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Microstructural characteristics of oxide layers formed on Mg–9 wt%Al–1 wt%Zn alloy via two-step plasma electrolytic oxidation

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ABSTRACT

A study investigated the formation and microstructural features of the oxide layer formed on Mg–9 wt%Al–1 wt%Zn alloy coated by two-step plasma electrolytic oxidation (PEO) where an acid electrolyte with K_2ZrF_6 was used for the second PEO coating after the initial coating was done in an alkaline electrolyte. The microstructure, chemical compositions, and constituent compounds of the oxide layers were observed using scanning electron microscopy, electron probe micro-analyzer, and X-ray diffraction, respectively. The microstructural observations showed that the micropores caused by plasma discharge were formed in the oxide layers which were comprised of three different parts, namely, inner, intermediate, and outer layers from the substrate to the surface of the sample. The outer layer contained the highest concentration of Zr element whose amount decreased toward the substrate whereas the concentration of Mg element increased in the order of outer, intermediate, and inner layers. This finding suggested that the outer oxide layer was mainly comprised of ZrO_2 compound while both ZrO_2 and $Mg_2Zr_5O_{12}$ compounds existed together as the main compounds in the intermediate oxide layer.

1. Introduction

Growing interest has been poured into the development of Mg alloys in the fields of electronics and automobile industry owing to their low density, high specific strength, and good machinability [1–3]. Despite their excellent properties, however, the poor corrosion resistance of Mg alloy samples limited the industrial applications in the numerous fields in which the high corrosion resistance was strongly required [4,5]. In order to protect bare Mg alloy samples from severe corrosion environment, several surface treatments, such as chromating, anodizing, and plasma electrolytic oxidation (PEO), have been used extensively to improve the corrosion properties of Mg alloy samples by creating the oxide layer on the top of the Mg alloy samples [6–8]. To date, PEO has been regarded as an eco-friendly surface reforming method that would generate the oxide layer on the metal surface with the excellent adhesion as intense plasma discharges with high energy state activated the plasma-enhanced electrochemical reactions in the electrolyte [9,10]. The surface morphologies of the oxide layer on Mg alloy sample subjected to PEO coating depended highly on processing variables, such as chemical compositions of the electrolyte, electrical parameters, and post treatments [11–14]. The chemical composition of the electrolyte was most important in determining the microstructure and chemical compounds of the oxide layer.

According to the recent investigations on the effects of chemical additives in the electrolyte [15–19], the oxide layers with various Zr-compounds which could be fabricated by adding K_2ZrF_6 into the electrolyte during the PEO process were desirable for enhancing the corrosion resistance. Luo et al. [15] reported that the incorporation of ZrO_2 compound into the oxide layer formed in zirconate electrolytes was propitious to improve the corrosion resistance of AZ91D Mg alloy at relatively high temperature. Liu et al. [16] demonstrated that the Zr-compounds, such as $Mg_2Zr_5O_{12}$ and ZrO_2, were beneficial for both passivation effect against the corrosion and compactness of the oxide layer formed on AM50 Mg alloy. Few studies, however, have been made to investigate the formation of the oxide layer containing Zr-compounds, in terms of the microstructural variation, chemical composition, and constituent phases affecting the corrosion resistance. Recently, Wang et al. [17] suggested that when K_2ZrF_6 was added to the alkaline electrolyte in order to form the Zr-compounds, the plasma discharges on Mg alloy samples were difficult to take place during PEO coating since the formation of the dielectric layer was apparently restricted which was associated with the instability of the electrolyte. On the other hand, the use of K_2ZrF_6 in the acid

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electrolyte could cause the noticeable anodic spark, which led to the growth of the oxide layer in Mg samples [16].

To alleviate the instability of the electrolyte as well as the difficulty in forming the oxide layer in the electrolyte with K_2ZrF_6, thus, we propose two-step PEO coating approach where an acid electrolyte with K_2ZrF_6 is used for the second PEO coating after the initial coating is made in a phosphate alkaline electrolyte. Then, the microstructure and chemical composition, and constituent phases of the oxide layer fabricated via two-step PEO coating of Mg–9 wt%Al–1 wt%Zn alloy sample were investigated.

2. Experimental

Prior to the PEO process, Mg–9 wt%Al–1 wt%Zn alloy samples with a size of $20 \times 30 \times 2$ mm^3 were mechanically polished with 1000 grit emery paper and subsequently rinsed with distilled water. The samples were then cleaned ultrasonically in ethanol. Two-step PEO coating was conducted utilizing a 6.5 kW DC power supply (Unicorntech, 65010D) in conjunction with stirring and cooling systems. The electrolytic cell consisted of a 2 l glass-vessel with a sample holder and stainless steel of dimensions 15×25 cm^2 was used as cathode. The chemical compositions and electrochemical properties of the electrolytes are listed in Table 1. The alkaline and acid electrolytes are denoted as 'Bath A' and 'Bath B', respectively. Two-step PEO coating comprised two individual PEO coatings within Baths A and B in a sequent manner. First PEO coating was conducted in Bath A for 60 s because the sample would be covered fully with the thin coating layer which might prevent the dissolution of Mg substrate further during second PEO coating. Then, the sample was pulled out from Bath A and immersed in Bath B which was prepared in a different vessel. Second PEO coating for 600 s was made in Bath B containing K_2ZrF_6 compound which might be known to trigger effectively the growth kinetics of the newly-formed oxide layer with fairly good compactness. To prevent the effects of PEO electrical parameters on the growth behavior of the oxide layer during two-step PEO coating, the current density, frequency, and duty ratio were fixed as 100 mA/cm^2, 500 Hz, and 30%, respectively. Schematic illustration of sequent two-step PEO coating is shown in Fig. 1.

The microstructure and chemical compositions of the surface of Mg alloy sample were collected using a field-emission scanning electron microscopy (SEM) equipped with an energy dispersive X-ray spectrometer (EDS). The composition profile of the cross section was examined by an electron probe micro-analyzer (EPMA). The Cu Kα radiation was used for the present X-ray diffraction analysis operated in Bragg–Brentano mode. The wide scan was performed from 20° to 80° with a step size of 0.05°.

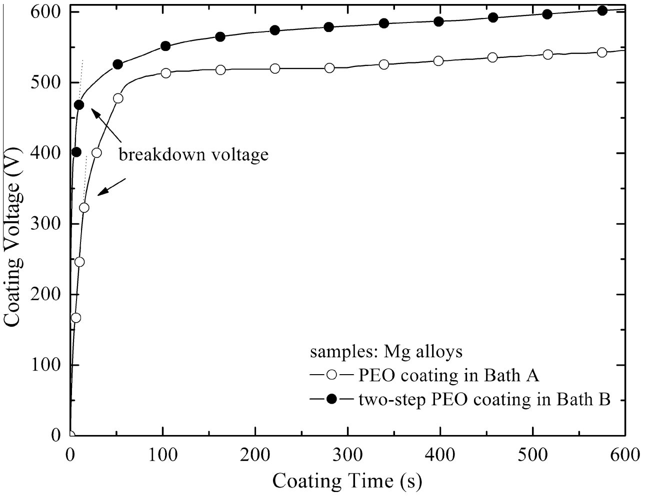

Fig. 2. Coating voltage vs. coating time of Mg alloy sample during two-step PEO coating in Bath B and PEO coating in Bath A.

3. Results and discussion

The coating voltage vs. coating time curve of the present sample processed by two-step PEO coating in Bath B is shown in Fig. 2, and this curve is also compared to that of the sample processed by PEO coating in Bath A during the same time. As reported earlier, the coating voltage of the sample increased steeply due to the partial dissolution of the substrate as well as the occurrence of the thin passivation film working as an insulator at the beginning of PEO

Table 1
Compositions and electrochemical properties of the electrolytes used.

	KOH (M)	$Na_3PO_4 \cdot 12H_2O$ (M)	H_3PO_4 (M)	K_2ZrF_6 (M)	pH	EC (mS/cm)
Bath A	0.02	0.03	–	–	12.2	10.4
Bath B	–	–	0.02	0.02	2.7	7.4

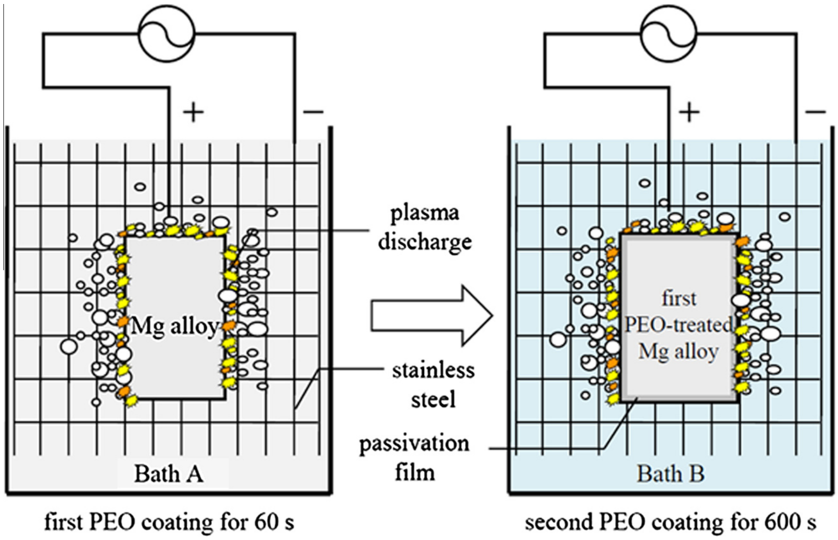

Fig. 1. Schematic illustration of the sequent two-step PEO coating.

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