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Electrochemical corrosion properties of CeO_2-containing coatings on AZ31 magnesium alloys prepared by plasma electrolytic oxidation

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ABSTRACT

Plasma electrolytic oxidation (PEO) of AZ31 Mg alloys was performed in CeO_2 particle-containing Na_2SiO_3-based electrolytes, and electrochemical corrosion properties of CeO_2-incorporated PEO coatings were investigated. The CeO_2 particles were incorporated into the coatings at early stage and were preferentially located in the outer porous layer filling the defects such as pores. The potentiodynamic and electrochemical impedance spectroscopy tests in 3.5 wt% NaCl solution indicated that the corrosion resistance of AZ31 Mg alloy was significantly improved by CeO_2 incorporation. The high impedance of CeO_2-containing PEO coated Mg alloy was still maintained after 40 h immersion in 3.5 wt% NaCl solution.

1. Introduction

Magnesium (Mg) and its alloys have been used in a wide range of lightweight applications such as construction, automobiles, aerospace, computer parts, mobile phones, and sporting goods [1,2]. However, high chemical reactivity and poor corrosion and wear resistance limit their widespread uses in many applications [3,4]. One of the effective ways to improve the corrosion resistance is a surface modification by protective coatings, which prevent the contact with environment [5,6]. A number of coating technologies are available for Mg and its alloys [7–13]. Among them, plasma electrolytic oxidation (PEO) based on the traditional anodic oxidation has proven to be promising because it can produce a thick, hard, and well adherent ceramic-like coating that has the potential to enhance the corrosion and wear resistance [14–16]. The properties of PEO coatings depend on numerous parameters [17–21], but the chemical composition of the electrolyte is known to play a decisive role in determining the properties of PEO coatings [22–27]. The presence of forsterite (Mg_2SiO_4), spinel ($MgAl_2O_4$), $Mg_3(PO_4)_2$, and MgF_2 along with MgO and $Mg(OH)_2$ in the PEO coatings is considered to be beneficial for the improvement of corrosion resistance [23,28–33].

To further improve the corrosion resistance, several attempts have been made to produce PEO coatings containing more stable oxides and compounds such as TiO_2, ZrO_2, $Mg_2Zr_5O_{12}$, Al_2O_3, and silica, by modifying the constituents of the electrolytes [34–40]. Rare earth metals, especially cerium (Ce), are commonly employed in the chemical conversion coatings and anodizing [41,42]. CeO_2 is known to improve the corrosion resistance in other systems such as galvanized steel and Ni-based alloy [43], but it was limitedly employed in PEO process. The formation of PEO coating on Mg alloy in the silicate electrolyte containing cerium nitrate ($Ce(NO_3)_3$) was not successful [44]. CeO_2 was effectively incorporated into the PEO coating after the conversion coating as a pretreatment and this combined process reduced the porosity of the coating and improved the corrosion resistance of Mg alloy [45]. However, to the best of our knowledge, one step direct process for CeO_2 incorporation during PEO of Mg alloys using CeO_2 particles (or sol) has not been demonstrated.

In this study, plasma electrolytic oxidation of AZ31 Mg alloy was conducted in CeO_2 particle-containing sodium silicate (Na_2SiO_3)-based electrolyte, and electrochemical corrosion properties of CeO_2-containing PEO coatings on AZ31 Mg alloy were evaluated by potentiodynamic test and electrochemical impedance analysis (EIS).

2. Experimental

2.1. Plasma electrolytic oxidation (PEO)

Commercially available AZ31 Mg alloy was used as the substrate for PEO. The AZ31 plates (17 × 23 × 3 mm) were ground using abrasive papers successively finer up to # 2000 grit and ultrasonically cleaned in ethyl alcohol and then dried prior to PEO treatment. The sodium silicate-based aqueous solution (Na_2SiO_3 (10 g/l) + KF

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(3 g/l)) was used as the electrolyte, and the CeO_2 particle (<5 μm, 99.9%, Aldrich) concentration in the electrolytic solution was varied from 0 to 40 g/l (0.24 M). A flat stainless steel plate (50 × 100 × 1 mm) was used as a counter electrode and the distance between two electrodes was 6 cm. PEO was conducted at constant current density of 5 A/dm^2 for 10 min using a DC pulse power supply, and the temperature of electrolytes was maintained at 15 °C by a magnetic stirrer in solution and a water cooling system. A pulse frequency and a duty cycle were fixed at 100 Hz and 6%, respectively. After the PEO treatment, the specimens were washed with ethyl alcohol and then dried.

2.2. Characterization of PEO coatings

The phases of the PEO coatings were analyzed by X-ray diffraction (XRD, M18XHF-SRA) using Cu K_α radiation ($\lambda = 0.154$ nm) at 40 kV and 200 mA between 2θ values of 20° and 60° with a step size of 0.02° at a scanning rate of 1°/min. The surface and cross-sectional morphologies of the coatings were observed using a scanning electron microscopy (SEM, JSM-5600, JEOL, Tokyo, Japan) after Au deposition by sputtering. The elemental composition of the PEO coatings was determined by energy dispersive X-ray spectroscopy (EDS) at an acceleration voltage of 20 kV using an ISIS 300 system (Link Analytical, Oxford Instruments). The microstructural characteristics of the PEO coating were further examined by high resolution transmission electron microscopy (HRTEM, Technai F20, FEI). The cross sectional TEM specimen was prepared by a conventional method. The sample was cut, ground with SiC papers successively to #2000 grit, and then polished using diamond paste to 1 μm. The polished sample of about 100 μm thickness was disk-cut and dimpled. After that, the specimen was further thinned using an ion miller (PIPS 691). The elemental distribution was also detected by EDS.

2.3. Electrochemical corrosion tests

The corrosion resistance of the PEO coatings was determined by potentiodynamic test using an EG & G potentiostat/galvanostat (model 273) with a corrosion software (model 352) in 3.5 wt% NaCl solution at pH 7.0. The potentiodynamic test was conducted using three-electrode cell (model K0235 Flat Cell) with a coated sample as a working electrode, a saturated calomel electrode (SCE) as a reference electrode, and a platinum sheet (20 × 20 mm) as a counter electrode. The one side of PEO coated sample was ground to the bare alloy and contacted with a conducting plate for electrical connection and the other side was exposed to the electrolyte through a hole of the end plate (area 1 cm^2). After 10 min of initial delay to stabilize the open-circuit potential (OCP), the potentiodynamic polarization tests were conducted from −2.0 to −1.0 V (vs. SCE) at a scan rate of 1 mV/s. Electrochemical impedance spectroscopy (EIS) was carried out in 3.5 wt% NaCl solution using an ac impedance analyzer (IM6, Zahner Electrick, Germany) after 10 min of initial delay reaching a stable OCP. The frequency was varied from 10^5 to 0.1 Hz at interval of 10 points per decade with a 10 mV sinusoidal perturbation with respect to the OCP. A platinum (20 × 20 mm) was used a counter electrode and SCE electrode was used as a reference electrode. The obtained EIS data were analyzed by the software (ZMAN version 2.0) and best-fitted to the appropriate equivalent circuit models. The corrosion tests were repeated at least three times for the reliability and reproducibility.

3. Results and discussion

3.1. Characteristics of PEO coatings

Fig. 1 shows the voltage transients at constant applied current density of 5 A/dm^2 during PEO. Similar to the previous reports [27,28], the cell voltage rapidly increased to ~250 V within 15 s, and then it gradually increased and reached a plateau of ~500 V after 5 min. The specimens were oxidized 5 more minutes in a stable sparking condition. The sparking during PEO with CeO_2 present could not be observed due to the opacity of the electrolytes. The transient curves were not noticeably affected by CeO_2 addition, but the final voltage was slightly reduced in the presence of CeO_2 particles [35,39].

The XRD patterns of PEO coatings are shown in Fig. 2 along with that of the untreated AZ31 Mg alloy. The PEO coatings were mainly composed of Mg, Mg_2SiO_4 forsterite, and CeO_2. The peak intensity of CeO_2 gradually increased with CeO_2 concentration in the electrolyte. The formation of Mg_2SiO_4 indicates that Mg^{2+} ions reaching the oxide/solution interface reacted with SiO_4^{4-} anions in aqueous solution to form Mg_2SiO_4 in the local high temperature environment [24]. The presence of CeO_2 in the XRD patterns implies that CeO_2 particles were successfully incorporated into the oxide coatings during PEO process. The reported isoelectric point of CeO_2 is pH = 6.5 [46], and the zeta potential measured by electrophoresis method (ELS-8000, Otuska, Japan) was −39.5 mV in the present electrolytic solution (Na_2SiO_3 + KF, pH = 13). Thus, it is expected

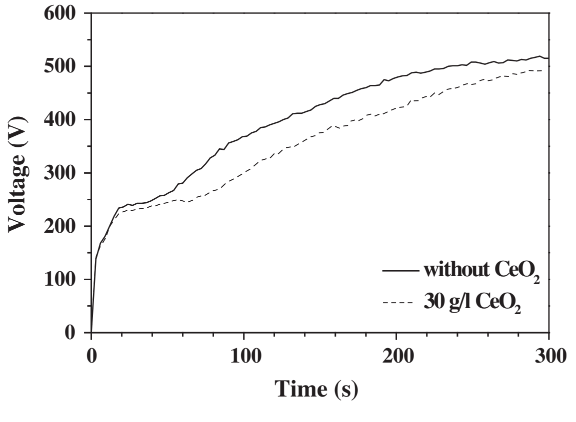

Fig. 1. Voltage transients during PEO of AZ31 Mg alloys at a constant applied current density of 5 A/dm^2 with (30 g/l) and without CeO_2 addition in sodium silicate-based electrolytes. No significant difference is seen with CeO_2 addition except a slightly lower final voltage.

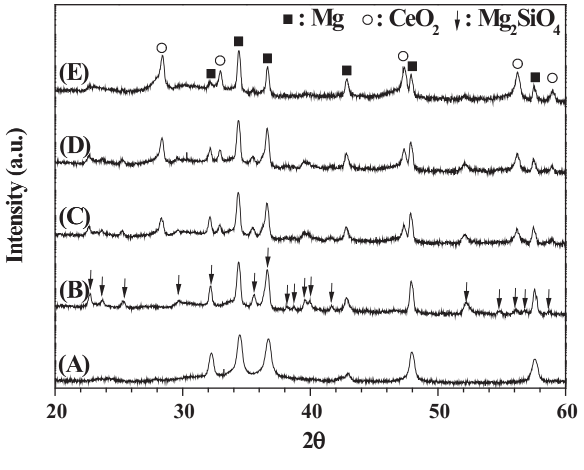

Fig. 2. XRD patterns of (A) uncoated AZ31 Mg alloy and PEO coatings obtained in (B) 0, (C) 10, (D) 20, and (E) 30 g/l CeO_2 particle-containing electrolytes. The CeO_2 content in the PEO coatings gradually increased with CeO_2 concentration in the electrolytes.