



Effect of Electrolyte Concentration on the Structure and Corrosion Resistance of Anodic Films Formed on Magnesium through Plasma Electrolytic Oxidation



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ARTICLE INFO

Article history:

Received 11 September 2016

Received in revised form 20 April 2017

Accepted 20 April 2017

Available online 23 April 2017

Keywords:

Magnesium

Plasma Electrolytic Oxidation

Electrolyte Concentration

Corrosion Resistance

ABSTRACT

The thickness and corrosion resistance of films formed on AZ31 magnesium alloys through plasma electrolytic oxidation for the same amount of electricity supplied increased with decreasing electrolyte concentration irrespective of the current density. For all electrolytes of phosphate, silicate, and aluminate, the initial bending/breakdown voltage increased linearly with the logarithm of the decreasing electrolyte concentration and exhibited no dependence on the current density. The chemical composition of the films was independent of all electrolysis conditions such as electrolyte concentration, current density, and anodization time. This behavior is explained by a mechanism in which anion incorporation is governed by a chemical reaction/precipitation under plasma but not by the electric field, unlike the case for conventional anodizing of valve metals without sparking. The corrosion resistance of the films tended to increase as a function of the logarithm of the film thickness, irrespective of the electrolyte species and electrolysis conditions.

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1. Introduction

The surface treatment of magnesium and magnesium alloys has attracted considerable attention owing to increasing demands for their use as the lightest practical metal in various industrial areas such as in automobiles, train carriages, architectural materials, electrical appliances, and biomedical devices including implants and stents. In particular, AZ31 alloys, which can be easily modified to a thin plate by rolling or press-forming (unlike AZ91 alloys), are receiving much attention with an effort to improve its corrosion resistance.

An anodic oxidation process has commonly been used for years to produce a sufficiently corrosion resistant surface [1–3] because the corrosion resistance of bare magnesium is substantially low [4–11], although much effort for the improvement has been focused on alloying [12,13]. Among several types of surface treatments, anodization with spark discharges at a high voltage called plasma electrolytic oxidation (PEO) or micro-arc oxidation

(MAO) has been applied for magnesium [3,14,15] more often than for typical valve metals (Ta, Nb, Zr, Al, Ti, Hf, and W) [16]. This is due to the limited rectification property of the oxide film on magnesium with an incomplete valve effect (Ag, Cd, Fe, Mg, Si, Sn, Zn, and Zr) [17]. In general, except for low voltage anodization in the range of 5–7 V [14], conventional anodization without sparking is not suitable for magnesium to obtain a dense and thick protective oxide film. The PEO process produces thick and hard ceramic-like coatings of several tens of microns in thickness, with the incorporation of species originating from the electrolyte used and improved corrosion and wear resistance [14,15,18–28]. In the PEO process, a high anodic voltage of more than 200 V is applied and intense sparking with visible light emission is generated on the oxide surface that induces a plasma state. According to the Pourbaix diagram [4], hydroxide film is formed on magnesium only in the alkaline region. Therefore, besides fluoride and/or chromate including electrolytes such as Dow17 [3,15,29], alkaline solutions containing phosphate [23,30–35], silicate [25–28,36–42], and aluminate [43–46] are often used as electrolytes in PEO for magnesium alloys. It was reported that the anodic films formed in a Na₃PO₄ solution exhibited a higher corrosion resistance than that of films formed in other electrolytes [18,19]. However, when we

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used mixed electrolytes and PEO was carried out using a pulsed power supply, a mixed electrolyte of silicate and phosphate with a proportion of phosphate of approximately 20% resulted in the highest corrosion resistance [24]. The microstructures (e.g., diameter and number of pores/spherical cavities) of the anodic films formed under sparking were strongly affected by the degree of sparking, such as the size, number, and appearance frequency of sparks, and not only by the formation voltage itself [23]. Compared to numerous fundamental studies on anodic film growth on aluminum [47], anodizing mechanism of magnesium, especially, by PEO process, for controlling the oxide composition, microstructure, film thickness, crystallinity, as well as other properties is not yet fully understood.

In the present study, to reveal the anodizing mechanism of magnesium under sparking discharge through a PEO process, the effect of the electrolysis conditions on the composition, microstructure, thickness, and corrosion resistance of anodic films was investigated with a focus on the electrolyte concentration as well as the electrochemical formation behavior. Sodium phosphate was the main electrolyte used for the PEO process. Moreover, sodium silicate and sodium aluminate were used for the process.

2. Experimental

The magnesium specimens used were obtained from an extruded plate of AZ31 B alloy with a thickness of 1 mm cut into pieces to give a working area of 5 cm². The chemical composition of the alloy is listed in Table 1. The specimens were degreased in acetone in an ultrasonic bath for 3 min prior to further use. Before anodization, the specimens were pretreated in a mixed acid solution of 10 vol.% HNO₃–2 vol.% H₃PO₄ for 20 s followed by dipping in a 5 wt.% NaOH solution at 80 °C for 1 min to obtain a clear and bright appearance on the surface. Direct current (DC) anodization was carried out with different concentrations (0.0625–0.5 mol·dm⁻³) of Na₃PO₄, Na₂SiO₃, and NaAlO₂ solutions at a constant current in the range of 100–600 A·m⁻² at 25 °C.

The morphology of anodic film obtained by the PEO process was evaluated using field-emission scanning electron microscopy (FESEM, JEOL JSM-6701F) and three-dimensional laser scanning microscopy (KEYENCE VK-X200). Elemental analysis was performed over an area of 250 × 200 μm² using energy-dispersive X-ray spectroscopy (EDX) with a JEOL EX-54175JMU spectroscope attached to an SEM (JEOL JSM-6380LA). To obtain further details of the film structure, transmission electron microscopy (TEM; JEOL JEM-2100F, operated at 200 kV) was also used. Electronically-transparent sections were prepared using focused ion beam milling (FIB; Hitachi SMI3050SE). The sample's chemical composition was investigated using energy-dispersive X-ray spectroscopy (EDX; JEOL JED-2300T). In this analysis, the diameter of the incident electron beam was set to 1 nm. The thickness of the anodic films was measured using a dual-type current thickness meter (Sanko electronic laboratory SME-1). The average value of 10-point measurements was used in the present work.

The corrosion resistance of the films was evaluated using an immersion test in a 0.1 mol·dm⁻³ NaCl aqueous solution at 30 °C for 100 h. The ratio of the average corrosion area was determined from a photographic image of the surface using image analysis software available in the public domain, Image J.

Table 1
Chemical composition of AZ31B magnesium alloy (wt.%).

Mg	Al	Zn	Mn	Si	Cu	Fe	Ni
Balance	3.34	1.13	0.35	0.02	0.001	0.002	0.0001

3. Results and Discussion

3.1. Anodization behavior and film structure

Typical voltage–time (V–t) curves for constant current density anodization of AZ31 B alloys at 200 A·m⁻² in Na₃PO₄ solutions with different electrolyte concentrations and the changes in the surface appearance during electrolysis are shown in Fig. 1. The voltage increased almost linearly with time due to dense oxide layer growth up to the first bending (breakdown) voltage, suggesting a change in the film structure from a barrier type to a porous type, accompanied by moderate electric breakdown (Fig. 1a). In the case of a 0.5 mol·dm⁻³ Na₃PO₄ solution, many small sparks illuminated and moved around the surface followed by a gradual increase in voltage oscillation when the slope of V–t curve decreased at approximately 150 V until the voltage increased up to 200 V after 20 min, as shown in Fig. 1b. After the voltage reached 200 V, strong voltage oscillation with intense sparking discharge and gas evolution started, followed by an increase in the spark size and strength and a decrease in the number of sparks. Shi et al. [26] measured the change in oxygen evolution content with the V-t transient when anodizing AZ91D in silicate solution. They found that the oxygen evolution that lowered the current efficiency became vigorous when the formation voltage increased and intense sparking appeared. The spark color also changed from whitish to orange, suggesting Na incorporation in the film. Sparks were localized at the specimen edge after 30 min in the case of 0.25 mol·dm⁻³ Na₃PO₄ and after 20 min when the concentration was increased to 0.5 mol·dm⁻³ (see Fig. 1b). In the case of 0.25 mol·dm⁻³ Na₃PO₄, the slope of the V–t curve changed at a higher voltage, i.e., approximately 200 V, and the start of strong voltage oscillation was delayed to approximately 250 V. This suggests that a certain thickness (or a certain oxide resistance) is needed for the start of voltage oscillation induced by a strong breakdown, i.e., intense spark discharge on the film. A detailed study on the initial anodization behavior of magnesium will be published elsewhere. Nevertheless, it is noted that prolonged anodization durations such as 60 min resulted in excess dissolution of the substrate edges where intense sparking was concentrated. Although the sparking discharge is extremely beneficial for PEO anodization through its assistance with oxide film growth, excess sparking caused by the localization has to be avoided. In the case of 0.125 mol·dm⁻³ Na₃PO₄, the voltage increase started after about 30 min. That is, a certain concentration of electrolyte is necessary to start the growth of an anodic oxide layer through PEO.

The surface and cross-sectional SEM images obtained after 10 min of anodization in 0.5 mol·dm⁻³ Na₃PO₄ at 200 A·m⁻² with the amount of electricity supplied was 120 kC·m⁻² are shown in Fig. 2. A large number of spherical voids/cavities with different sizes up to 10 μm were dispersed in the uneven oxide layer with a thickness ranging from 5 to 50 μm as shown in Fig. 2(b). This lava-like structure of the film implies that the anodic film was formed in a molten state caused by plasma and solidified after rapid cooling. Since the emergence of large-sized plasma caused by intense sparking discharge moved from place to place, the film thickness differs significantly depending on the location. As indicated in the TEM images (see Fig. 2(c)), the PEO film was mostly amorphous, but numerous crystallites shown as dark spots in the size of 30 nm (see the inset in (c)) were dispersed. Small pores of sizes of less than approximately 1 μm were predominantly located near the interface area between the substrate and the film. EDX point analysis assigned as the square A in Fig. 2(c) of the film, that is a typical PEO film area, revealed that the content of P was significantly high (see Fig. 2(d) A). As previously reported [23,48,49], the PEO film formed in Na₃PO₄ solution mainly comprises amorphous magnesium phosphate and crystalline

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