

## Influence of potassium pyrophosphate in electrolyte on coated layer of AZ91 Mg alloy formed by plasma electrolytic oxidation

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**Abstract:** The effect of potassium pyrophosphate in the electrolyte on plasma electrolytic oxidation (PEO) process for AZ91 Mg alloy was investigated. The morphologies and chemical compositions of the coating layer on the AZ91 Mg alloy were evaluated and corrosion resistance was also estimated by potentiodynamic polarization analysis. The coating layer on AZ91 Mg alloy coated from the Bath 2 containing 0.03 mol/L of potassium pyrophosphate for 360 s exhibited considerably dense structure and contained 11%–18% (mass fraction) of phosphorous. The higher content of phosphorous of coating layer coated from Bath 2 could be detected at the bottom of oxide layer, which strongly implied that the phosphorous ion might be concentrated at the barrier layer. Corrosion potential of coating layer of AZ91 Mg alloy increased and corrosion current density decreased with increasing the concentration of potassium pyrophosphate. The polarization resistance ( $R_p$ ) of coating layer of AZ91 Mg alloy coated from Bath 2 was  $4.65 \times 10^7 \Omega/\text{cm}^2$ , which was higher than that ( $R_p = 3.56 \times 10^4 \Omega/\text{cm}^2$ ) of the sample coated from electrolyte without potassium pyrophosphate. The coating layer coated from Bath 2 containing 0.03 mol/L potassium pyrophosphate exhibited the best corrosion resistance.

**Key words:** plasma electrolytic oxidation; magnesium alloy; phosphorous; corrosion resistance

### 1 Introduction

Magnesium alloys have excellent physical and mechanical properties, such as high strength, low density and good castability. So they have been used in a lot of fields, such as mobile, aerospace, construction, and computer. Unfortunately, magnesium alloys have poor corrosion resistance, especially in acidic environments and in salt-water condition[1]. Conventional surface treatment methods such as cremating, non-cromating process are not satisfied. These processes have the disadvantages of low corrosion resistance and wastewater problems. Therefore, it is worth developing a new process of surface treatment to solve these problems. Plasma electrolytic oxidation (PEO) process is a relatively new surface treatment method to form oxide layer on magnesium alloys using an environmentally friendly process[2]. An important feature of PEO process is a plasma discharge that occurs at the metal/electrolyte interface when the applied voltage exceeds a certain critical breakdown value. The constituents of surface oxides contribute from substrate and the anodic complexes from the electrolyte. The

structures of PEO process depend on various processing conditions, including chemical composition and concentration of electrolyte, current density, and alloy composition of substrate[3–4]. Especially, the chemical composition of the electrolyte exerts a considerable influence on the property and formation of effective ceramic coating for Mg alloy. Moreover, some additives, such as phosphate, fluoride, and borate are commonly used[5]. In this study, the effect of potassium pyrophosphate in the electrolyte on PEO process for AZ91 Mg alloy was investigated. The morphologies and chemical compositions of the coating layer on the AZ91 Mg alloy were evaluated and corrosion resistance was estimated by potentiodynamic polarization analysis.

### 2 Experimental

Commercial AZ91 ingots were used as substrate in this study. AZ91 Mg alloy plates with 30 mm × 50 mm × 2 mm were ground to a grit of 1 000 by SiC paper, then rinsed with de-ionized water, ultrasonically cleaned in ethanol, and finally dried in warm air. PEO process was conducted at 20 kW. The equipment for PEO has a glass-vessel container with a sample holder as the

electrolyte cell, a stainless steel used as the cathode, and stirring and cooling system. Table 1 lists the chemical compositions of electrolyte for PEO process. The current density was controlled constant at  $50 \text{ mA/cm}^2$ . Temperature of electrolyte was maintained at  $20\text{--}30 \text{ }^\circ\text{C}$  during PEO process. The morphology and chemical compositions of the oxide layer were observed using a scanning electron microscope (TESCAN 510). Potentiodynamic polarization to evaluate corrosion resistance of the coated AZ91 Mg alloy was carried out using Reference 600 Potentiostat (Gamry Instruments). As we know, Mg alloy is sensitive to occur pitting corrosion in electrolyte or environment containing  $\text{Cl}^-$ .

**Table 1** Electrolyte compositions for PEO process in AZ91 Mg alloy

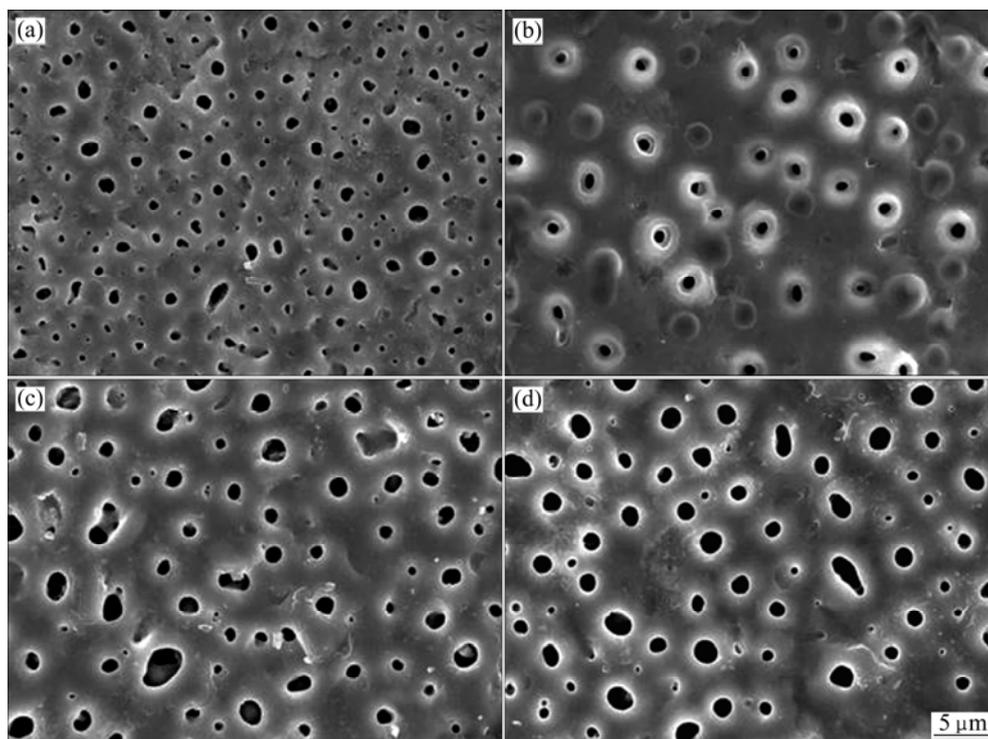
Bath No.	$c(\text{KOH})/(\text{mol}\cdot\text{L}^{-1})$	$c(\text{Na}_2\text{SiO}_3)/(\text{mol}\cdot\text{L}^{-1})$	$c(\text{K}_4\text{P}_2\text{O}_7)/(\text{mol}\cdot\text{L}^{-1})$	pH	$E_c/(\text{mS}\cdot\text{cm}^{-2})$
1	0.12	0.04	0	12.90	25.4
2	0.12	0.04	0.03	13.17	30.8
3	0.12	0.04	0.06	13.15	47.9
4	0.12	0.04	0.15	13.27	49.4

### 3 Results and discussion

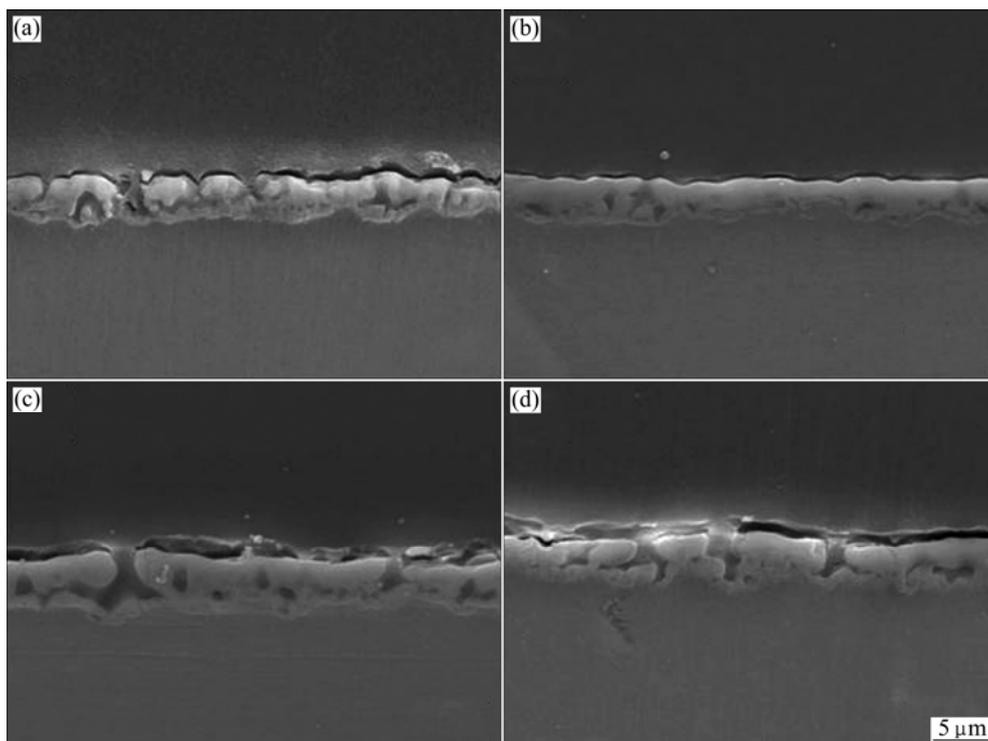
Fig.1 shows the surface morphology of oxide layer in AZ91 Mg alloy coated from the electrolyte with a variation of the concentration of the potassium

pyrophosphate for 360 s. As shown in Fig.1, coating layer of the AZ91 Mg alloy exhibited the typical surface morphology for PEO process regardless of the kinds of electrolyte. During PEO process, the metal surface was progressively covered with an oxide layer. The oxide layer showed surface morphology of dense crater-like microstructures with some round-shape shrinkage pores observed in the crater centers. Surface morphology with small-pore-size oxide layer in Bath 1 was observed (Fig.1(a)). The pore size on the surface of coating layer increased with increasing the concentration of the potassium pyrophosphate in the electrolyte. The coating layer coated from Bath 2 exhibited the most small size pores on surface.

The cross-sectional images of layer coated from the electrolytes with and without potassium pyrophosphate are shown in Fig.2. There were many micro pores and some micro cracks on surfaces of coating layer. These pores and cracks were neither connected with each other nor perforated through the whole coating layer. Previous studies showed that pores in the coating layer were formed by gas bubbles thrown out of micro-arc discharge channels while cracks were resulted from thermal stress due to rapid solidification of molten oxide in the relatively cool electrolyte[2]. In the ordinary way, the coating layer formed on the AZ91 Mg alloy applied in the PEO process was composed of two different layers: an outer porous layer and an inner barrier layer, which is a very thin layer with thickness of  $100\text{--}300 \text{ nm}$ [4–5].



**Fig.1** Surface morphologies of oxide layer of AZ91 Mg alloy in electrolyte containing various concentrations of potassium pyrophosphate coated for 360 s: (a) Bath 1; (b) Bath 2; (c) Bath 3; (d) Bath 4



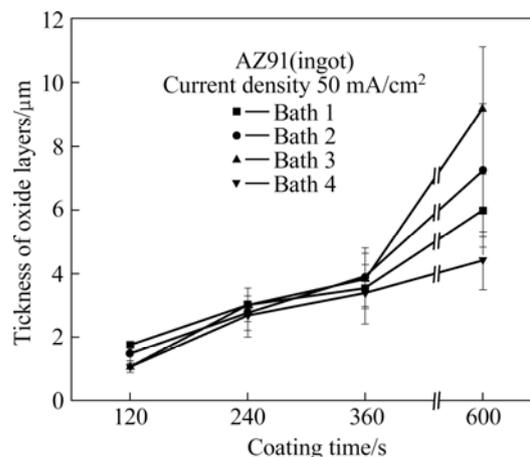
**Fig.2** Cross-sectional images of oxide layer of AZ91 Mg alloy in electrolyte containing various concentrations of potassium pyrophosphate coated for 360 s: (a) Bath 1; (b) Bath 2; (c) Bath 3; (d) Bath 4

The structure of coating layer was different with the variation of the concentration of potassium pyrophosphate. The sample coated from Bath 2 with potassium pyrophosphate exhibited relative uniform structure, compared with the other conditions (Fig.2(b)).

Fig.3 show the changes of the coating thickness as a function of the coating time coated from electrolytes with a variation of the potassium pyrophosphate. It was observed that coating thickness increased with increasing coating time regardless of kinds of electrolytes. However, the exfoliation between the coated layer and the matrix occurred in the Bath 3 and Bath 4 over 600 s.

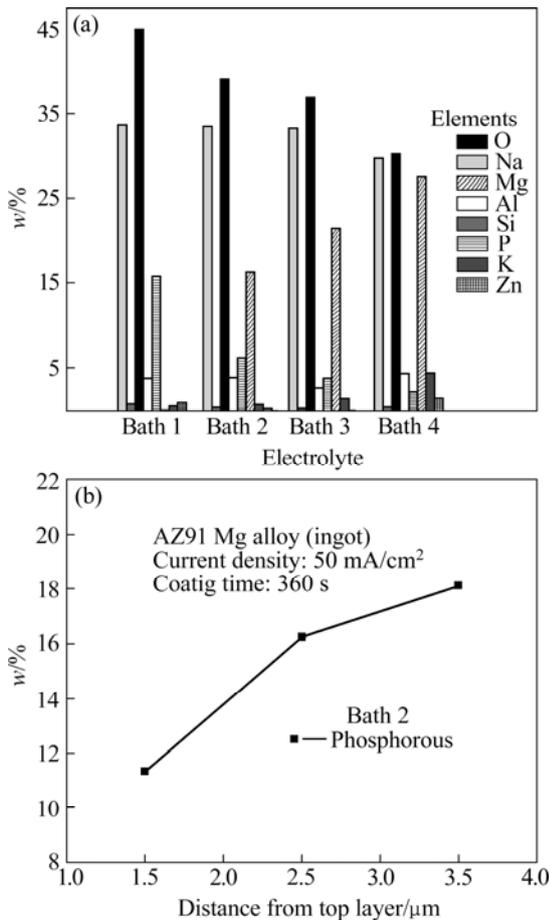
The growth rate of coating layer on the AZ91 Mg alloy was same treated until 360 s with and without potassium pyrophosphate. Thickness of coating layer treated until 360 s was measured to be  $\sim 3.8 \mu\text{m}$ . The growth rate of coating layer on AZ91 Mg alloy coated after 360 s exhibited far different with kinds of electrolytes. The growth rate of coating layer coated from Bath 3 is faster than that of the other conditions. However, the surface roughness of the coating layer increased due to the increase in the diameters of the pores on the surface of coating layer. Other researchers reported that the coating layer had an influence on the surface roughness[6–7].

From the result of the EDS analysis of the oxide layer on the cross-section of AZ91 Mg alloy, the component of the oxide layer coated from the electrolyte



**Fig.3** Variation of thickness of PEO coatings formed in electrolytes containing various concentrations of potassium pyrophosphate

containing potassium pyrophosphate consisted of oxygen, phosphorous, silicon, magnesium, and aluminum, which strongly supported that phosphorous was successfully incorporated in oxide layer (Fig.4(a)). The contents of phosphorous ions in the oxide layer coated from the electrolytes for 360 s increased with increasing the concentration of potassium pyrophosphate in the electrolyte. The content of phosphorous ion existed in the coating layer coated from Bath 4 was detected to be about 30%. In the case of the sample coated for 360 s, the contents of phosphorous ions existed in the porous



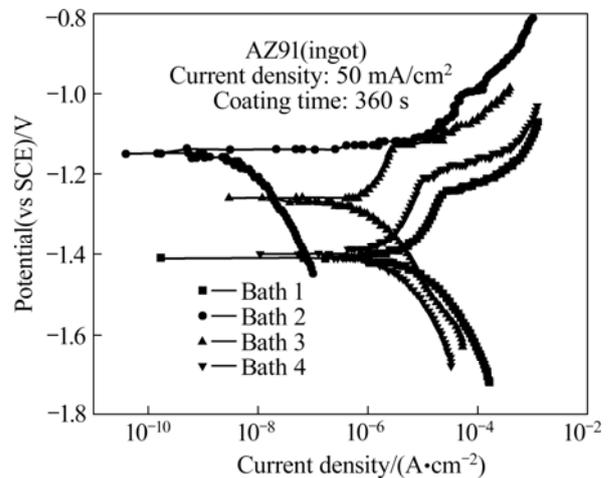
**Fig.4** Energy-dispersive plot of oxide layer on AZ91 Mg alloy treated from Bath 2 for 360 s

layer and barrier layer were measured to be 11% and 18%, respectively (Fig.4(b)). In the other words, the higher content of phosphorous could be detected at the bottom of oxide layer, which strongly implied that the phosphorous ion might be concentrated at the barrier layer.

Corrosion resistance of the coating in the AZ91 Mg alloy was evaluated by electrochemical potentiodynamic polarization in 3.5% NaCl solution. Fig.5 exhibits the potentiodynamic polarization curve of coating layer of AZ91 Mg alloy coated from the electrolyte with a variation of the concentration of potassium pyrophosphate. It is well known that corrosion potential and current density of coated samples were often used to characterize corrosion protective property of the coating [8–9]. In general, it was reported that the high corrosion potential and low corrosion current density of the coating exhibited a low corrosion rate and a good corrosion resistance[8]. Corrosion potential of coating layer of AZ91 Mg alloy increased and corrosion current density decreased with increasing the concentration of potassium pyrophosphate. In the case of the sample coated from Bath 4 with the high content of phosphorous ion, corrosion potential and corrosion current density were

similar to the sample coated from Bath 1 without potassium pyrophosphate. Especially, corrosion current density of coating layer of AZ91 Mg alloy coated from Bath 2 containing 0.03 mol/L potassium pyrophosphate was three orders lower than that of coating layer of AZ91 Mg alloy coated from Bath 1 without potassium pyrophosphate. The corrosion potential ( $\phi_{\text{corr}}$ ), corrosion current density ( $J_{\text{corr}}$ ), and anodic/cathodic Tafel slopes ( $b_a$  and  $b_c$ ) were derived from these data. Based on the approximately linear polarization behavior near OCP, the polarization resistance ( $R_p$ ) values were determined from Stern-Geary equation[10]:

$$R_p = \frac{b_a * b_c}{2.303 J_{\text{corr}} (b_a + b_c)} \quad (1)$$



**Fig.5** Potentiodynamic polarization curves of oxide layer on AZ91 Mg alloy coated from electrolyte containing various concentrations of potassium pyrophosphate

The results of potentiodynamic polarization are summarized in Table 2. The polarization resistance ( $R_p$ ) of coating layer of AZ91 Mg alloy coated from Bath 2 was  $4.65 \times 10^7 \Omega/\text{cm}^2$ , which was higher than that ( $R_p = 3.56 \times 10^4 \Omega/\text{cm}^2$ ) of the sample coated from electrolyte without potassium pyrophosphate. It was reported that some additives such as phosphate and fluoride were very commonly used for the formation of stable products ( $\text{Mg}_3(\text{PO}_4)_2$  or  $\text{MgF}_2$ )[7]. These stable products could act as barrier layer preventing magnesium substrate from corrosion in most corrosive intermediate. Phosphate was useful to enhancing the corrosion resistance of inner barrier layer of PEO process. The corrosion resistance of all the samples can be ranked as: Bath 2 > Bath 3 > Bath 4 > Bath 1. The coating layer formed on the surface of AZ91 Mg alloy in electrolyte containing phosphorous ions fabricated by PEO process provided effective corrosion protection to substrate in electrolyte containing  $\text{Cl}^-$  ions.

**Table 2** Results of potentiodynamic corrosion tests of four samples in 3.5% NaCl solution

Bath No.	$\phi_{\text{corr}}/V$	$J_{\text{corr}}/(A \cdot \text{cm}^{-2})$	$R_p/(\Omega \cdot \text{cm}^{-2})$
1	-1.41	$1.96 \times 10^{-5}$	$3.56 \times 10^4$
2	-1.14	$1.22 \times 10^{-8}$	$4.65 \times 10^7$
3	-1.22	$2.27 \times 10^{-6}$	$3.85 \times 10^6$
4	-1.40	$4.77 \times 10^{-6}$	$5.26 \times 10^5$

## 4 Conclusions

The effect of potassium pyrophosphate in electrolyte on PEO process for AZ91 Mg alloy was investigated. The pore size on the surface of coating layer increased with increasing concentration of the potassium pyrophosphate in the electrolyte. The structure of coating layer was different with the variation of the concentration of potassium pyrophosphate. The sample coated from Bath 2 with potassium pyrophosphate exhibited relatively uniform structure, compared with the other conditions. The contents of phosphorous ions in the oxide layer coated from the electrolytes for 360 s increased with increasing the concentration of potassium pyrophosphate in the electrolyte. Corrosion potential of coating layer of AZ91 Mg alloy increased and corrosion current density decreased with increasing the concentration of potassium pyrophosphate. The polarization resistance ( $R_p$ ) of coating layer of AZ91 Mg alloy coated from Bath 2 was  $4.65 \times 10^7 \Omega/\text{cm}^2$ , which was higher than that ( $R_p=3.56 \times 10^4 \Omega/\text{cm}^2$ ) of the sample coated from electrolyte without potassium pyrophosphate. Phosphate was useful to enhancing the corrosion resistance of inner barrier layer of PEO process. The coating layer coated from Bath 2 containing 0.03 mol/L potassium pyrophosphate exhibited the best corrosion resistance.

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