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Growth process of plasma electrolytic oxidation films formed on magnesium alloy AZ91D in silicate solution

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Abstract

In order to get a clear picture for describing the growth process of the oxide film formed on magnesium alloy AZ91D under plasma electrolytic oxidation (PEO) in alkaline silicate solution, the characteristics of PEO films formed at different reaction stages were systemically investigated. The results of morphologies, compositions and electronic properties indicated that the PEO films had a different growth behavior as the PEO treatment proceeding. At the initial stage (before the occurrence of sparking), the growth rate of PEO films was low, the elements (O, Mg, Al and Si) contents were varied obviously and the donor concentration in the film was kept at a high level. After sparking occurred, the PEO films showed a higher growth rate due to the high transfer rate of ions and electrons and the existence of plasma reactions; simultaneously, the films formed on α- and β-phase exhibited different growth rate. With treated time increased, the thickness of PEO films and transfer resistance to ions and electrons were also increased; thereby, the growth rate of the PEO films was decreased gently.

Keywords: Magnesium alloy AZ91D; PEO film; Oxidation process; Capacitance measurement; Semiconducting properties

1. Introduction

Plasma electrolytic oxidation (PEO) [1–4] developed from conventional anodic oxidation, has been brought for surface modification of magnesium and its alloys due to some significant properties of the PEO films, such as good adhesion, high hardness and high corrosion resistance [4–7]. PEO treatment on magnesium alloys has been developed for several decades and a number of studies focused on the dependence of films performance on PEO conditions (such as electrolyte composition [5], voltage model [8], treated time [9], heating treatment [10] and so on). Recently, some researches also outlined the film growth process on magnesium alloy [11,12]. However, systemic investigations on the variation of structure, composition and electronic properties of the films formed on magnesium alloys during PEO process were seldom reported.

In view of barrier effect of PEO films composed of outer porous layer and inner barrier layer [13,14], transportation of electrons and ions between electrolyte and magnesium electrode with PEO films would be some certain influenced. This makes the magnesium electrode exhibit different electrochemical behavior in comparison with bare metal electrode, but similar to that of semiconducting or insulating electrode. Thus, some methods used to study semiconducting electrodes can be adopted to investigate the properties of magnesium electrode with PEO films. Capacitance measurement based on Mott–Schottky (MS) theory [15–17] is a conventional technique to probe electronic properties of a semiconducting electrode in aqueous electrolyte. The slope changing of MS curves often indicates the intrinsic changing of semiconducting electrode due to concentrations variation of donor or acceptor. Thus, electronic properties of semiconducting magnesium electrodes can be probed by capacitance measurement.

The aim of this work is to reveal the growth process of PEO films and to develop a proper PEO treatment mode for magnesium alloys. The PEO films formed at different reaction stages (treated at different cell potential and for different time) in alkaline silicate electrolyte were prepared. SEM and EDAX were, respectively, used to examine the morphologies and composition of those PEO films. Meanwhile, capacitance measurement was

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carried out in PEO electrolyte to evaluate the donor or accepter levels of the PEO films. Then, PEO films growth process was detailedly analyzed based on the above-mentioned results.

2. Experimental

2.1. Samples and solutions

Rectangular samples (with dimensions 10 mm × 10 mm × 25 mm) made of die-cast magnesium alloy AZ91D (Al 8.5–9.5%, Zn 0.50–0.90%, Mn 0.17–0.27%, Mg balance) were used as working electrodes. The working electrodes were sealed with epoxy resin leaving only the polished square surface with an area of 1 cm^2. For clearly observation of the surface morphologies of samples after PEO treatment, the working surface of magnesium electrodes were successively ground with a series of SiC papers and finally polished with diamond paste, then degreased in ethanol and distilled water before PEO treatment. Graphite electrodes were used as counter electrodes. The PEO films used for characteristic measurements were prepared under pulse voltage model and the cell potential were increased step by step till a certain value, then the magnesium electrode was oxidized under this value for some time. The universal PEO electrolyte containing silicate (15–20 g/L Na_2SiO_3 and 3–8 g/L KOH) was used. The same electrolyte was used for capacitance measurement. All solutions were made of analytical grade reagents and distilled water.

2.2. Test methods

The surface morphologies and chemical composition of PEO films were examined by XL-30FEG scanning electron microscopy (SEM) with energy dispersive analysis of X-rays (EDAX). Elemental mapping in the cross-section of PEO films was measured by S-3400N scanning electron microscopy. The thickness of PEO films was measured by HCC-25 eddy-current equipment.

Capacitance measurements were conducted using a conventional three electrodes electrochemical cell with the Mg samples as working electrode, a platinum plate as auxiliary electrode and a saturated calomel electrode (SCE) as reference. Capacitance measurements with variable anodic over potential from 0.5 to −0.5 V (SCE) was performed at fixed frequency of 1000 Hz by PAR 2273 potentiostat in cathodic direction with a potential scanning rate of 20 mV/s. All experiments were carried out at room temperature.

3. Results and discussion

3.1. Morphology characteristics of PEO films

The surface morphologies of AZ91D alloy samples formed at different stages of PEO process were shown in Fig. 1. It can be seen that the magnesium alloy AZ91D substrate (Fig. 1a) is consisted of α- and β-phase ($Mg_{17}Al_{12}$). When magnesium electrode was anodized at 100 V for 30 s, a few granular products were formed on its surface while the original phase structure still visible clearly (Fig. 1b). As cell potential was increased to 150 V and stabilized at this potential for 30 s, a large amount of small gas bubbles occurred on the sample surface during PEO process. The surface including both α- and β-phase of magnesium electrode were covered by a thin and uniform oxide film that was composed of many fine granular particles as shown in Fig. 1c. Because this potential (150 V) has not reach the spark discharge potential of magnesium alloy AZ91D in the alkaline silicate solution, the anodizing process was similar to that of the conventional anodic oxidation one. That is to say that the film formation was obeyed the conventional anodic oxidation reactions. On the magnesium electrode, Mg^{2+} was formed by dissolution of magnesium from the substrate under the effect of electric filed (reaction (i)). Most of the gas produced on the anodic electrode was oxygen generated by decomposition of OH^- [18] (as the reaction (ii)):

$$Mg \rightarrow Mg^{2+} + 2e^- \text{ (anodic dissolution)} \quad \text{(i)}$$

$$4OH^- \rightarrow O_2 + 2H_2O + 4e^- \text{ (side reaction)} \quad \text{(ii)}$$

The formation of uniform granular products on magnesium alloy AZ91D can be attributed to the outward migration of Mg^{2+} and inward migration of ${SiO_3}^{2-}$ and OH^- under the effect of high potential. When the concentrations of Mg^{2+}, ${SiO_3}^{2-}$ and OH^- reached a critical value in the electrode/electrolyte interface, film formation reactions would take place. Such as $Mg(OH)_2$ and Mg_2SiO_4 would be formed by the following reactions (iii) and (iv), respectively:

$$Mg^{2+} + 2OH^- \rightarrow Mg(OH)_2 \quad \text{(iii)}$$

$$2Mg^{2+} + {SiO_3}^{2-} + 2OH^- \rightarrow Mg_2SiO_4 + H_2O \quad \text{(iv)}$$

The products resulted from the above reactions would deposit on and cover the surface of magnesium electrode. After the electrode was taken out of electrolyte and desiccated, magnesium oxide (MgO) would be produced by dehydration reaction of $Mg(OH)_2$ as reaction (v):

$$Mg(OH)_2 \rightarrow MgO + H_2O \quad \text{(v)}$$

When the cell potential was not too high (150 V), these reactions would uniformly take place on the magnesium electrode in alkaline silicate solutions. Thus a thin oxide film formed under 150 V would uniform and cover the whole electrode surface (both α- and β-phase). The thickness measurement indicated that the thin oxide film was about 2 μm (in Fig. 2). This thin oxide film would act as a barrier layer, which not only effectively separates magnesium substrate from electrolyte but also inhibits the transfer of electron and ions between electrolyte and metal substrate. Thus, a high electric field would be formed in the thin oxide barrier layer during the following process when the applied potential was increased further. The high electric field intensity accumulated in the thin oxide layer was the indispensable conditions for spark discharge in the following PEO process.

When the cell potential reached about 200 V, which was over the breakdown potential of the thin oxide film formed on the magnesium electrode, there were numerous bright fine sparks