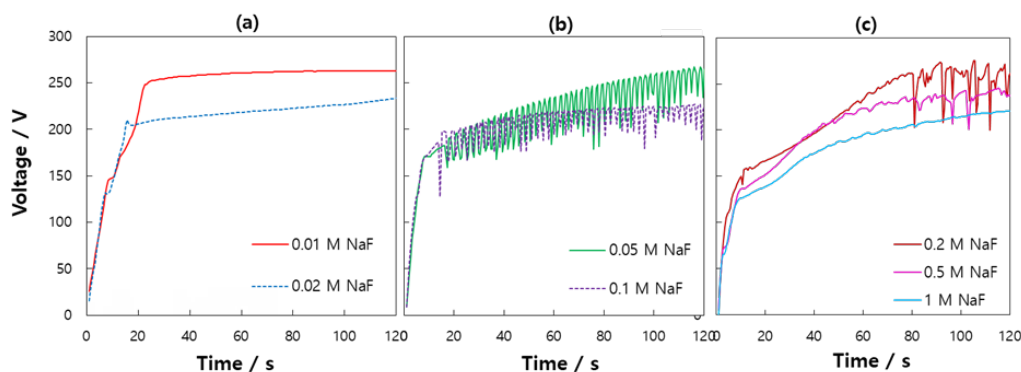


Fig. 1. Voltage–time curves of AZ31 Mg alloy at  $50\text{mA/cm}^2$  in aqueous electrolytes containing various NaF concentrations from 0.01 M to 1 M.

AZ31 Mg alloy with time at a constant applied current density of  $50\text{mA}/\text{cm}^2$  in aqueous electrolytes containing various NaF solutions from 0.01 M to 1 M. There were observed three different voltage-time behaviors, depending on the concentration of NaF in deionized water. When NaF concentration is lower than 0.02 M, the voltage of AZ31 Mg alloy increased linearly up to about 130 ~ 150 V within 10 s and then increased again up to more than 200 V after showing a short voltage plateau. The voltage increasing rate was suddenly lowered after the second sharp increase and reached steady-state values more than 200 V.

If NaF concentration is between 0.05 M and 0.1 M, the voltage of AZ31 Mg alloy showed large fluctuations about 30 ~ 50 V periodically after a linear increase up to about 170 V, as can be seen in Fig. 1(b). When NaF concentration is higher than 0.2 M, the linearly increased voltage in the initial stage increased is lowered and periodic voltage

fluctuations were not observed up to 60 s. Irregular voltage fluctuations appeared in 0.2 M and 0.5 M NaF solutions after about 60 s but any voltage fluctuations were not observed during anodic oxidation of AZ31 Mg alloy in 1 M NaF solution.

The surface and cross-sectional morphologies of AZ31 Mg alloy after 2 min of anodic oxidation treatment at  $50\text{mA}/\text{cm}^2$  in various NaF solutions are given in Figs. 2 and 3, respectively. The AZ31 Mg alloy surface after the anodic oxidation treatment in 0.01 M and 0.02 M NaF solutions contains large size pits (Figs. 2(a) and 2(b)) and thin oxide layer is formed along the surface (Figs. 3(a) and 3(b)). Considering that the voltage in Fig. 1(a) reached very high values more than 200 V without any fluctuations, it seems reasonable to conclude that the thin anodic oxide layer is broken locally and it can be recovered immediately after breakdown of the oxide layer by applied high electric field during

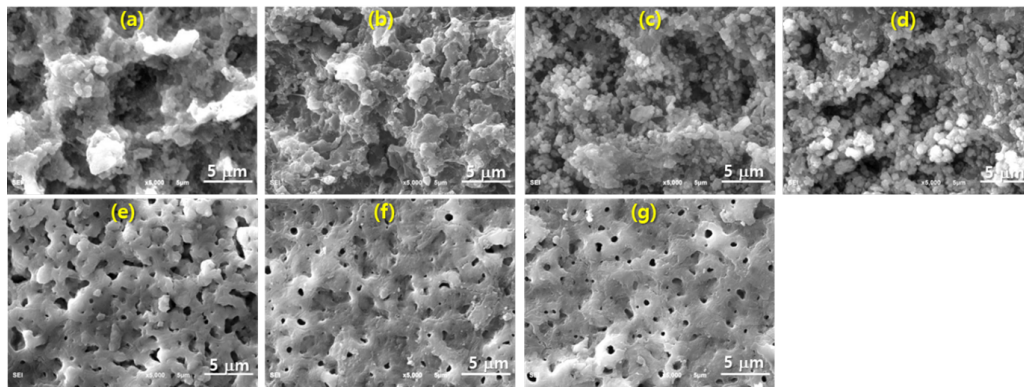


Fig. 2. SEM surface images of AZ31 Mg alloy after anodic oxidation for 2 min at  $50\text{mA}/\text{cm}^2$  in aqueous solutions containing various NaF concentrations of (a) 0.01 M, (b) 0.02 M, (c) 0.05 M, (d) 0.1 M, (e) 0.2 M, (f) 0.5 M and (g) 1 M.

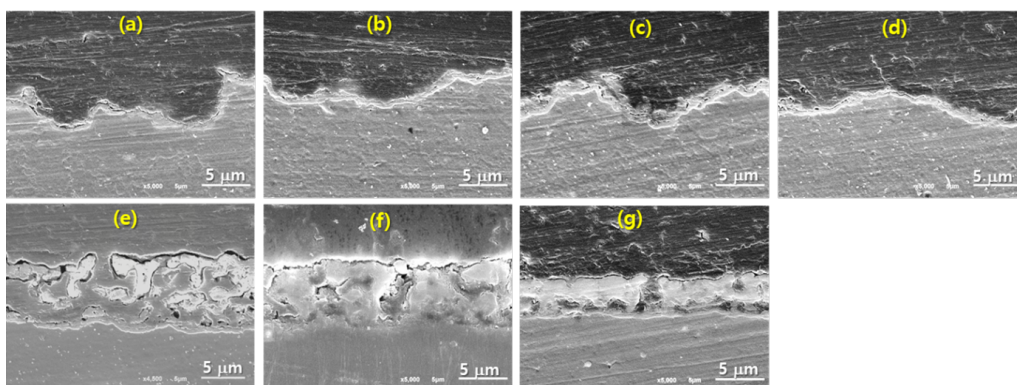


Fig. 3. SEM cross-sectional images of AZ31 Mg alloy treated anodically for 2 min at  $50\text{mA}/\text{cm}^2$  in aqueous solutions containing various NaF concentrations of (a) 0.01 M, (b) 0.02 M, (c) 0.05 M, (d) 0.1 M, (e) 0.2 M, (f) 0.5 M and (g) 1 M.

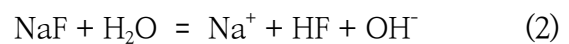
anodic treatment of AZ31 Mg alloy in 0.01 M and 0.02 M NaF solutions.

In 0.05 M and 0.1 M NaF solutions (Fig. 1(b)), the anodic oxidation voltage showed large periodic fluctuations and large number of small particles were observed on the surface (Figs. 2(c) and 2(d)). The periodic fluctuations of voltage more than 30 mV during anodic oxidation treatment suggest that anodic oxide films are broken easily and it is recovered slowly after breakdown of the oxide layer by applied high electric field in 0.05 M and 0.1 M NaF solutions.

In 0.2 M, 0.5 M and 1 M NaF solutions, the surface of AZ31 Mg alloy obtained after 2 min of anodic oxidation treatment revealed the formation of typical PEO films with pores (Figs. 2(e) ~ 2(g)). The PEO films formed on AZ31 Mg alloy in NaF solutions were observed to be highly porous and porosity decreased with increasing NaF concentration. The PEO films became denser and thinner with increasing NaF concentration. Cracks were observed in the PEO films formed in 1 M NaF solution but they were not formed in 0.2 M and 0.5 M NaF solutions. It should be mentioned that no visible arcs were generated during anodic oxidation treatment in NaF solutions but PEO films with irregular pores were formed in NaF solutions containing more than 0.2 M.

In order to understand the formation

mechanism of PEO films on AZ31 Mg alloy in NaF solutions, it is necessary to consider the role of both  $F^-$  and  $OH^-$  ions in not only formation of anodic oxide layer but also dielectric breakdown of the oxide layer. Fig. 4 presents the changes in pH with NaF concentration in deionized water. The pH value was lower than 6 and it did not change so much with NaF concentration when it is lower than 0.1 M. However, interestingly, the pH value increased linearly with increasing NaF concentration more than 0.2 M. The increased pH with increasing NaF concentration can be explained by equations (1) and (2), which represent removal of  $H^+$  ions and generation of  $OH^-$  ions, respectively.



During the application of anodic voltage in aqueous solution containing NaF, the increased voltage reflects thickening of resistive surface layer, which could be by the formation of  $Mg(OH)_2$  and  $MgF_2$  according to equation (3) and (4),

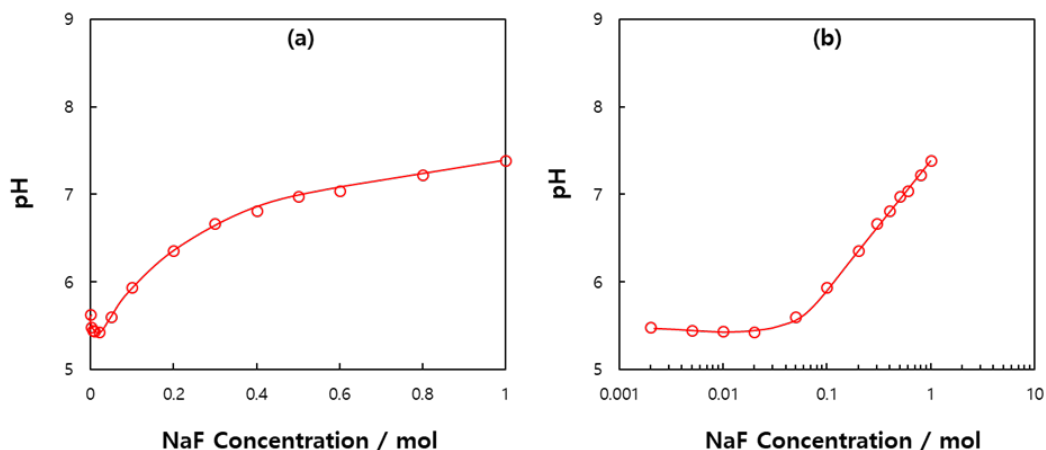
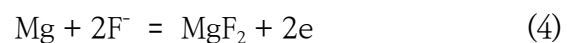


Fig. 4. Plots of solution pH versus NaF concentration in (a) linear and (b) semi-logarithmic scale.

For growth of PEO films, dielectric breakdown of oxide layer followed by immediate formation of anodic oxide at the same position is essential. In general, the dielectric breakdown could occur by the ingress of  $\text{OH}^-$  ions into the surface layer under applied high electric field, which induce local heating and finally rupturing the surface layer locally. However, considering that concentration of  $\text{OH}^-$  ions in 0.01 ~ 1 M NaF solutions in this work is lower than  $10^{-6}$  mole, as depicted in Fig. 4, it is plausible that ingress of  $\text{F}^-$  ions into the surface oxide layer by the applied high electric field could result in dielectric breakdown and formation of oxide layer. Thus, it should be pointed out that PEO films can be formed on AZ31 Mg alloy in aqueous solutions with pH 6.5 ~ 7.5 by  $\text{F}^-$  ions without help of  $\text{OH}^-$  ions if NaF concentration is more than 0.2 M in deionized water.

#### 4. Conclusions

Anodic oxidation behavior of AZ31 Mg alloy was investigated as a function of NaF concentration in deionized water at 50 mA/cm<sup>2</sup> by voltage-time curves and observation of surface and cross-sectional morphologies of the anodically treated samples for 2 min. Three different voltage-time behaviors appeared with concentration of NaF in deionized water. When NaF concentration is lower than 0.02 M, the voltage of AZ31 Mg alloy increased linearly with time in the initial stage and then reached a steady-state value more than 200 V and large size pits and thin oxide layer were formed on the surface. If NaF concentration is between 0.05 M and 0.1 M, the voltage of AZ31 Mg alloy showed large periodic fluctuations between 30 and 50 V and large number of small particles were observed on the surface. When NaF concentration is higher than 0.2 M, highly porous PEO films were formed without visible arcs on the AZ31 Mg alloy surface.

The porosity of PEO film on AZ31 Mg alloy decreased with increasing NaF concentration and it became denser and thinner with increasing NaF concentration. Cracks were observed in the PEO films formed in 1 M NaF solution but they were not formed in 0.2 M and 0.5 M NaF solutions. It is concluded that PEO films can be formed on AZ31 Mg alloy in aqueous solutions with pH 6.5 ~ 7.5 by  $\text{F}^-$  ions without help of  $\text{OH}^-$  ions if NaF concentration is more than 0.2 M in deionized water.

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