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Effect of current density on corrosion resistance of micro-arc oxide coatings on magnesium alloy

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Abstract: Oxide coatings were prepared on magnesium alloys in electrolyte solution of Na_2SiO_3 at different current densities (3, 4 and 5 A/cm^2) with micro-arc oxidation process. X-ray diffractometry (XRD) results show that the oxide coatings formed on magnesium alloys are mainly composed of MgO and $MgAl_2O_4$ phases; in addition, the content of MgO increases with increasing the current density. The morphology and surface roughness of the coatings were characterized by confocal laser scanning microscopy (CLSM). The results show that the surface roughness (R_a) decreases with increasing the current density. Moreover, the electrochemical corrosion results prove that the MgO coating produced in the electrolyte Na_2SiO_3 at current density of 5 A/cm^2 shows the best corrosion resistance.

Key words: magnesium alloy; micro-arc oxidation; current density; corrosion resistance

1 Introduction

Magnesium alloys are attractive for applications in the automobile and aerospace industries because of their relatively low density and high damping capacity as compared to other structural metals[1−4]. However, magnesium has a number of undesirable properties including poor corrosion and wear resistance, poor creep resistance and high chemical reactivity, which have limited their more extensive use in many applications. Techniques for solving these problems include electroplating, chemical plating, anodic oxide coating, chemical conversion coating, physical vapor deposition, surface coating, laser surface treatment and so on, but all of these methodologies have specific limitations[5−7].

Micro-arc oxidation (MAO) is a relatively new and promising surface treatment method used to form a thick oxide coatings on magnesium substrate by plasma discharge in aqueous solution on substrate surface under high voltage. The deposition process of MAO implies electrochemical, plasma chemical and thermal chemical reactions taking place in the electrolyte[8−10]. The quality of MAO coating can be controlled by compositions of electrolyte, temperature of electrolyte, treatment time and voltage, anodic current density, etc [11−15]. Generally, current density is one of the most important parameters affecting microstructure and properties of the coating. However, there is little research about the effects of current density on the oxide coatings on magnesium alloys. In this work, the effect of current density on the corrosion resistance of the coatings formed on magnesium alloys was analyzed. It is expected that the preliminary results can be significant in promoting the further application of MAO process about magnesium alloy.

2 Experimental

2.1 Preparation of MAO coatings on magnesium alloy

Rectangular coupons (10 mm×20 mm×3 mm) of AZ91D magnesium alloy were used as substrates in the experiment. Prior to the MAO treatment, the specimens were polished with SiC abrasive paper (up to1000 grit) and degreased in acetone and distilled water. MAO units used in this work mainly consist of electrolyte bath with stirring and cooling systems and a power supply with approximate 1 000 V of the maximum voltage amplitude. The MAO process was performed in alkaline electrolyte containing 15 g/L Na_2SiO_3 and 3 g/L NaOH. The temperature of the electrolyte was controlled at 20−30 ˚C. For the power supply, its frequency was 500 Hz. The

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current density varied at 3, 4 and 5 A/dm^2 at the coating surface was maintained by controlling the voltage amplitude in the deposition process.

2.2 Characterization of MAO coatings

The phase composition of the coatings was identified with X-ray diffractometer (Model D/Max 2500PC Rigaku, Japan) operated with Cu K_α. The X-ray generator settings were 50 kV and 50 mA, and the scans were acquired from 20° to 80° (in 2θ). The microstructure and surface roughness of the coatings were observed by confocal laser scanning microscope (Olympus OLS3000, Japan), which uses advanced image processing software and allows the construction of three-dimensional images of the object, topographical maps, and the surface roughness values of the coatings could also be obtained.

2.3 Corrosion resistance tests

The corrosion resistances of the substrate and the coatings prepared at different current densities were evaluated by means of a three-electrode corrosion cell. 3.5% (mass fraction) NaCl solution was used as corrosive medium. A platinum electrode was used as counter electrode and a saturated calomel electrode (SCE) was used as reference. The working electrode had an area of 1 cm^2 in contact with the electrolyte. The potentiodynamic polarization curves were scanned from −2.2 V to −2.0 V at a rate of 10 mV/s with a potentiostat EG&G model 273. The surface morphologies of the oxide coatings after the corrosion resistance tests were characterized by SEM.

3 Results and discussion

3.1 Effect of current density on microstructure and surface roughness of micro-arc oxidation coating

As is known there are three main steps underlying the formation of MAO coatings: firstly, a number of discharge channels are formed for the breakdown of the low conductive oxide layer and the alloy elements are melted out of the substrate to the channels; then, the alloy elements react with the electrolytic elements and get oxidized; at last, the oxidized material is ejected to the coating surface and cooled by the electrolyte. The above processes are repeated all through the MAO process, leading to the increase of the coating thickness. Therefore, the morphology and structure of the coating are quite dependent on the oxidation process. Fig.1 illustrates the two-dimensional and three-dimensional images of the coatings formed on the magnesium alloy in a bath containing 20 g/L Na_2SiO_3 and 3 g/L NaOH at different current densities for 40 min. The micrographs clearly indicate that the pores present on the coating surface as dark circular spots and distribute all over the surface of the ceramic coatings. It is also apparent that the number of pores is increased, while the diameter of the pores is apparently decreased with increasing the current density. In Fig.2(a), some micro cracks inevitably appear on the coating due to the rapid solidification of the molten MgO in the discharge channel. In contrast to this, more unsealed micro-pores are found to exist in the coating formed at the current densities of 4 A/dm^2 and 5 A/dm^2.

The corresponding three-dimensional images of the coatings are also displayed in Fig.1. Though the coatings take on the similar surface figures, the wave crest and trough of the agglomeration vary depending on the current density, which causes different surface roughness. The results of surface roughness measured with the software attached to the CLSM are presented in Table 1. It is clearly that the surface roughness decreases with increasing the current density. The change of surface morphologies can be exclusively contributed to the effect of current density, which determines the applied voltage in the MAO process. The higher the applied voltage in the process, the higher the energy for the micro-pores to sinter together. Therefore, the higher the current density, the smaller the dimension in the discharge channel, and the lower the surface roughness in the surface appearance.

Table 1 Thickness and surface roughness of MAO coatings formed at different current densities

Current density/(A·dm^{-2})	R_a/μm	R_q/μm
3	8.727 5	13.625 8
4	7.624 3	11.726 3
5	7.425 9	10.956 2

3.2 Effect of current density on composition of micro-arc oxidation coating

Fig.2 shows X-ray diffraction patterns of oxide coatings formed on magnesium alloys by micro-arc oxidation in a bath containing 15 g/L Na_2SiO_3 and 3 g/L NaOH at current densities of 3, 4 and 5 A/dm^2 for 40 min, respectively. It is obvious that the MAO coating consists of MgO and $MgAl_2O_4$ phases. It is known that the magnesium oxide is produced by plasma thermal chemical reactions in the discharging channels. The phase is thermodynamically stable at all testing temperatures, whereas is metastable. The magnesium oxide should be formed by plasma thermal chemical reactions in the discharge channels. When the current density is higher, the discharge spark can burn for a long time in MAO process. So, the discharge product can be transformed completely into the phase. In addition, the content of MgO in the coatings has no apparent variation

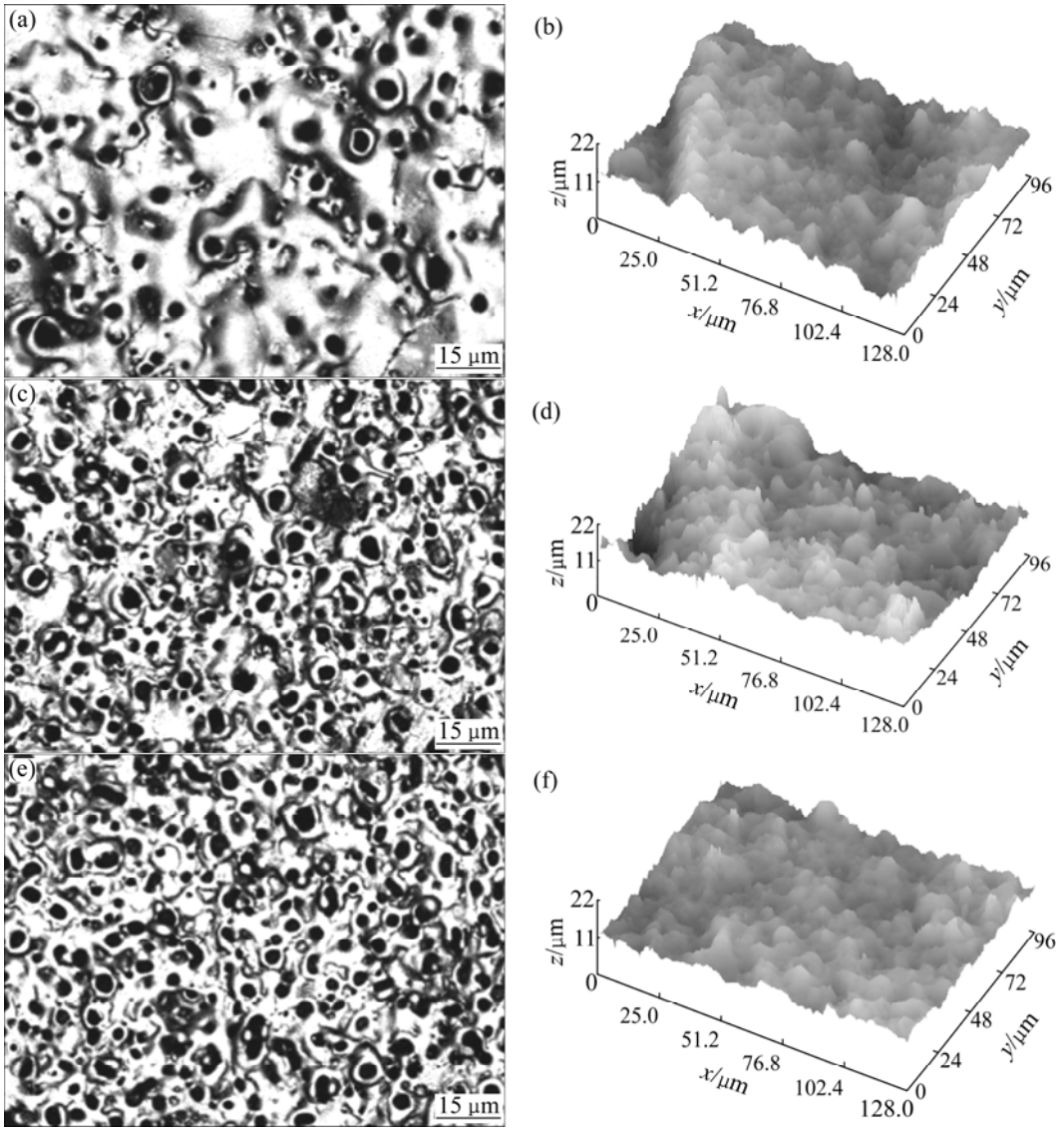

Fig.1 Surface CLSM images and corresponding three-dimensional images of ceramic coatings formed at different current densities: (a), (b) 3 A/dm^2; (c), (d) 4 A/dm^2; (e), (f) 5 A/dm^2

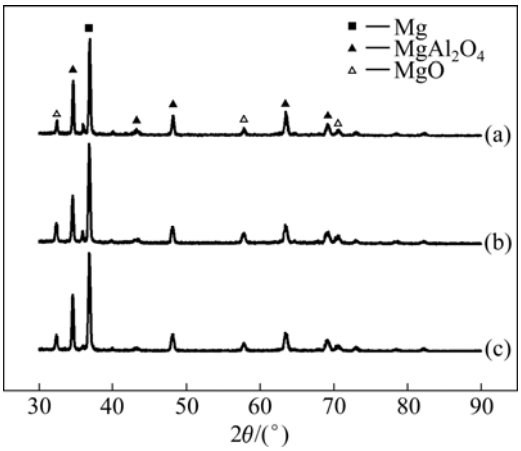

Fig.2 XRD patterns of MAO coatings formed on magnesium alloys at different current densities: (a) 3 A/dm^2; (b) 4 A/dm^2; (c) 5 A/dm^2

with the current density. However, the content of $MgAl_2O_4$ in the coating formed at the current density of 5 A/dm^2 is decreased compared to the other two coatings fabricated at current densities of 3 and 4 A/dm^2, respectively. It is well known from the previous study that, the content of $MgAl_2O_4$ has a strong effect on the corrosion resistance of the MAO coating.

3.3 Effect of current density on corrosion resistance of micro-arc oxidation coating

In order to evaluate the corrosion resistance provided by ceramic coatings, potentiodynamic polarization curves were performed. The representative polarization curves for magnesium alloys coated with ceramic coatings by micro-arc oxidation and for the substrate are shown in Fig.3. It is obvious that the sample

treated by micro-arc oxidation has a good corrosion protective property compared with the magnesium substrate; furthermore, the coating fabricated at current density of 5 A/dm^2 shows the best corrosion resistance. This may be attributed to the morphology and roughness of the coatings discussed above. It has been reported that the main corrosion form of magnesium alloy in NaCl solution is pitting corrosion[16]. Therefore, the micro-pores of the MAO coatings have detrimental effect on the corrosion performance. Larger pores augment the real exposed area to the corrosive solution and they may concentrate more corrosion medium than little ones. The excellent corrosion resistance is possibly attributed to compact structure of the coating fabricated in electrolyte containing 20 g/L Na_2SiO_3 and 3 g/L NaOH at the current density of 5 A/dm^2. The corresponding surface morphologies of oxide films after corrosion tests formed at different current densities are shown in Fig.4.

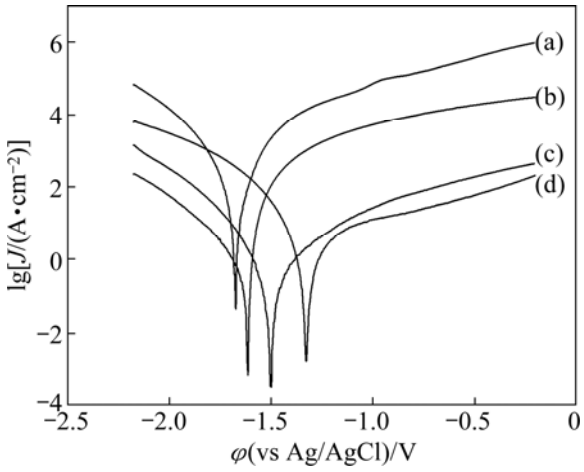

Fig.3 Polarization curves of substrate and ceramic coatings formed at different current densities: (a) Substrate, magnesium alloy; (b) Coating, 3 A/dm^2; (c) Coating, 4 A/dm^2; (d) Coating, 5 A/dm^2

4 Conclusions

1) The current density has a strong effect on the corrosion resistance of MAO coatings.

2) By changing the current density, the MAO coatings possess different compositions and microstructures, as well as the corrosion resistances. The oxide coatings consist mainly of MgO and $MgAl_2O_4$ phases. However, the content of $MgAl_2O_4$ in the coating formed at current density of 5 A/dm^2 decreases compared to the other two coatings fabricated at current densities of 3 and 4 A/dm^2.

3) As a result, the coating formed at current density of 5 A/dm^2 shows the better corrosion resistance than the other MgO coatings.

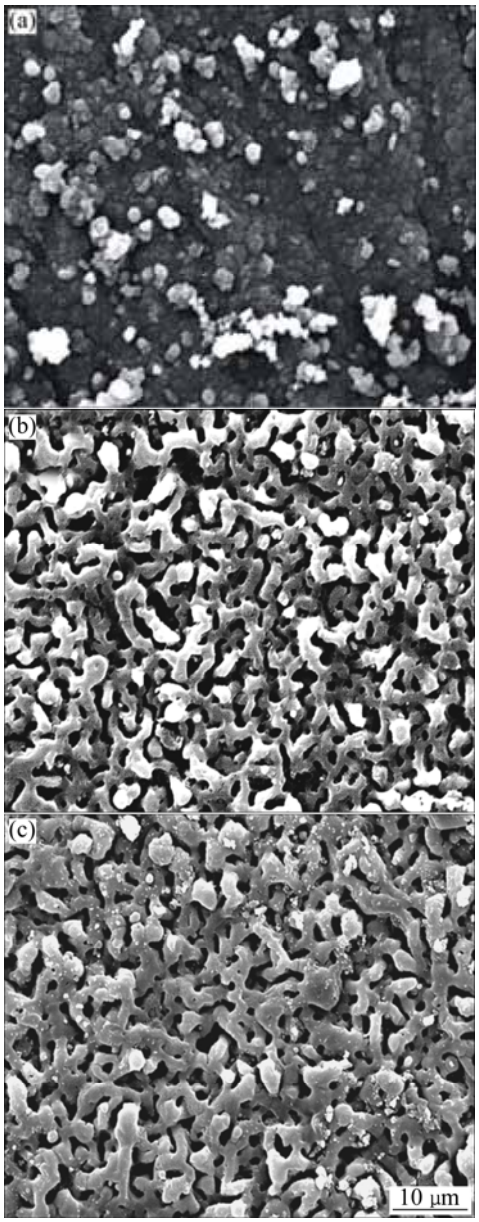

Fig.4 Surface morphologies of oxide films formed at different current densities after corrosion tests: (a) 3 A/dm^2; (b) 4 A/dm^2; (c) 5 A/dm^2

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