Effects of CH₃OH Addition on Plasma Electrolytic Oxidation of AZ31 Magnesium Alloys*

HE Yongyi (何泳仪), CHEN Li (陈砺), YAN Zongcheng (严宗诚), ZHANG Yaley (张亚磊)

College of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, China

Abstract  Plasma electrolytic oxidation (PEO) films on AZ31 magnesium alloys were prepared in alkaline silicate electrolytes (base electrolyte) with the addition of different volume concentrations of CH₃OH, which was used to adjust the thickness of the vapor sheath. The compositions, morphologies, and thicknesses of ceramic layers formed with different CH₃OH concentrations were determined via X-ray diffraction (XRD), energy-dispersive spectroscopy (EDS), and scanning electron microscopy (SEM). Corrosion behavior of the oxide films was evaluated in 3.5 wt.% NaCl solution using potentiodynamic polarization tests. PEO coatings mainly comprised Mg, MgO, and Mg₂SiO₄. The addition of CH₃OH in base electrolytes affected the thickness, pores diameter, and Mg₂SiO₄ content in the films. The films formed in the electrolyte containing 12% CH₃OH exhibited the highest thickness. The coatings formed in the electrolyte containing different concentrations of CH₃OH exhibited similar corrosion resistance. The energy consumption of PEO markedly decreased upon the addition of CH₃OH to the electrolytes. The result is helpful for energy saving in the PEO process.

Keywords: plasma electrolytic oxidation, methanol, vapor sheath, ceramic films

PACS: 52.77.Dq

DOI: 10.1088/1009-0630/17/9/07

(Some figures may appear in colour only in the online journal)

1 Introduction

Plasma electrolytic oxidation (PEO), which is also called micro-arc oxidation, spark anodizing, anode spark electrolysis, or plasma electrolytic anode treatment, has elicited considerable interest as an environmentally friendly technology because of its high efficiency and easy production [1-3] in fabricating ceramic coatings with exceptional properties on light metals (e.g., Al, Mg, and Ti) [4-7]. PEO ceramic films exhibit corrosion resistance [8,9], wear resistance [10], strong adhesion [11,12], thermal shock resistance [13], and high thermal emissivity [13-16]. PEO discharge occurs when the applied voltage reaches a critical value corresponding to the breakdown of an initial insulating oxide layer [17,18]. This insulating layer compels the high applied voltage to form a strong electric field between the metal surface and electrolytes, thereby resulting in a strong discharge. A vapor sheath forms on the metal surface that also works as an insulating layer following the initiation of the discharge. The vapor sheath is formed by vaporization and electrolysis of the solvent in the electrolytes given the high applied voltage between the electrodes during conventional oxidation.

Various solvent types lead to different gaseous compositions of the vapor sheath. For example, the addition of methanol in the electrolytes produces additional carbon dioxide compared with the products of hydrogen and oxygen with water as a solvent. When the applied voltage reaches a critical value, the vapor sheath breaks down, followed by the breakdown of the oxide layer [19]. Subsequently, the discharge initially occurs at the weakest dielectric point, in which dopants and defects exist on the metal surface.

Yerokhin et al. [20] indicated that the vapor sheath was formed on the metal surface because of the formation of H₂ and O₂. Furthermore, they found that glow discharges could ignite in the gaseous media at the oxide–electrolyte interface, which resulted in heating, melting, and quenching of the underlying oxide layer. Relevantsev et al. [21] demonstrated the presence of gas bubbles containing negative oxygen ions during PEO. Their results showed that discharge extinction was a consequence of the expansion and cooling of gas bubbles. Gupta et al. [22] found that the implosion of gas bubbles caused the release of stored energy into the gas layer and the transfer of kinetic energy to the surface of the work piece. The energy could be high enough

---

*supported by National Natural Science Foundation of China (No. 21376088), the Project of Production, Education and Research, Guangdong Province and Ministry of Education (Nos. 2012B091000063, 2012A090300015), and Guangzhou Science and Technology Plan Projects of China (No. 2014Y2-00042)
to quench the surface and yield a unique surface microstructure. Guo et al. 23 pointed out that oxygen gas produced from the oxidation of water or hydroxyl was evenly adsorbed on the metal surface, which was covered with a thin dielectric film and surrounded by a continuous vapor sheath. Moreover, the vapor sheath in the anodic film impeded the transport of cations and anions to form new film materials, thereby decreasing the current efficiency during PEO. Hussein et al. 24 proposed three plasma discharge models: metal-oxide interface discharge (type B) and oxide-electrolyte interface discharge types within the upper (type A and type C) coating layers. Localized melt channels, which were sites of ionic diffusion from the electrolytes and plasma reactions, were formed through the oxide layer for type B. However, how the vapor sheath formed at the electrolyte-oxide layer interface obstructs ionic immigration, remains unclear. Types A and C corresponded to the discharges caused by the breakdown of the vapor sheath in small holes near or under the relatively deep surface. Hence, the vapor sheaths performed an important function in PEO. However, studies on vapor sheaths and the effects of their thicknesses on discharge intensities and growth of PEO films were few.

In this study, CH$_3$OH was added in alkaline silicate electrolytes to adjust the thickness of the vapor sheath because of its low evaporation enthalpy and dielectric constant. The effects of CH$_3$OH addition on the surface morphologies, compositions, thicknesses and corrosion resistance of oxide films, as well as the energy consumption of PEO, were investigated. In addition, the function of the thickened vapor sheath on the growth of PEO coatings was clarified.

2 Experiments

2.1 Preparation of PEO films

Prior to oxidation, AZ31 magnesium alloy sheets (dimensions, 10 mm×10 mm×5 mm; mass fraction: Al 3.1074%, Mn 0.4219%, Zn 0.9075%, balance magnesium) were polished using a waterproof abrasive paper with a grit of up to 4000. Subsequently, the alloy sheets were degreased with acetone in an ultrasonic bath and rinsed with distilled water. A homemade DC power supply was used to provide 0-1500 V voltage and 0-5 A current. Samples of magnesium alloys and stainless steel were used as anodes and cathodes, respectively. The electrolytes comprised 4.0 g/L KOH and 20.0 g/L Na$_2$SiO$_3$ (base electrolyte) with CH$_3$OH (volume concentration, 0% to 20%). The applied voltage and experiment duration were 300 V and 30 min, respectively. PEO coatings were also formed in base electrolytes with and without 8% CH$_3$OH for durations ranging from 30 min to 120 min at a constant voltage of 300 V. During PEO, the solution temperature was kept below 40°C by circulating cooling water and stirring. The voltage and current were measured using data acquisition systems at 5 Hz.

2.2 Characterization of PEO films

The phase compositions of PEO films were investigated via X-ray diffraction (XRD, D8 ADVANCE, Bruker, Germany) with Cu-K$_\alpha$ radiation (λ=1.5418 Å) at a step size of 0.05° and a scan range of 2θ=20°-90°. Scanning electron microscopy (SEM S-3700N, Hitachi Ltd., Japan) was employed to observe both the surface morphology and, through observation of sample cross sections, coating thickness of the PEO layers. The PEO treated samples were mounted with resin and polished to a mirror finish then sputtered with a gold film to make them conductive before SEM analysis. The measurements of coating thickness were carried out on cross sectional SEM images of samples taken at five different locations and their average values were calculated. Elemental compositions of the oxide coatings were determined via energy-dispersive spectroscopy (EDS) affiliated with SEM.

2.3 Corrosion testing

Corrosion resistance of the oxide films formed with different concentrations of CH$_3$OH was assessed by potentiodynamic polarization tests using the Autolab system in 3.5 wt.% NaCl solution, temperature of the solution was kept at 294±298 K. Samples were sealed with epoxy resin and immersed into the solution with 0.5 cm$^2$ exposed areas. A saturated calomel electrode (SCE) and a platinum plate were used as a reference and counter electrode, respectively. After 30 min of initial delay, polarization tests of samples were performed at a sweeping rate of 1 mV/s from −500 mV versus the open circuit potential towards a more noble direction.

3 Results and discussion

3.1 Phase composition, morphologies and components of PEO films

Fig. 1 shows the XRD patterns of PEO coatings formed in the electrolytes with different volume concentrations of CH$_3$OH. The sharp diffraction peaks suggested the crystallinity of the produced films. The diffraction peaks of magnesium oxide (MgO) and magnesium silicate (Mg$_2$SiO$_4$) regardless of the amount of added CH$_3$OH in the electrolytes. Typical phases of PEO coatings were produced in the silicate solution 25,26. CH$_3$OH addition failed to form other phases. The intensity of the peaks corresponding to the alloy substrate was strong because the oxide films exhibited porous structures, and X-rays could easily penetrate and reach the substrate. Fig. 1 shows that the characteristic peak intensities of Mg$_2$SiO$_4$ were weak and the change of its content was not noticeable. The possible reason
HE Yongyi et al.: Effects of CH<sub>3</sub>OH Addition on Plasma Electrolytic Oxidation of AZ31 Magnesium Alloys

was that thin ceramic layers were produced by the DC power sources [18] and the content of Mg<sub>2</sub>SiO<sub>4</sub> was low.

![Fig. 1](image1.png)

**Fig. 1** XRD patterns of PEO films formed in 4.0 g/L KOH + 20.0 g/L Na<sub>2</sub>SiO<sub>3</sub> electrolytes with different volume concentrations of CH<sub>3</sub>OH for 30 min

Fig. 2 illustrates the SEM micrographs of oxide films on the magnesium alloy substrate formed with different volume concentrations of CH<sub>3</sub>OH. All the PEO coatings exhibited porous microstructures and volcano top-like pores. Open or sealed pores that were unevenly distributed on the coating surface were considered as ‘footprints’ of plasma discharge channels [27]. The melting products around the volcano pores indicated that the plasma temperature on the magnesium alloy surface during PEO was high at about 2 × 10<sup>4</sup> K [18]. The addition of CH<sub>3</sub>OH into the electrolyte markedly changed the surface morphology of the PEO films. The average diameter of the pores decreased with increasing volume concentration of CH<sub>3</sub>OH. The number of large open pores initially decreased upon the addition of CH<sub>3</sub>OH. However, this amount slightly increased when the added CH<sub>3</sub>OH exceeded 12% [Fig. 2(e) and (f)].

Increasing the CH<sub>3</sub>OH concentration from 0% to 20% decreased the boiling point of aqueous methanol solution from 100°C to 81.48°C. The vaporization temperature of the electrolytes decreased because of the smaller evaporation enthalpy of CH<sub>3</sub>OH (35.21 kJ/mol) compared with that of H<sub>2</sub>O (40.67 kJ/mol). Considering the physical properties of CH<sub>3</sub>OH, the proportion of this compound in the vapor sheath significantly increased to 58.70% upon the addition of 20% CH<sub>3</sub>OH. Hence, the vapor sheath was easily formed, and more CH<sub>3</sub>OH was vaporized with increasing CH<sub>3</sub>OH concentration, which increased the thickness of the vapor sheath. Fig. 2 shows that when the volume concentration of CH<sub>3</sub>OH was increased, much smaller pores were formed on the surface. Pore size could be associated with the discharge type. The formation of small pores implied that discharge types A and C from the breakdown of the vapor sheath frequently occurred on the micro holes of the oxide film [24]. Both the number of large open pores and the average pore diameter decreased because of a large group of discharge types A and C with low intensities. The breakdown of thickened vapor sheaths became difficult for CH<sub>3</sub>OH concentrations exceeding 12% so that when discharges were ignited on a specific location, it lasted for a long time. This result can be attributed to the formation of large open pores shown in Fig. 2(e) and (f).

![Fig. 2](image2.png)

**Fig. 2** SEM micrographs showing the surface morphology of oxide films for different volume concentrations of CH<sub>3</sub>OH: (a) 0%, (b) 4%, (c) 8%, (d) 12%, (e) 16%, (f) 20%

Fig. 3 depicts the elemental contents in oxide films in the electrolytes with different CH<sub>3</sub>OH concentrations. The results revealed that the PEO coatings were mainly composed of O, Mg, and Si. Yao et al. [28] indicated that the electrolyte composition and ionic species influenced the constituents of PEO films. Mg was incorporated into the layers from the magnesium substrate; Si was from the PEO electrolyte containing sodium silicate. However, the derivation of O was complicated because its sources came from anions (e.g., OH<sup>-</sup> and SiO<sub>3</sub><sup>2-</sup>) or from oxygen dissolved in PEO electrolytes [17]. Fig. 3 shows that the atomic concentration of Si in oxide films decreased with increasing CH<sub>3</sub>OH concentration in the electrolyte. Si could be used to trace the interactions between the electrolytes and the coating surface during plasma discharge because the element was derived from sodium silicate electrolytes. The decreased Si content suggested that the thickened vapor sheath impeded the transmission of SiO<sub>3</sub><sup>2-</sup> from the electrolytes as the concentration of CH<sub>3</sub>OH increased. Therefore these ions could not diffuse into the discharge channel to react with Mg<sup>2+</sup> and OH<sup>-</sup> and form Mg<sub>2</sub>SiO<sub>4</sub> precipitates on the surface. Hence, it could be inferred that the Mg<sub>2</sub>SiO<sub>4</sub> content also decreased with increasing volume concentrations of CH<sub>3</sub>OH.
3.2 Growth of PEO films

Fig. 4 illustrates the average thickness of PEO coatings formed in the base electrolytes with different CH$_3$OH concentrations for 30 min at 300 V voltage. The PEO films ranging from 2 $\mu$m to 3.5 $\mu$m were thin because the homemade DC power supply was used. Generally speaking, the thickness of PEO layers increased with the conductivity of the electrolytes [29,30]. When the amount of added CH$_3$OH was increased, the conductivity of the electrolytes was reduced, which decreased the intensity of micro-arc discharges. Therefore, the PEO films should be thinner. However, in this study, the average thickness first increased gradually with increasing volume concentration of CH$_3$OH. The thickness reached its maximum value for 12% CH$_3$OH and decreased afterwards. Given the smaller dielectric constant of CH$_3$OH (32.6) compared with that of H$_2$O (78.3), the vapor sheath formed with CH$_3$OH easily breaks down at the same voltage. The densities of micro-arc discharge types A and C on specific locations of metal surfaces would increase. Sintering and densification of the growing oxides could be accelerated. Hence, the thickness of PEO coatings increased with thickening vapor sheath because of increased CH$_3$OH concentration. However, the thickness of the vapor sheath continuously increased so that it was difficult to break it down. The intensities of micro-arc discharges decreased and consequently caused a decrease in density, which contributed to a decrease in the thickness of PEO films. The thick vapor sheath functioned as a barrier to prevent ionic diffusion into the discharge channels; chemical and physical reactions between the electrolyte and the ceramic surface in these ions were obstructed [31], which resulted in PEO with a low activity. Therefore, the thickness decreased when the CH$_3$OH concentration was increased to 20%. When the volume concentration of CH$_3$OH exceeded 20%, arc discharges were noticeable on the metal surface and PEO was difficult to continue. The produced layers were sufficiently thin so that they could hardly cover the substrate surface and reveal ideal properties for PEO films.

Previous studies on PEO films prepared in alkaline silicate electrolytes reported that their thickness was proportional to the processing time [15,32]. Fig. 5 reveals that the thickness of coatings produced in different electrolytes increased with the duration. The PEO films produced in the electrolytes containing 8% CH$_3$OH were thicker than those in the base electrolytes for the same duration time at a voltage of 300 V, which was consistent with previously mentioned results. Figs. 4 and 5 demonstrate that thicker vapor sheaths formed with appropriate amounts of CH$_3$OH were beneficial to the growth of PEO films.

3.3 Corrosion resistant properties of PEO films

The corrosion resistance of the coatings is evaluated by electrochemical potentiodynamic polarization in 3.5% NaCl solution. Fig. 6 shows the potentiodynamic curves of the films formed in electrolytes containing different concentrations of CH$_3$OH. The corrosion potential ($E_{corr}$), corrosion current density ($i_{corr}$) and corrosion resistance ($R_{corr}$) derived from the potentiodynamic curves are shown in Table 1.
Corrosion potential and corrosion current density of the samples are often used to characterize the corrosion resistant property of the films. The high corrosion potential and low corrosion current density of the films suggest a low corrosion rate and a high uniform corrosion resistance performance. The results shown in Fig. 6 and Table 1 demonstrate that the coatings formed with different concentrations of CH$_3$OH have a close $E_{\text{corr}}$, $i_{\text{corr}}$ and $R_{\text{corr}}$, indicating that the corrosion resistance of PEO films is similar. Different surface structures (pore diameter), thicknesses and phase compositions of ceramic layers have a significant effect on the corrosion performance of the films. On one hand, larger micro-pores increase the real exposed area to the corrosive solution. On the other hand, an increase in coating thickness improves corrosion resistance. The number of large micro-pores of films first decreased with the addition of CH$_3$OH then increased slowly, while the thickness of coatings showed the opposite trend. Besides, the ceramic layers have the same phase compositions. As a result, the corrosion resistance of porous films formed with different concentrations of CH$_3$OH is similar.

### 3.4 Energy consumption of PEO process

The energy consumption of PEO for various CH$_3$OH concentrations added in the base electrolyte was investigated and given as follows:

$$E = \int_0^t V_I dt,$$

where $V_I$ is the instantaneous voltage, $I_t$ is the instantaneous current, and $t$ is the duration time of the PEO process. The voltage and current were measured using data acquisition systems at 5 Hz. All values of $E$ were calculated and recorded by a computer program automatically (Table 2). $E$ markedly decreased with increasing CH$_3$OH concentration and reached a minimum value at 16%.

<table>
<thead>
<tr>
<th>Volume concentration of CH$_3$OH (%)</th>
<th>Energy consumption (W)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>6857.6</td>
</tr>
<tr>
<td>4</td>
<td>3404.3</td>
</tr>
<tr>
<td>8</td>
<td>3303.6</td>
</tr>
<tr>
<td>12</td>
<td>2819.8</td>
</tr>
<tr>
<td>16</td>
<td>2693.1</td>
</tr>
<tr>
<td>20</td>
<td>2769.0</td>
</tr>
</tbody>
</table>

The energy was mainly consumed to heat the electrolytes and form the vapor sheath during PEO. Hence, $E$ of the formation and breakdown of the vapor sheath during oxidation determined that for the entire PEO. Given the evaporation enthalpy of CH$_3$OH smaller than that of H$_2$O, the vapor sheath formed with CH$_3$OH and H$_2$O as a result of Joule heat consumed less energy than that formed with H$_2$O only. Besides, as the relationship between current and time is shown in Fig. 7, at first the current increased with time. Then the current decreased quickly, suggesting that breakdown of the dielectric barrier layer happened, and then discharge took place. The current decreased slowly to a relatively low value (7-8 mA) without the addition of CH$_3$OH, but the current decreased more quickly and to a lower value (2-6 mA) with the addition of CH$_3$OH. So the breakdown of the vapor sheath consumed less energy when CH$_3$OH was added in the electrolyte. However, excess CH$_3$OH thickened the vapor sheath; thus, more energy was needed to break it down. The results revealed that $E$ increased when the CH$_3$OH concentration reached 20%.

![Fig.7](image)

**Fig. 7** Variation of currents with time added with different CH$_3$OH concentrations in base electrolyte: (a) 0-1800 s and (b) 1800-1800 s
4 Conclusions

The addition of CH$_3$OH in the electrolytes decreased the average pore diameter of PEO coatings. Transformations of phase compositions were unchanged except for the reduction in Mg$_2$SiO$_4$ content. The film thickness increased with duration during PEO. However, the oxide films produced in the electrolytes with 8% CH$_3$OH were thicker than those in the base electrolytes for the same experiment duration. The thickness of PEO coatings increased with CH$_3$OH concentration and reached a maximum value at 12%; subsequently, the thickness was reduced with further addition of CH$_3$OH. The results indicated that ionic diffusion from electrolytes into the discharge channels was impeded because of a CH$_3$OH-induced increase in the thickness of the vapor sheath. Moreover, the thickened vapor sheath contributed to the increased density of micro-arc discharges and the growth of PEO films. The energy consumption of PEO markedly decreased with increasing CH$_3$OH concentration, but the coatings showed similar corrosion resistance. The result is helpful for energy saving in the PEO process.

Acknowledgments

The authors also gratefully acknowledge the support from the Guangdong Provincial Laboratory of Green Chemical Technology.

References


Plasma Science and Technology, Vol.17, No.9, Sep. 2015

(Manuscript received 10 September 2014)
(Manuscript accepted 2 February 2015)
E-mail address of corresponding author
YAN Zongchong: zcyang@scut.edu.cn