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Anodic Oxide Films Formed on AZ31 Magnesium Alloy by Plasma Electrolytic Oxidation Method in Electrolytes Containing Various NaF Concentrations

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Abstract

The present work was conducted to investigate the effects of NaF concentration in phosphate and silicate-containing alkaline electrolyte on the morphology, thickness, surface roughness and hardness of anodic oxide films formed on AZ31 Mg alloy by plasma electrolytic oxidation (PEO) method. The PEO films showed flat surface morphology with pores in the absence of NaF in the electrolyte, but nodular features appeared on the PEO film surface prepared in NaF-containing electrolyte. Numerous pores ranging from 1 to 20 μm in size were observed in the PEO films and the size of pores decreased with increasing NaF concentration in the electrolyte. Surface roughness and thickness of PEO films showed increases with increasing NaF concentration. Hardness of the PEO films also increased with increasing NaF concentration. It was noticed that hardness of inner part of the PEO films is lower than that of outer part of them, irrespective of the concentration of NaF. The low hardness of PEO films was explained by the presence of a number of small size pores less than 2 μm near the PEO film/substrate interface.

Keywords : Plasma electrolytic oxidation, Anodic oxide film, Magnesium alloy

1. Introduction

Mg alloys have been developed for automobile and mobile equipments because of their low density of 1.7 g/cm^3 which is 30% lighter than Al. One of the problems of Mg alloys, which has limited their wide applications, is their poor corrosion resistance. So, a number of researchers have tried to develop surface treatment method to improve their corrosion resistance. Plasma electrolytic oxidation (PEO) method is one of the promising surface treatment methods for Mg alloys. The PEO treatment method is used to form an anodic oxide film on valve metals using micro arcs generated by dielectric breakdown of the oxide film under high electric field [1-13].

PEO film on AZ31 Mg alloy has been studied by many authors. 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 has been conducted in many different aqueous electrolytes containing silicates [4, 14-16], fluorides [5, 8], phosphates, borates and stannite electrolytes. Verdure et al. [17] reported that all the elements in the electrolytes could be included in the PEO films on AM60 Mg alloy. Sealing of the PEO films to improve their corrosion protective property has been tried by immersion in boiling water [18], alkaline phosphate and silicate [19], stannite [20] and E-paint solution [21]. Although a number of such works have been conducted to elucidate the effects of electrolyte

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compositions on the formation of PEO films on Mg alloys, still there is lack of information about the effects of fluoride ions on the PEO film characteristics on AZ31 Mg alloy.

In this work, PEO films were formed on AZ31 Mg alloy in aqueous alkaline solutions containing various NaF concentrations, and their morphologies, thickness, surface roughness and hardness were examined in view of Nave concentration in the electrolyte.

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) was used for this work. The alloy plate of 1 mm thickness was cut into 9 × 70 mm size and the edges were abraded with # 400 Sic paper. Clean and smooth surface of the specimen was prepared by using a blade-abrading method [22] and masked using a tape, leaving 10 cm^2 of exposed area. The masked specimen was used for PEO treatment. The PEO films were formed by the application of a 0.2 ms width positive pulse current at 2200 Hz using a pulse power supply in 0.7 M NaOH + 0.15 M Na_3PO_4 + 0.175 M Na_2SiO_3 solution containing various concentrations of Nave from 0.1 M to 0.5 M at 20°C. 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. Another AZ31 Mg alloy plate was used as the counter electrode. The surface and cross-section of the PEO films were observed using SEM (Scanning Electron Microscopy, JSM-6610LV) and the surface roughness was measured by surface roughness tester (MITUTOYO, SJ-400). Hardness of the PEO films were measured using a micro hardness tester and a scratch test method increasing the load from 1 to 20 N was used.

3. Results and Discussion

Surface morphologies of PEO (plasma electrolytic oxidation) films on AZ31 Mg alloy are displayed in Fig. 1 with the concentration of NaF in phosphate and silicate-containing alkaline electrolyte. In the absence of NaF in the electrolyte, the PEO film showed relatively flat surface with large number of pores ranging from 1 to 5 mm. In the presence of 0.1 M NaF into the electrolyte, nodular features appeared on the PEO film surface and large size pores were observed between the nodules. It is interesting to note that small size pores about 1 mm diameter was located within the nodules. By adding more NaF into the electrolyte, nodular features became clearer. The nodular structure is not the same shape as those reported in the literature [23,24] because small size pores are observed within the nodules. The nodular structure observed in this work rather resembles the pancake structure where a pore is located at its center [24, 25-27].

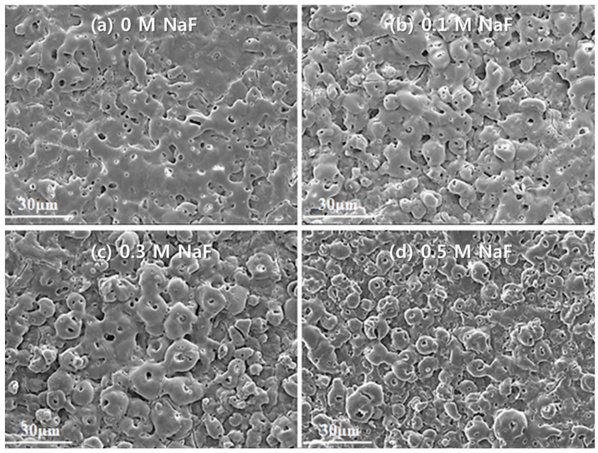

Fig. 1. Surface morphologies of PEO films formed for 10 min on AZ31 Mg alloy using pulse current in 0.7 M NaOH + 0.15 M Na_3PO_4 + 0.175 M Na_2SiO_3 solution containing various concentrations of NaF at 20°C.

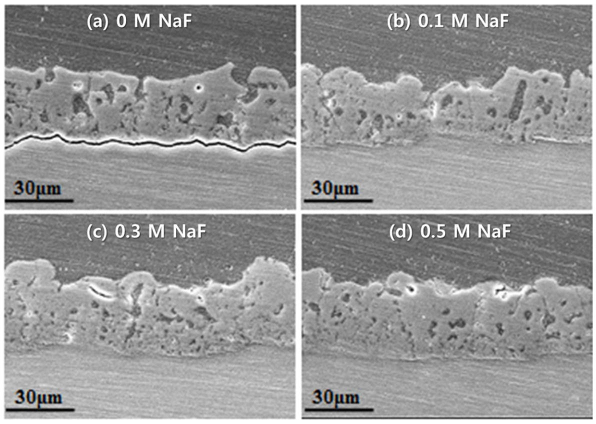

Fig. 2. Cross-sectional morphologies of PEO films formed for 10 min on AZ31 Mg alloy using pulse current in 0.7 M NaOH + 0.15 M Na_3PO_4 + 0.175 M Na_2SiO_3 solution containing various concentrations of NaF at 20°C.

The porous morphologies of PEO films with NaF concentration can be more clearly seen in their cross-sections as demonstrated in Fig. 2. A number of pores were observed in the PEO films and the size of pores showed a decreasing tendency with increasing NaF concentration in the electrolyte. It is also noted that large size pores are dispersed in the middle and outer

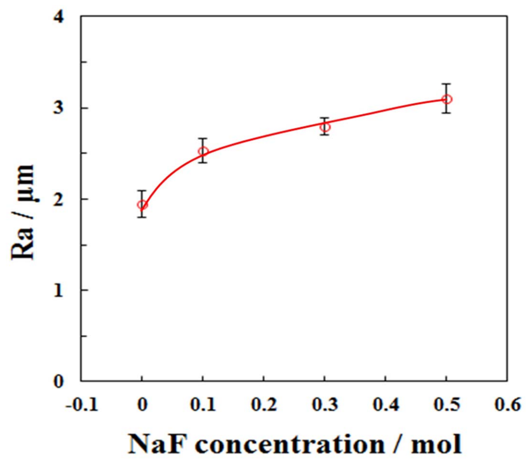

Fig. 3. Surface roughness of PEO films formed for 10 min on AZ31 Mg alloy using pulse current in 0.7 M NaOH + 0.15 M Na_3PO_4 + 0.175 M Na_2SiO_3 solution containing various concentrations of NaF at 20°C.

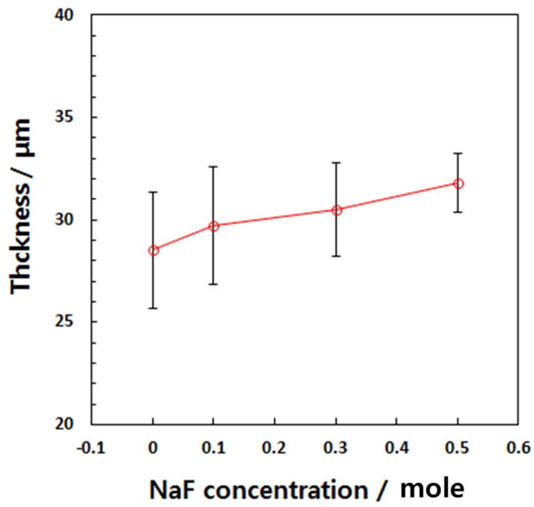

Fig. 4. Thickness of PEO films formed on AZ31 Mg alloy using pulse current in 0.7 M NaOH + 0.15 M Na_3PO_4 + 0.175 M Na_2SiO_3 solution containing various concentrations of NaF at 20°C.

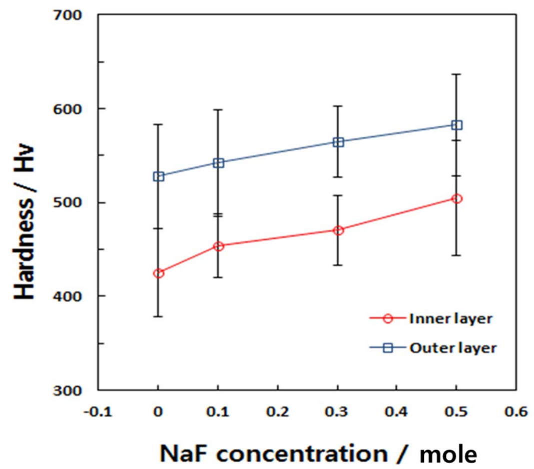

Fig. 5. Variations in hardness of PEO films at outer and inner parts of the PEO films formed for 10 min on AZ31 Mg alloy using pulse current at 20°C in 0.7 M NaOH + 0.15 M Na_3PO_4 + 0.175 M Na_2SiO_3 solution containing various concentrations of NaF.

parts of the films and large number of small size pores less than 2 μm are distributed in the inner part of the PEO films, irrespective of NaF concentration.

The line profiles of PEO film surface showed relatively irregular shapes and the PEO film/substrate interface showed relatively flat line profiles. A crack was observed at the PEO film/substrate interface in the absence of NaF in the electrolyte (Fig. 2(a)), but no interfacial crack was found in the presence of NaF (Fig. 2(b)), indicating that the adhesion of PEO films on AZ31 Mg alloy is markedly enhanced by adding NaF in an alkaline electrolyte. It is worth mentioning that there are no cracks developed across the PEO films fabricated in relatively high concentration of phosphate and silicate-containing alkaline solution.

Surface roughness of the PEO films increased with increasing NaF concentration in the electrolyte, as shown in Fig. 3. The increased surface roughness is attributed to the formation of nodular structure in Fig. 1. Surface roughness of PEO films was reported to decrease with increasing NaOH concentration owing to decrease of pore size in the PEO films [28]. Thus, it should be mentioned that structural evolution of PEO films, such as formation of nodular structure or changes in pore size, could be a key factor for changing the surface roughness of anodic oxide films on Mg alloy.

More than 25 μm thick PEO films were formed on AZ31 Mg alloy and the PEO films become slightly thickened with NaF concentration in the electrolyte, as illustrated in Fig. 4. The PEO film thickness on AZ31 Mg alloy was reported to increase with increasing NaOH concentration [28, 29]. The presence of F^- and OH^- ions in electrolyte could contribute to the formation of MgF_2 and $Mg(OH)_2$ so that anodic films can be more efficiently formed. However, still the detailed processes of more efficient formation of PEO films by NaF or NaOH concentration, are not clearly understood. So, more studies about the efficiency of PEO film formation in various electrolyte compositions should be carried out, and some new findings about the effect of carbonate ions on the PEO film formation will be presented in a following paper.

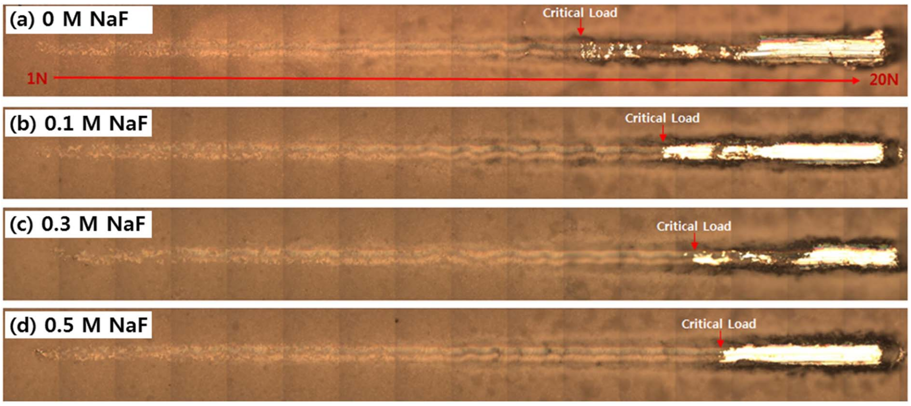

Fig. 6. Scratch test results of the PEO films on AZ31 Mg alloy by increasing the load from 1 N to 20 N. The PEO films were prepared for 10 min at 20°C using pulse in 0.7 M NaOH + 0.15 M Na_3PO_4 + 0.175 M Na_2SiO_3 solution containing various concentrations of NaF.

Hardness of the PEO films formed on AZ31 Mg alloy was measured at inner and outer parts and the results are presented in Fig. 5. It is interesting to note that the hardness of inner part is lower than that of outer part. Anodic oxide films formed on Al7075 alloy in sulfuric acid solution showed lowered hardness towards the oxide surface due to more chemical attack by longer contact with acid electrolyte [30]. Since there is no difference of contact time for different positions of the PEO films with the electrolyte, the lower hardness of inner part than outer part can not be explained by chemical attack of electrolyte. Instead, the presence of large number of small size pores in inner part of the PEO film, as shown in Fig. 2, could explain the lower hardness of inner part than outer part.

Hardness of the PEO films was also observed to increase with increasing NaF concentration in the alkaline electrolyte (Fig. 5). Fig. 6 exhibits scratch test results for the PEO film-covered surface on AZ31 Mg alloy prepared in various NaF concentrations. A critical load needed for the exposure of bare metal surface increased with increasing NaF concentration in the electrolyte, which confirms again the improved hardness of the PEO films with NaF concentration.

4. Conclusions

Morphologies, thickness, surface roughness and hardness of anodic oxide films formed on AZ31 Mg alloy were investigated in terms of NaF concentration in phosphate and silicate-containing alkaline electrolyte. Nodular features were found on the PEO film surface fabricated in NaF-containing alkaline electrolyte but flat morphology without nodules was obtained in the electrolyte without addition of NaF. A number of pores ranging from 1 to 20 μm in size were observed in the PEO films and the size of pores decreased with increasing NaF concentration in the electrolyte. It was also observed that large number of small size pores less than 2 μm are distributed in the inner part of the PEO films, independent of NaF concentration in the electrolyte. Surface roughness and thickness of PEO films increased with increasing NaF concentration. Hardness of the PEO films was also found to increase with increasing NaF concentration. It is noted that hardness of outer part of the PEO films is higher than that of inner part of it. The low hardness in the inner part of the PEO films is attributed to the presence of large number of small size pores in the film. Adhesion of the PEO film on AZ31 Mg alloy was found to be enhanced by adding NaF in an alkaline electrolyte.

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