ELECTROCHEMICAL RESPONSE OF ZrO_2-MgO LAYER ON Mg ALLOY VIA PLASMA ELECTROLYTIC OXIDATION FOLLOWED BY ANNEALING TREATMENT

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Introduction

Plasma electrolytic oxidation (PEO) is a surface treatment method which forms an oxide layer on Mg alloy in the plasma state generated by applying an extremely high anodic potential in wet conditions [1]. The structural morphologies processed by PEO technique depend on electrolyte including chemical composition, concentration and electrochemical parameters. It is important to determine an appropriate electrolyte in order to improve the corrosion resistance of an oxide layer on Mg alloy.
Skeldon *et al.* [2] demonstrated the influence of ZrO_2 incorporation on the corrosion resistance of Mg materials. Indeed, Hwang *et al.* [3] reported that the polarization resistances of the Mg oxide layers were enhanced by subsequent annealing treatment since the phase transformation of the oxide layer due to the dehydration reaction during annealing. However, few researches have explored how the corrosion behavior of Mg alloy would be altered if two beneficial effects coming from both the addition of ZrO_2 to the electrolyte and the subsequent annealing are combined. Therefore, the main purpose of the present study is to investigate the influences of ZrO_2 incorporation in the electrolyte and the annealing treatment on the surface morphology, chemical composition, and corrosion response of the PEO-treated Mg alloy.

Experimental

A commercial Mg alloy plate (Mg-8.29Al-0.83Zn-0.31Mn in wt%) was cut into 30 × 50 × 2 mm specimens, which were polished with #1000 SiC papers and rinsed with distilled water. PEO coatings were performed with a 20 kW power supply using stainless steel as the counter electrode in an electrolyte containing 0.09 M KOH + 0.05 M KF + 0.01 M $K_4P_2O_7$ (Cell A). Specially, the electrolyte containing 0.07 M ZrO_2 were referred to as Cell B. The applied current density was fixed at 50 mA/cm^2. After PEO coating, the specimen was subsequently annealed at 150 ^oC.
The surface morphologies of the oxide layers were observed utilizing a scanning electron microscope (SEM). Also, the corrosion behavior of the oxide layer was evaluated using electrochemical impedance spectroscopy (EIS) consisting of three electrodes: PEO-coated Mg alloy specimen as a working electrode, a platinum mesh as a counter electrode, and an Ag/AgCl electrode as a reference electrode.

Results and discussion

Fig. 1 shows the surface morphologies of the PEO-coated Mg alloy under three different conditions: specimens coated in Cell A and B and the other coated in Cell B, followed by subsequent annealing. The SEM micrographs of the oxide layers in Mg alloy coated in the electrolytes without and with ZrO_2 are represented in Figs. 1(a) and (b), respectively. In general, when a strong dielectric voltage exceeded the critical voltage, plasma bubbles and melting oxides can be thrown out through the channel, causing the micro-channels and pores during PEO coating [1]. Thus, the surfaces of both specimens possessed a number of pores with an average size of ~1 μm. It is found that the surface structure of the specimen with ZrO_2 differed from that without ZrO_2. Fig. 1(c) exhibited the surface morphology of the oxide layer in Mg alloy coated in Cell B, followed by annealing treatment at 150 ^oC. Despite the annealing treatment, the average size and distribution of micro-pores remained stationary; however, annealing treatment may lead to a change in a fraction of oxide compounds in PEO-coated Mg alloy specimen.
Fig. 2 shows that good fitting results were made between the experimental data and iterated

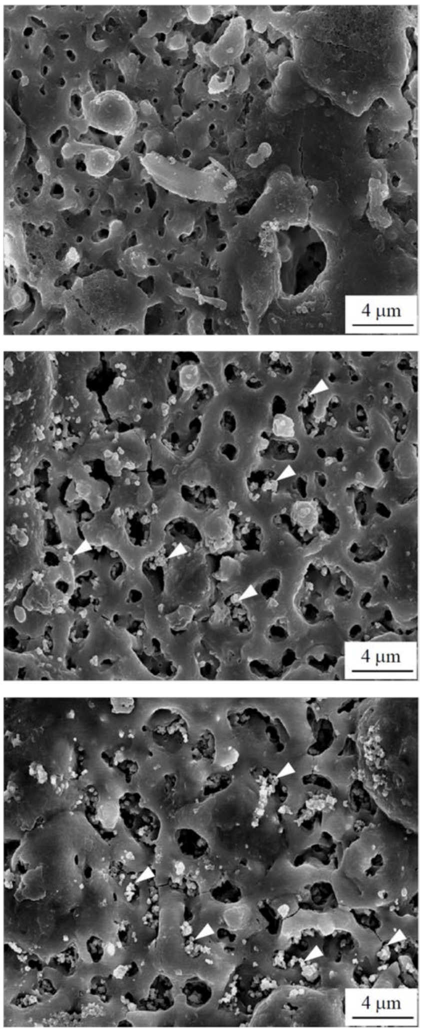

Fig. 1 SEM images showing the surface morphologies of the PEO-coated Mg alloy specimens: (a) without ZrO_2, (b) with ZrO_2, and (c) with ZrO_2 followed by annealing treatment. The arrows in Figs. 1(b) and (c) indicated the ZrO_2.

results based on the equivalent circuit model [4]. The corresponding values of the equivalent elements are listed in Table 1. According to Table 1, the values of R_o and R_i would tend to be increased in the order of the specimens coated in the electrolytes without ZrO_2, with ZrO_2, and

Table 1 Fitting results of the PEO-coated Mg alloy specimens based on the equivalent circuit model. Subscripts of *o* and *i* stand for the outer and inner oxide layers, respectively.

	R_s ($\Omega\cdot cm^2$)	R_o ($k\Omega\cdot cm^2$)	R_i ($k\Omega\cdot cm^2$)
without ZrO_2	21.3	1.03	88.7
with ZrO_2	20.1	13.2	217
with ZrO_2 + annealing	20.8	198	639

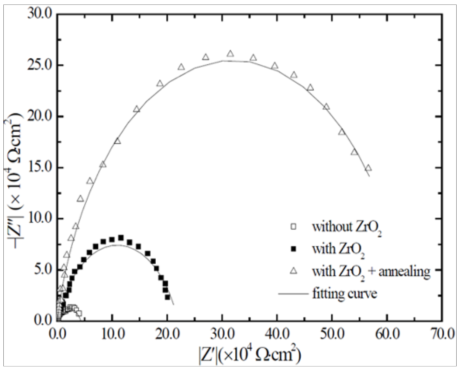

Fig. 2 Impedance test data of the PEO-coated Mg alloy specimens and the fitting results of their electrochemical plots based on the equivalent circuit model.

the specimen coated with ZrO_2, followed by annealing. Among all conditions here the specimen via PEO coating with ZrO_2 and subsequent annealing revealed the best corrosion resistance values of outer and inner layers. It was concluded that the combination of ZrO_2 incorporation and transformation of the Mg oxide layer by subsequent annealing was desirable for enhancing the anti-corrosion properties of Mg alloy.

Conclusions

The effects of ZrO_2 and annealing treatment on morphological changes and corrosion characteristics of the PEO-coated Mg alloy were investigated. Abundant ZrO_2 were successfully incorporated into the oxide layer during PEO coating. They uniformly existed and decreased the volume fraction of micro-pores, which might enhance the corrosion resistance. According to EIS analysis based on the equivalent circuit model, the oxide layer including ZrO_2 together with the annealing treatment could be selected for achieving a good electrochemical property.

References

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