Fluoride effect on plasma electrolytic oxidation coating formed on Mg-Al alloy in alkaline electrolytes

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Abstract
Plasma electrolytic oxidation (PEO) is an effective protection technique developed for light alloys, such as aluminum, magnesium and titanium alloys. PEO electrolytes often contain fluorides, yet their functionality is not well understood during the oxide layer formation and growth. In the present work, we tracked the fluoride evolvement contained in PEO ceramic protective layer formed on AZ91 magnesium alloys. It is found that a fluoride rich layer with 1–2 μm thickness is often formed at the coating/substrate interface and nanocrystalline MgO islands with size of 20–60 nm are found to be embedded in amorphous coating substrate.

1. Introduction
As an effective sparking anodizing treatment technique, plasma electrolytic oxidation (PEO) has been used to produce surface corrosion protection layer for magnesium and its alloys for about 50 years old [1]. PEO process utilizes high voltage microdischarge process based on a fundamental electrolyte of dilute silicate or phosphate-silicate solutions along with some additives, such as fluoride. It can form a coherent, ceramic-type coating over the anode surface along with diffusion and mass transport of second phase materials [2, 3]. Under the conditions of chemical conversion, a thin magnesium fluoride (MgF2) film can be formed on magnesium by immersion in a solution containing fluoride anions. Mu and Han investigated the effect of potassium fluorozirconate electrolyte on pure magnesium disks and found that the contained fluoride, for instance, MgF2, which has improved the coating performance [4]. Liu et al revealed a similar PEO coating formed in this fluoride-containing electrolyte [5]. In fact, it is well known to use the fluoride-containing electrolyte in commercial PEO processes for magnesium alloys, such as DOW17, HAE, Magoxid, Tagnite, Keronite etc. In most cases, MgF2 is formed among other compounds [6, 7]. Aleksey et al found the negative current is not contributed to surface charging, but associated with the changes of the coating’ chemical or morphological characterization [8]. In this study, we investigated the fluoride evolvement during the process of PEO coating formed on Mg-Al alloy in alkaline electrolyte solution.

2. Experimental

2.1. Materials and PEO procedure
The AZ91 magnesium alloy samples used in this study were produced by self-made casting process. The weight ratio (wt%) of the main alloy elements is: Al8.1, Zn0.85, Mn0.27, and Mg balance. Typical dimensions of the samples are 50 × 30 × 10 mm³. Main components of the aqueous electrolyte are (NaPO3)₆ and Na₃AlF₆ and the detailed electrolyte composition is listed in table 1. pH value of the electrolyte lies in the range of 11–12 before PEO. The electric regime was a high frequency (700 Hz) bipolar pulse generator. The electrolyte temperature was below 35 °C during the coating process. The counter electrode was a stainless steel plate. The duty cycle is fixed as 0.3 and the mean voltage of the negative electrical pulse was set at −60 V. Depending the microdischarge stage, the experiment utilized a method of step-down current control as shown in figure 1.
During this process, a large initial electric current density $i_0$ ($7–9\text{ Adm}^{-2}$) was first used to initiate the oxidation process, during which the output voltage increased from 0 V to about 200 V ($U_0$). When the electric current density $i_1$ was reached to the range of 4–6 Adm$^{-2}$, the output voltage continued to increase. When the voltage $U_1$ reached 420 V, the electric current density $i_2$ was set a much smaller value of 0.5–1 Adm$^{-2}$ and then kept for the rest processing time. The entire PEO process lasted for 15 min and it is found the above step-down current control approach creates the most stable and effective processing results. After cleaning, the PEO samples are kept in a drying chamber and ready to examination.

2.2. Microscopic and composition analysis of the oxide coatings

2.2.1. SEM study
PEO coatings are investigated with scanning electron microscopy (SEM, JXA-8800R) for chemical composition and morphology. For cross-sectional analysis, the processed AZ91 samples were embedded in epoxy resin block. Due to the low conductance of the oxide layers, the samples were sputter-coated with a thin layer of carbon prior to microstructure observation.

2.2.2. TEM study
Transmission electron microscopy (TEM, Philips Tecnai F20) analysis was used to obtain more detailed structural and compositional information along the cross-section of the PEO layer. The cross-section specimens were prepared by the sandwich method, where a pair of samples were glued surface-to-surface to form a sandwich before being thinned mechanically down to about 80 $\mu$m in thickness, followed by a subsequent perforation using Ar ion milling, which was shown in figure 2. It is noted due to the brittleness and porous nature of the oxide film, special care is needed during the latter stage of Ar ion milling for the TEM specimen preparation to prevent coating abscission.

3. Results

3.1. General observations of the AZ91 Mg alloy PEO process
The typical appearance of microdischarges during the plasma electrolytic oxidation is shown in figure 3. Sparking and gas evolution were the two major phenomena. During the initiation process, a large number of sparks are generated in the form of moving discrete white microdischarges on the sample surface.
Accompanying the increasing voltage, a portion of microdischarges turn yellow, grow larger, and move at a lower speed. Then in the stable state all of the microdischarges turn yellow and there is apparent decrease in the microcharge spatial density.

3.2. Morphology and composition analysis of the oxide films with SEM

Figure 4 compares the surface morphology and corresponding composition mapping between the neighboring areas with and without the surface oxide layer. The right portion of the SEM image shows the surface of the PEO layer while the oxide layer on the left portion of the image has been stripped. Figures 4(b)–(c) show the surface elemental distribution obtained from the same region as in the SEM, where the grey scale reflects the abundance of the corresponding individual element. The element distribution is uniform across the respective oxidized and stripped regions but that fluorine concentration in the stripped region is much higher than that in the unmoved region.

Closer look at the surface morphology and corresponding composition mapping of the PEO formed oxide is shown in figure 5. The surface oxide layer formed by PEO contains randomly distributed local discharged channels and melted spots with various sizes. Individual discharge channel has crater-like opening with its central axis perpendicular to the substrate surface. The discharge channel opening has a thickened pancake shape containing microcracks. Surface analyses of Mg, P and O show uniform distribution of these elements. Fluorine signal is very weak, indicating a low surface concentration of the element.

The PEO film in the cross-section mode provides further information on the morphology and composition distribution of elements in the oxide film. As shown in figure 6, the oxide layer has a uniform thickness and a high concentration of voids can be observed close to the oxide/substrate interface. Element analyses show that Mg, O and P are uniformly distributed across the PEO film thickness, but the F distribution is not uniform across the film thickness and there exists a clear fluoride rich layer at the coating/substrate interface. This F rich layer has a thickness of 1–2 μm. EDX spectrum collected from this interfacial region confirms the existence of a relative high concentration of fluorine, as shown in figure 7.
3.3. TEM analysis

To better understand the PEO layer microstructure and composition distribution, TEM investigations have been conducted. Figure 8 shows the TEM cross-sectional micrograph of the surface layer. This PEO layer is mostly amorphous and includes higher concentration of nanocrystalline MgO particles distributed towards surface and the MgO nanoparticles have sizes between 20–60 nm. These MgO nanocrystals can be characterized by the (111), (200), (220) and (222) diffractions from the selected area electron diffraction (SAED). As showed in figure 2, the TEM sampling method can’t ensure the thinner film analysis region located within the fluoride rich layer. The result shows that no crystalline fluoride phases (MgF$_2$, NaMgF$_3$, etc) was detected. TEM image shows a cavity located close to coating/substrate interface. Except for the cavity, the amorphous oxide layer has a dense and uniform appearance.

![Figure 4](image1.png)

**Figure 4.** (a) SEM morphology of the PEO coating, and corresponding composition distribution of (b) magnesium, (c) phosphorous, (d) oxygen, and (e) fluorine.

![Figure 5](image2.png)

**Figure 5.** (a) SEM morphology of discharge channels within PEO coating, (b) surface morphology and the related element mapping of (c) magnesium, (d) phosphorous, (e) oxygen, and (f) fluorine.
Using the TEM mode, the related elemental compositions were shown in Figure 9. Here only the layer close to the interface was analyzed, in this region with an average thickness of about 3 μm, fluorine had a relative stable concentration with a slow drop from interface. In contrast, oxygen concentration within this thickness has two distinct distribution regions: a high concentration region close to the substrate interface and a lower concentration towards the oxide surface.

4. Discussion

4.1. Effect of fluorine on the oxide layer formation
The formation of the fluoride enrichment zone at the coating/substrate interface is closely related to the fluoride in electrolyte and we believe the fluoride influence can come from the following three contributions. First, prior to the sparking process, fluorine ions in electrolyte stimulate the formation of a passivation layer on the magnesium alloy surface [9]. And once the PEO process is initiated, there is growth of MgF₂ at the substrate/coating interface in addition to the magnesium oxide and hydroxide formation [10]. In the meanwhile, the

![Figure 6](image6.png)

Figure 6. (a) SEM morphology of the PEO cross-section layer and the related element mapping of (b) magnesium, (c) phosphorous, (d) oxygen, (e) fluorine.

![Figure 7](image7.png)

Figure 7. EDX spectrum at the PEO layer/substrate interface.
enrichment of fluoride within the initial oxide supplies additional electrons, which can alter the electrical character of the coating and helps the initiation of dielectric breakdown according to the conventional electron avalanche theory \[11\]. Finally, after the discharge damping, fluoride will enter the discharge channel with electrolyte and reacts with magnesium at the bottom of pores to form the fluoride rich area as observed in figure 5(f). The growth of new oxide mainly locates at the coating/substrate interface, and the inward propulsion of fluoride enrichment zone into the magnesium substrate causes further film thickening \[12\]. Figure 10 shows the evolution process of the fluoride rich layer during the course of the PEO coating growth.

4.2. MgO nanocrystal and cavity formation mechanism

The existence of nanocrystals in amorphous oxide films formed on Al and Ti substrates has been reported by several groups \[13–16\]. In general, the nanocrystalline islands are believed to form during the following two stages. In the first step, when the initially formed amorphous film was very thin and the electric field strength in the film can be high enough to enable a sufficient ionic flow to stimulate the growth of MgO nuclei. This crystallization induced by electric field, or by the sporadic electric discharge, was observed by Vermilyea, Yahalom, Zahavi and Schimizu \[17\]. In the second stage, subsequent microdischarge breakdown will cause an increase in oxidation rate and a change in chemical and physical properties of the formed coating. In addition, ejected Mg particles from substrate can be imbedded, oxidized and converted into MgO crystalline inclusions in the amorphous coating \[11, 18, 19\].

The sealed cavities formed in the oxide film can be related to the oxygen generation at the interface between the MgO nanocrystals and amorphous matrix, with oxygen bubbles formed and embedded within the latter.

Figure 8. (a) TEM image of the PEO coating, (b) corresponding SAED pattern.
These bubbles could grow, and either be sealed in the coating to form cavities contained in the oxide film or eventually be released by bubble rupture at the film surface.

4.3. Relationship between the fluorine enrichment zone and the barrier layer

The presence of a barrier layer between the bulk porous oxide film and substrate was first demonstrated by Bradford et al. and Gulbransen et al. during their investigation of the passivation process using electrochemical methods. In general, it was hypothesized that this barrier layer of anodic film formed on magnesium alloy is mainly MgO [10, 21] with fluorine species incorporated in this layer. The fluorine in enrichment region formed in this study can be an indicator which the coating propelled inward to the magnesium substrate.

Figure 9. (a) TEM micrograph of cross-section of the PEO coating and the related element distribution, (b) magnesium, (c) phosphorous, (d) oxygen, and (e) fluorine.
5. Conclusions

During the PEO coating of AZ91 magnesium alloy, the fluoride contained in the electrolyte solution played an important role on the growth process and a fluoride-enriched layer of about 1–2 μm in thickness was formed at the coating/substrate interface.

The fluoride layer was mainly composed of the amorphous substrate, nanocrystal MgO particles with 20–60 nm size and some cavities. The formation of the MgO nanocrystal may be closely related with the imbedding and subsequently oxidizing of the direct ejected particles of Mg substrate.

The oxygen content in the inner layer was higher than that in the outer layer while the content of fluorine was even in both layers, which suggested that the so-called barrier layer was included in this fluoride zone, and that the fluorine may be only a retained marker during the course of the barrier layer propelling inward to magnesium substrate.

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