



High-corrosion resistance of the microarc oxidation coatings on magnesium alloy obtained in potassium fluotitanate electrolytes



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ABSTRACT

Microarc oxidation (MAO) coatings were prepared on AZ91D magnesium alloys in the electrolytes containing 10 ml/L triethanolamine and various concentrations of potassium fluotitanate, sodium hexametaphosphate, and sodium hydroxide. The corrosion resistances of the MAO coatings were evaluated using electrochemical impedance spectroscopy (EIS). Based upon corrosion the resistance of the coatings, an optimized electrolyte that was composed of 8.0 g/L K_2TiF_6 , 8.0 g/L $(NaPO_3)_6$, 3.0 g/L NaOH and 10.0 ml/L TEA was obtained. The coating that was formed at 6 A/dm² was mainly composed from MgO, $Mg_3(PO_4)_2$, Mg_2TiO_4 , and amorphous phases. The coating exhibited excellent corrosion resistance due to its larger coating thickness, smaller amount of micropores and cracks, and the existence of more stable compositions.

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1. Introduction

Poor corrosion resistance of magnesium alloys has severely limited their use in many applications [1]. An effective solution is to form an anti-corrosion protective coating on the alloys [2]. Microarc oxidation (MAO), which is based upon conventional anodic oxidization technology, has been developed and applied for the surface treatment of magnesium alloys. This technique can fabricate high-quality coatings with high hardness values, large adhesion strengths, and increase in corrosion resistance [3–6]. As such, MAO has become one of the most remarkable techniques utilized for the improvement of the corrosion resistance of magnesium alloys.

The corrosion resistance of MAO coating mainly depends on its thickness, composition, and microstructure [7–9]. According to previous studies, electrolyte compositions affects the microstructure, composition, and properties of the MAO coating because these elements can be incorporated into the coating during MAO [10]. Several types of electrolytes, such as silicate [11,12], aluminate [13,14], and phosphate [15,16], have been used to prepare MAO coatings. In general, the MAO coatings formed in those electrolytes are mainly composed of a MgO phase with some other electrolyte-related compounds [e.g., Mg_2SiO_4 , $Mg_3(PO_4)_2$, $MgAl_2O_4$, or MgF_2]. These coatings cannot provide sufficient long-term corrosion protection to the substrate because MgO is not stable in neutral or acidic environments [4,17]. One promising solution to this problem is the incorporation of stable oxides and/or other stable compounds, such as Nb_2O_5 , ZrO_2 , TiO_2 , $Mg_2Zr_5O_{12}$, CeO_2 , MgF_2 , or ZrF_4 , in the MAO coatings by modifying the compositions of the electrolytes. [9,18–25]. These

oxides and compounds could be imbedded into the coatings during the MAO process to improve the corrosion resistance. However, many of these electrolytes used in the MAO for the magnesium alloys with the modified compositions cannot be used for long periods (relatively unstable) [26]. As a result, small sparks were previously formed on the specimen surface, and uniform MAO coatings could not be obtained [27]. Thus, the development of a more stable and new electrolyte for the preparation of MAO coatings with excellent corrosion resistance is still necessary.

In our previous work, a suitable electrolyte composed of potassium fluotitanate (K_2TiF_6), sodium hexametaphosphate [$(NaPO_3)_6$], sodium hydroxide (NaOH), and triethanolamine (TEA) has been exploited to prepare the MAO coating that contains Mg_2TiO_4 and TiO_2 . This MAO coating showed excellent corrosion resistance [27]. Moreover, the electrolyte is very stable and could be used normally for over two months.

Herein, to further improve the corrosion resistance property of the MAO coating, the electrolyte composition (K_2TiF_6 , $(NaPO_3)_6$ and NaOH) was optimized. The structures, components, and morphologies of the coatings were investigated using XRD, EDS, and SEM, and the corrosion resistances of the MAO coatings were evaluated using the electrochemical impedance method.

2. Experimental

2.1. Materials

Rectangular specimens of the AZ91D magnesium alloys were used as substrates for the MAO coatings. Prior to the MAO treatment, the specimens were sequentially polished with 240-, 400-, and 600-grit SiC abrasive paper, and were then subsequently degreased in acetone. All

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of the solutions were prepared using analytical grade reagents and deionized water.

2.2. Preparation of the MAO coatings

The electrolyte used in the present work was an aqueous solution containing $(\text{NaPO}_3)_6$, NaOH, K_2TiF_6 , and $(\text{HOCH}_2\text{CH}_2)_3\text{N}$. A pH meter (PHS-25, Shanghai Leici Instrument Factory, China) and conductivity tester (DDS-11A, Shanghai Leici Instrument Factory) were used to measure the pH and conductivity of the electrolytes, respectively. For the MAO processes, magnesium alloy and stainless steel were used as the anode and cathode, respectively. The MAO coating was carried out by using a pulsed electrical source providing positive pulse voltages (South – Central University for Nationalities, China). Pretreated magnesium alloy specimens were processed in various electrolytes under different current densities (RMS value) ranging from 3 to 10 A/dm^2 for 15 min with a fixed frequency of 200 Hz and a duty cycle of 15%. The temperature of the electrolyte during MAO was kept below 40 °C by using a constant mechanical stirrer and heat exchange system. After MAO, specimens were rinsed with deionized water and dried in warm air.

2.3. Characterizations of MAO coatings

The thickness of the MAO coatings was measured using an eddy-current coating thickness meter (Fisher-E110B, Germany). The surface morphology and elemental composition of MAO coatings were investigated through the use of a scanning electron microscope (SEM, S-530, Hitachi, Japan) that was equipped with an energy dispersive X-ray spectrometer (EDS, LINK ISIS, Oxford, UK). X-ray diffractometry (XRD, Rigaku 2000, Japan) was employed to investigate the phase composition of the coatings. Diffraction data were acquired over 2θ scattering angles ranging from 20° to 80° at a scanning speed of 6°/min and a step size of 0.020°. All of the obtained data were analyzed using Jade 6.0 software.

2.4. Corrosion resistance measurements

Electrochemical measurements were conducted using a CHI-660A electrochemical workstation in a three-electrode cell with a saturated calomel electrode (SCE) and a platinum sheet (15 mm × 15 mm) as the reference and counter electrodes, respectively. The MAO coating with an exposed area of 1 cm^2 was used as the working electrode, and a solution containing 3.5 wt.% NaCl was used as electrolyte. EIS

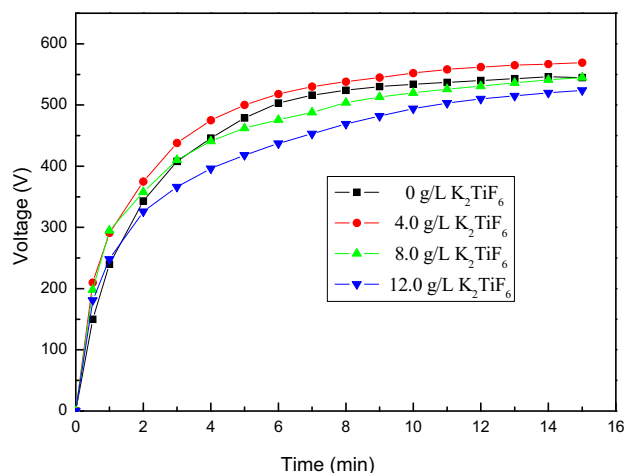


Fig. 2. Voltage–time curves during MAO process in the electrolyte containing 6.0 g/L $(\text{NaPO}_3)_6$, 3.0 g/L NaOH, 10.0 ml/L TEA and different K_2TiF_6 concentrations at a constant current density of 3 A/dm^2 .

measurements were conducted at an open circuit potential with an AC amplitude of 10 mV over a frequency range of 0.01–100 kHz.

A neutral salt spray test was used to estimate the barrier properties of the MAO coatings in a corrosive service environment according to the ASTM B117 standard procedure. The test was conducted under continuous spray conditions at a temperature of 35 ± 2 °C.

3. Results and discussion

3.1. Effects of K_2TiF_6 concentration

Fig. 1 shows the pH and conductivity of the electrolytes containing 6.0 g/L $(\text{NaPO}_3)_6$, 3.0 g/L NaOH, 10.0 ml/L TEA, and different concentrations of K_2TiF_6 . As the K_2TiF_6 concentration increase, the pH values gradually decreased, whereas the conductivity initially decreased and then increased. The electrolyte with K_2TiF_6 would generate K^+ , F^- , and Ti^{4+} through hydrolysis, which caused the variations in pH and conductivity. $\text{Ti}(\text{OH})_4$ sol particles can be formed by the reactions between Ti^{4+} and OH^- . Therefore, the pH values would decrease as the K_2TiF_6 concentration increases. Since the Na^+ and K^+ tended to absorb onto the $\text{Ti}(\text{OH})_4$ sol particles due to the double electrical layer, the electrolyte conductivity would decrease as the K_2TiF_6 concentration increases. Thus, K_2TiF_6 exerted both positive and negative effects on the pH values and conductivity of the electrolyte, respectively. The conductivity was the lowest in the electrolyte that contained 4.0 g/L K_2TiF_6 .

A voltage – time curve was used to investigate the influence of electrolyte composition on the MAO process. Fig. 2 shows the voltage – time responses of the MAO process in different electrolytes. According to previous studies, three or four stages of the MAO process can be distinguished in the voltage–time curves. Values of the breakdown and final voltages in the different electrolytes are listed in Table 1. Obvious differences in the breakdown and final voltages of the electrolytes were observed. The breakdown voltages depend upon the electrolyte conductivity, and they decreased with an increase in the electrolyte conductivity [28]. The electrical conductivity and melting point of the components that were formed in the anode/electrolyte interface are

Table 1
Breakdown voltage and final voltage in different electrolytes.

	Concentration of K_2TiF_6 (g/L)			
	0	4.0	8.0	12.0
Breakdown voltage (V)	220	240	200	180
Final voltage (V)	545	569	545	524

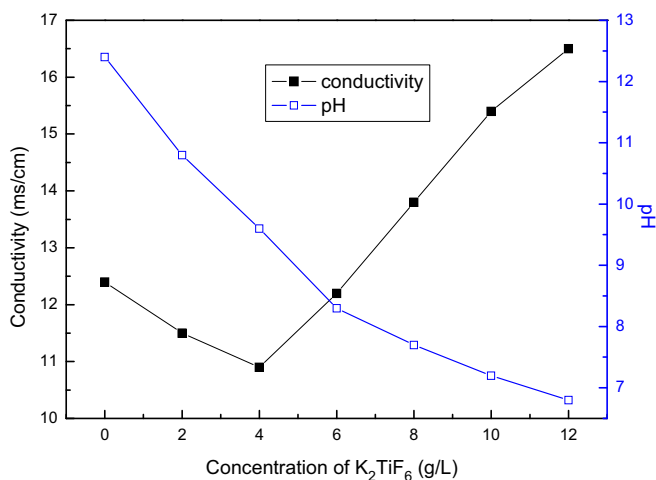


Fig. 1. The pH and conductivity of electrolyte containing 6.0 g/L $(\text{NaPO}_3)_6$, 3.0 g/L NaOH, 10.0 ml/L TEA and different K_2TiF_6 concentrations at 25 °C.

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