

EFFECTS OF OXIDATION TIME ON MICRO-ARC OXIDIZED COATINGS OF MAGNESIUM ALLOY AZ91D IN ALUMINATE SOLUTION

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Keywords: Magnesium alloy, Micro-arc oxidation, Coating, Corrosion resistance

Abstract

Micro-arc oxidation coatings were prepared on magnesium alloy AZ91D at different oxidation times in aluminate solution. The effects of the oxidation time on the microstructure, growth rate and corrosion resistance of the coatings were investigated. The results indicate that the coatings are uniform in thickness and mainly composed of $MgAl_2O_4$ and MgO . There were many residual discharging channels on the coatings surface. The coatings improved the corrosion resistance of magnesium alloy AZ91D considerably. With increased oxidation time, the crystalline substances content and thickness of the coatings increased, while the growth rate of the coatings decreased, and the resulting coatings surface had lower porosity and larger pore sizes. In addition, the corrosion resistance of the coatings on magnesium alloy AZ91D surfaces is superior to the magnesium alloy AZ91D substrate in the $NaCl$ solution, and the effect is more remarkable with longer oxidation times.

Introduction

Magnesium (Mg) and its alloys have low density and high specific strength, so they are being increasingly applied to various industries like automotive and consumer electronics. Effective coatings will facilitate further application of magnesium and its alloys.

Micro-arc oxidization (MAO, which also named as plasma electrolytic oxidation or anodic spark oxidation), based on conversational anodic oxidization technology, is a new promising surface treatment method of forming functional coatings such as anti-corrosion coatings, anti-wear coatings or bioactive coatings on valve metals (such as Al, Mg and Ti) in a suitable electrolyte by increasing the anodic voltage to a high stage, usually accompanied by intensive gas evolution and sparking phenomenon at the anode surface [1-3]. Recently, MAO has successfully been used for producing protective coatings on Mg and its alloys to enhance the corrosion resistance [4-9].

The presence of $MgAl_2O_4$ in a composite coating on metal substrates is desirable for corrosion resistance [10]. Our previous work has reported that the $MgAl_2O_4/MgO$ composite coatings on Mg and its alloys by MAO in an aqueous $NaAlO_2$ -containing electrolyte [8, 9, 11]. The coating firmly bonds to the substrate, exhibits a high microhardness and has improved considerably the corrosion resistance of the substrate. The effects of $NaAlO_2$ concentration in the electrolyte and the applied voltage on the structure, phase composition, microhardness and corrosion resistance of coatings have been studied, respectively. On the other hand, the oxidation time has been proven to be a crucial factor in the microstructure and properties of MAO-formed coatings in silicate electrolyte [12]. In this work, it is mainly for

above-mentioned reasons that the morphologies, phase components, and corrosion resistances of the MAO coatings prepared on Mg alloy AZ91D substrates at the different oxidation time in the $NaAlO_2$ -containing electrolytes were investigated.

Experimental procedures

Samples (20 mm×15 mm×6 mm) of die-cast Mg alloy AZ91D (chemical composition in wt. %: Al 8.5-9.5, Zn 0.5-0.90, Mn 0.17-0.27, Mg balance.) were used as substrate material. The samples were ground with abrasive papers and ultrasonically cleaned with acetone and distilled water prior to MAO treatment. For MAO, a pulse power supply was employed, and the Mg alloy AZ91D sample was used as an anode while a stainless steel cylinder container with electrolyte inside was used as a cathode. The electrolyte is mainly composed of $NaAlO_2$ and some additional additives prepared with deionized water. During MAO treatment of each Mg alloy AZ91D, the oxidation time was fixed at 5, 20, 40, and 60 minutes, respectively. The applied voltage, pulse frequency and duty circle was fixed at 480 V, 100 Hz and 25%, respectively. The electrolyte bath was water-cooled and its temperature was maintained lower than 30 °C. After the MAO treatment, the samples were washed with deionized water and dried at room temperature.

The morphologies and phase components of the samples were investigated using scanning electron microscopy (SEM; JSM-6460, Japan) and X-ray diffraction (XRD; D/MAX-2200PC, Japan), respectively.

The corrosion resistance of Mg alloy AZ91D before and after the MAO treatment was tested through Zennium-type electrochemical corrosion testing system produced by Germany's ZAJNER Company. The samples with an exposed area of 1 cm² were immersed in a 3.5 wt. % $NaCl$ solution prepared using analytical grade reagents in distilled water. After 10 minutes of initial delay, the scan was conducted with a constant rate 0.5 mV/s speed from -1.9 to -1.0 V. The reference electrode is a saturated calomel electrode (SCE), and the auxiliary electrode is a graphite electrode.

Results and discussion

Microstructure

The surface morphologies of the coatings formed at different oxidation time are shown in Figure 1. It can be seen in Figure 1 porous surface of the coating has been formed. There were many residual discharging channels on the coatings surface. As oxidation time increases, the resulting coatings surface has lower porosity, larger pore size and bigger melting particles. The coatings surface is composed of grains with different diameters,

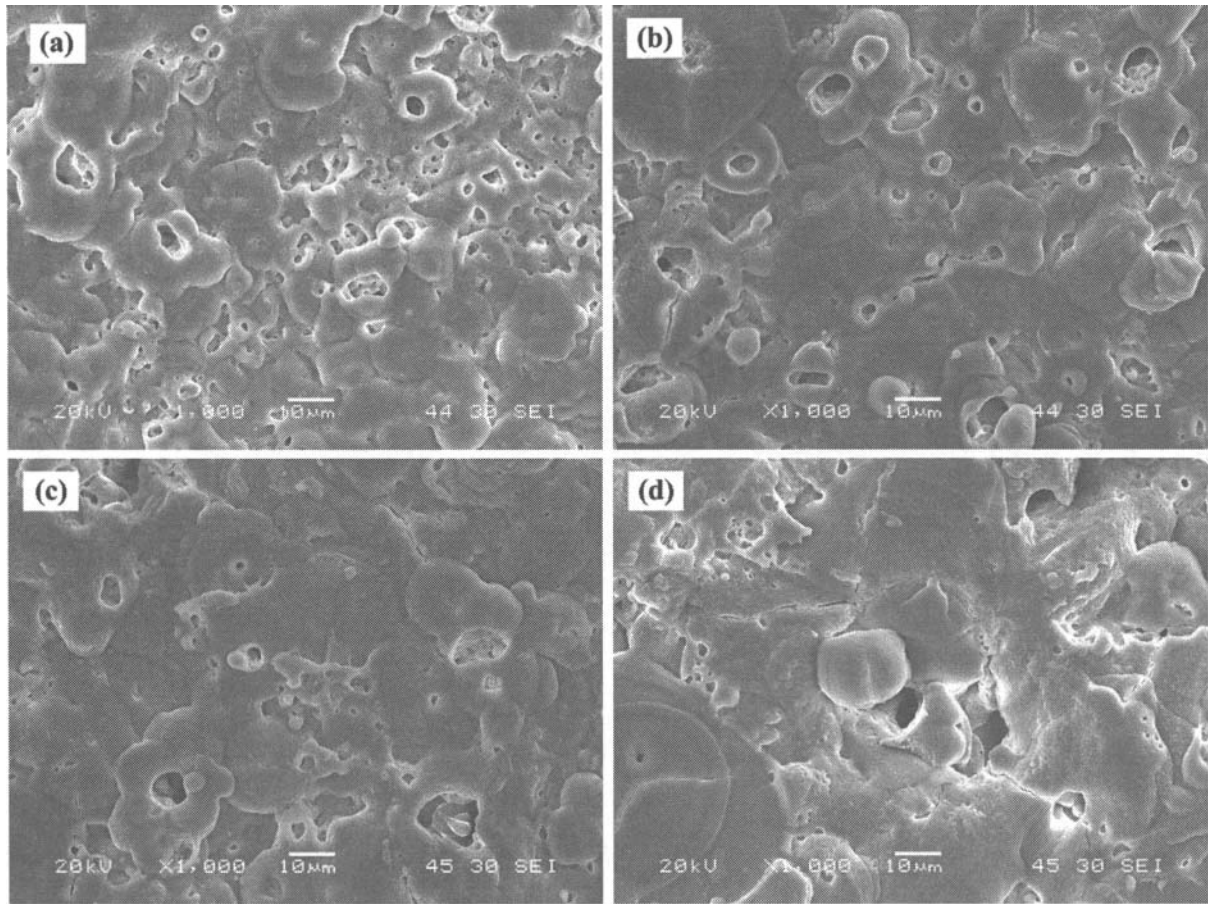


Figure 1. Surface morphologies of the coatings formed at (a) 5, (b) 20, (c) 40 and (d) 60 minutes.

which are melted and unevenly distributed on the coatings surface. The molten grains have integrated each other due to sintering effect during MAO process. The rough surface of coatings is due to uneven-melted solids. In addition, obvious extended micro cracks can be seen on the coatings surface. These micro cracks are caused by overlarge thermal stress in fast solidification of the melts when the coatings surface contact with the electrolytic solution [13].

Figure 2 shows the cross section of the coatings formed at different oxidation times. The thickness of the coating is approximately 21, 27, 30 and 32 μm , respectively. As oxidation time prolonged, the growth rate of MAO coatings was gradually decreased. The cross section of the coatings appears to be relatively uniform in thickness. However, even though they are not entirely transverse in the coatings, micro pores and micro flaws can be seen in Figure 2. It can also be seen in Figure 3 that the internal substrates are covered by a relatively intact protective layer, which are composed of relatively stable thermodynamically compounds. The preferential growth of coatings at a certain location is either due to the inherent electrochemical heterogeneity of basis Mg, or the concentration of current, or both, when sparking occurs. The preferential growth and the dielectric breakdown of coatings, together with the trapping and the

evolution of oxygen and aqueous vapor should be responsible for the above mentioned micro pores and micro flaws. It is also noticed that there is no apparent discontinuity in the interface of the coatings and substrates. This indicates that the coatings can bond tightly to the substrates.

Figure 3 shows the XRD patterns of the coatings formed at different oxidation time. The coatings are mainly composed of MgAl_2O_4 and MgO . With increasing oxidation time, the MgAl_2O_4 content of the composite coatings increases, while no significant variation is observed in the MgO content. This suggests that the AlO_2^- anions in the electrolytes react with the substrate during the MAO process, and the oxidation time has great influence on the composition of the coatings formed on Mg alloy AZ91D. In addition, as observed from the experiment, the phase components of the MAO coatings differ from the amorphous coating on Mg alloy treated by the anodic oxidation. MAO can make amorphous phase into crystalline phase through high temperature and high pressure instant sintering. The method can form a dense layer to increase the hardness and corrosion resistance of Mg alloy [2]. The instantaneous temperature in the micro-spark zone can reach 10^3 - 10^4 K [3], thus the oxide products synthesized by plasma chemical interactions possess a stable chemical thermodynamic property.

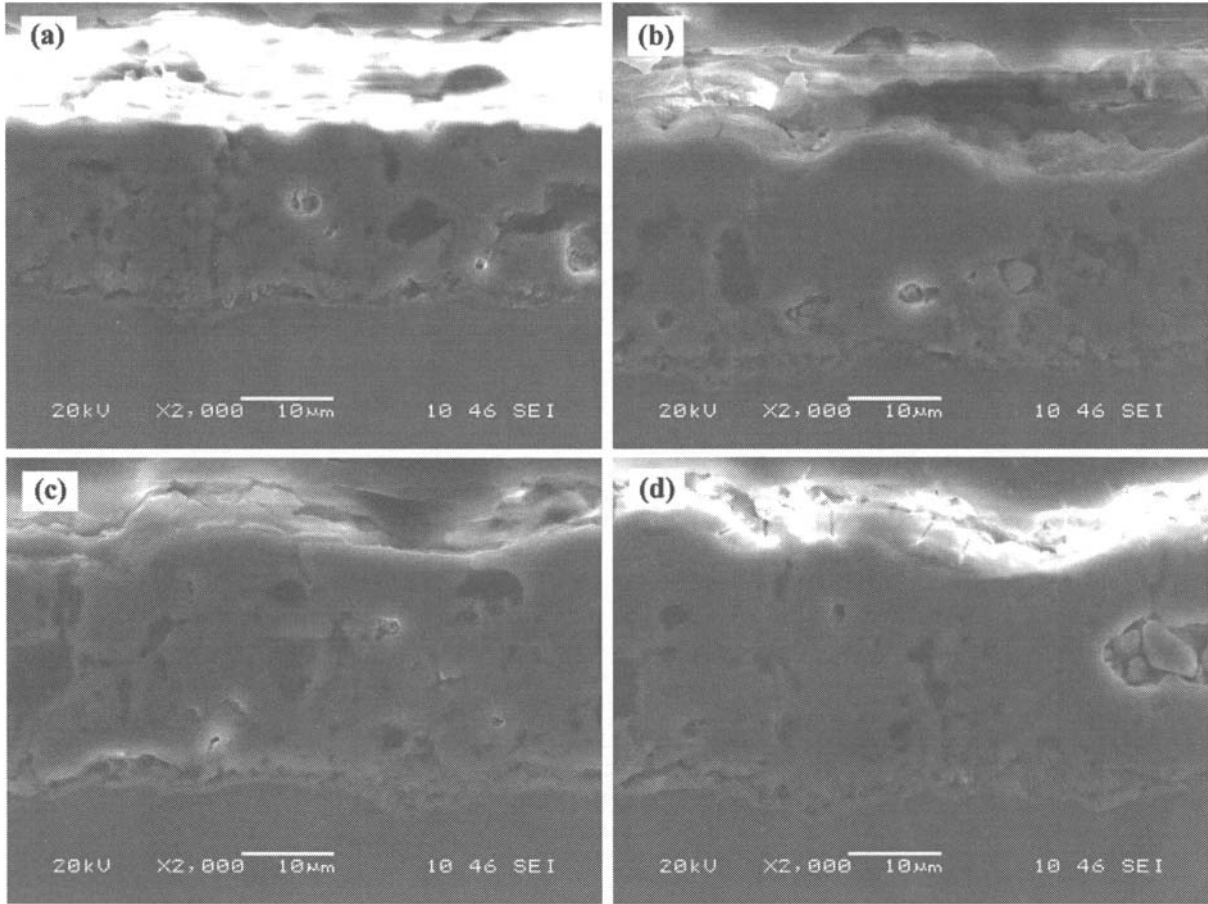


Figure 2. Cross-sectional morphologies of the coatings formed at (a) 5, (b) 20, (c) 40 and (d) 60 minutes.

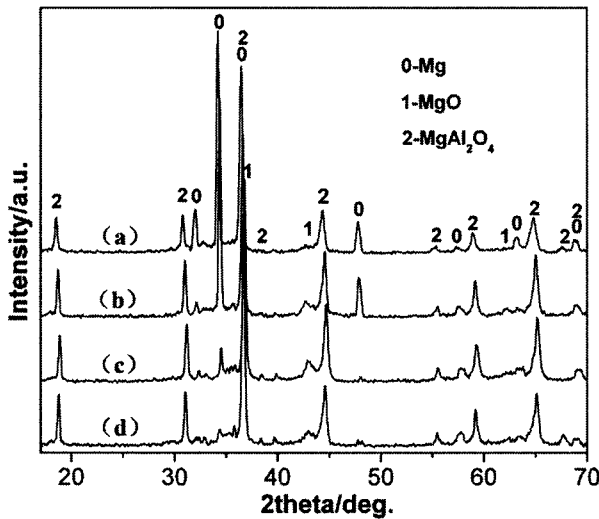
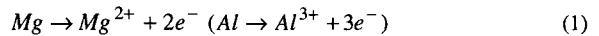
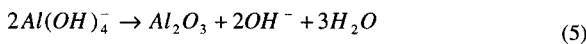
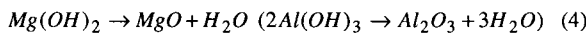
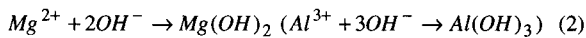


Figure 3. XRD patterns of the coatings formed at (a) 5, (b) 20, (c) 40 and (d) 60 minutes.

Above results demonstrate that a kind of MgAl₂O₄/MgO coating has been synthesized on Mg alloy AZ91D by the MAO. The presence of MgAl₂O₄ and MgO indicate that AlO₂⁻ and OH⁻ ions have incorporated into the coating intensively. A possible explanation for the formation of the coating is as follows.

During the MAO, due to the effect of the electric field, Mg²⁺ (Al³⁺) (reaction (1)) from the Mg alloy AZ91D substrate according to the reactions (2) and (3) combined with the OH⁻ and AlO₂⁻ from the NaAlO₂ solution to form Mg(OH)₂, Al(OH)₃ and MgAl₂O₄. Since the AlO₂⁻ is relatively unstable, it can partially interact with water in solution, forming Al(OH)₄⁻ [14]. An extreme high thermal energy generated by sparks caused the dehydration of the hydroxides (reactions (4) and (5)) [15]. Notably, the local temperature inside the discharge channels can reach 3000–10,000 K in the MAO process [6]. Therefore, the phase transformations caused by the high local temperature. It is known that the only compound present in the phase diagram of the MgO–Al₂O₃ system is MgAl₂O₄ [16], so, when micro-arcs rise, the reaction (6) can be generated.





Corrosion resistance

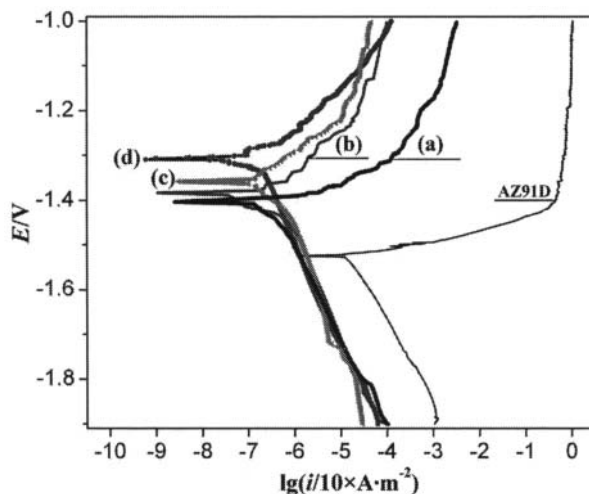


Figure 4. Polarization curves of the MAO-treated samples formed at (a) 5, (b) 20, (c) 40 and (d) 60 minutes and the Mg alloy AZ91D substrate in 3.5 wt. % NaCl solution.

Table.1 The result of potentiodynamic corrosion tests in 3.5 wt. % NaCl solution

Samples	E_{corr} (V)	i_{corr} ($\mu\text{A}/\text{cm}^2$)
AZ91D	-1.541	22.023
5 minutes	-1.425	1.748
20 minutes	-1.383	1.523
40 minutes	-1.352	1.202
60 minutes	-1.338	0.893

Figure 4 shows the potentiodynamic polarization curves of Mg alloy AZ91D and the samples treated at different oxidation time. It can be seen from the results that the anodic polarization curve of Mg alloy AZ91D enters the active dissolution zone when the potential reaches -1.524 V. The anodic current density of Mg alloy AZ91D electrode increases with the potential increasing in this zone. The anodic polarization curve of the each MAO-treated sample enters the active dissolution zone when the potential reaches -1.408, -1.387, -1.360 and -1.309 V, respectively, and the anodic current density of the each MAO-treated sample electrode increases with the potential increasing in this zone. The corrosion

potential (E_{corr}) and the corrosion current density (I_{corr}) data are shown in Table 1. The data clearly show that the corrosion resistances are enhanced by the MAO process. The corrosion potential of the MAO-treated samples increases and their corrosion current density decreases with increasing oxidation time. The results indicate that the coating formed at longer oxidation time has a lower corrosion rate and better corrosion resistance. After the corrosion test, large corrosion craters can be clearly observed by naked eye on Mg alloy AZ91D surface, but there are no visible changes on the coatings surface. When formed at 60 minutes, the corrosion current density of coating decreases by two orders of magnitude compared with the Mg alloy AZ91D and its corrosion resistance is greatly improved. The above results illustrate that the coatings provide effective corrosion protection for the Mg alloy AZ91D substrate in solutions containing Cl⁻. The effective corrosion protection provided by the MgAl₂O₄/MgO composite coatings can be attributed to intact microstructures and relatively stable chemical thermodynamic composition.

Conclusions

Through MAO process, MgAl₂O₄/MgO composite coatings with uniform thickness are directly prepared on Mg alloy AZ91D, and thus the surface property has been greatly improved. The coatings are mainly composed of MgAl₂O₄ and MgO. There were many residual discharging channels on the coatings surface. With the increase of the oxidation time, the crystalline substances content and the thickness of the coatings increase, while the growth rate of the coatings decrease, and the resulting coatings surface has lower porosity and larger pore size. When formed at 60 minutes, the coating is approximately 32 μm thick and has sufficient corrosion resistance. Such MgAl₂O₄/MgO composite coatings are expected to be an effective protection of Mg alloy substrates for its practical application.

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