

## Growth process and corrosion resistance of micro-arc oxidation coating on Mg-Zn-Gd magnesium alloys

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**Abstract:** A Mg-6Zn-3Gd (mass fraction, %) alloy, noted as ZG63, was coated by different micro-arc oxidation (MAO) processes, and the coating structure and corrosion resistance of the alloy were studied using scanning electron microscopy (SEM), glancing angle X-ray diffractometry (GAXRD) and various electrochemical methods. The micro-arc oxidation process consists of three stages and corresponds with different coating structures. In the initial stage, the coating thickness is linearly increased and is controlled by electrochemical polarization. In the second stage, the coating grows mainly inward and accords with parabolic regularity. In the third stage, the loose coating forms and is controlled by local arc light. The looser coating is mainly composed of MgSiO<sub>3</sub> and the compact coating is mainly composed of MgO. From micro-arc oxidation stage to local arc light stage, the corrosion resistance of the coated alloy firstly increases and then decreases. The satisfied corrosion resistance corresponds to the coating time ranging from 6 to 10 min.

**Key words:** Mg-6Zn-3Gd magnesium alloys; micro-arc oxidation; growth process; corrosion resistance

### 1 Introduction

Micro-arc oxidation (MAO) technique is a promising and effective method of surface treatment for aluminium and magnesium alloys because the MAO coating can improve the corrosion resistance and wear-resisting property of the alloys substantially[1–3]. Presently, the researches on MAO technique for magnesium alloys focus on influence of solution system and electrical parameter on property and microstructure of ceramic coating[4–7]. Nevertheless, study on ceramic coating formation and growth mechanism is little[8–11]. A few reports on growth process and phase structure of MAO are about tradition brand magnesium alloys rather than rare earth magnesium alloys[12–14]. The study of JIANG et al[15] indicated that the process of MAO involved three growth stages and the different growth stages have different growth manner and phase structure. However, growth regularity and property such as corrosion resistance of ceramic coating in the three growth stages have not been studied deeply[16–18].

In the present work, the growth mechanism and corrosion resistance of MAO coating on Mg-6Zn-3Gd-

0.5Zr (mass fraction, %) magnesium alloy are studied in order to provide experimental foundation in prevention of corrosion for magnesium alloys.

### 2 Experimental

The MAO coatings were prepared with 10 kW DC pulse micro arc oxidation system. The cast ingot of Mg alloy with a normal composition of Mg-6Zn-3Gd-0.5Zr (mass fraction, %) was cut into cubical samples with a dimension of 30 mm × 30 mm × 5 mm. The electrolyte temperature is controlled automatically at (25±5) °C. The pH value of this recipe solution was in the range of 11–12 before MAO. The time of MAO is from 18 s to 30 min under a constant current density of 3 mA/cm<sup>2</sup>. The thickness and mass of the coatings were measured using a coating thickness gauge (TT260) and an electronic balance, respectively. Before the experiment of weighing, the samples should be dried. The surface morphology of the anodic film was examined by scanning electron microscopy (SEM). The crystal structure of the anodic film was determined by glancing angle X-ray diffractometry (GAXRD) with a glancing incident angle of 0.5°. Potentiodynamic electrochemical

tests were carried out using a LK98C electrochemical analyzer. The electrochemical cell consisted of a three-electrode glass cell.

### 3 Results and discussion

#### 3.1 Growth process of ceramic coating on Mg-Zn-Gd magnesium alloys

Fig.1 shows the growth process of ceramic coating in the different stages. It is apparent that the longer the treating time of MAO, the thicker the ceramic coating is. The growth rate of ceramic coating is fast and is controlled by electrochemical polarization in the initial stage. In other words, the growth process of ceramic coating is controlled by interface reaction. The interface reaction can be described as



Therefore, the growth process of ceramic coating accords with linear regularity with data fitting software CurveExpert1.3 in the anodic oxidation stage. The formula of linear regularity can be described as  $Y=4.1X$ . The reason that growth rate of ceramic coating is fast has two aspects. One is the faster electrochemical reaction rate than ion migration rate, and the other is the formation manner of oxide in the initial stage. In the beginning, the growth of the oxide is along crystal lattice of matrix alloy, called false crystalline oxide, so that the growth rate is fast. With the ceramic coating thickening, the oxide coating disengages crystal lattice of matrix alloy and then grows according to own crystal lattice. The formation time of false crystalline oxide is short and the growth rate is fast, which can improve the combining force between matrix alloy and ceramic coating.

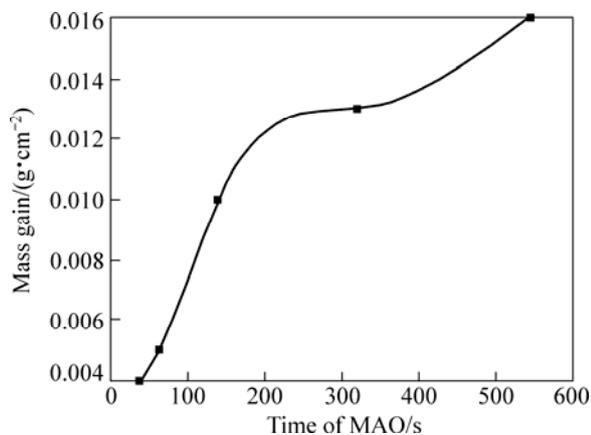


Fig.1 Growth process of ceramic coating in different stages

With the time increasing, the growth rate of ceramic coating decreases and the growth law never accords with liner regularity. In the micro-arc oxidation stage, data fitting software CurveExpert1.3 show that the growth

process of ceramic coating changes to parabolic regularity. The expression of parabolic regularity is  $Y=-4.9+4.38X-0.32X^2$ . Because oxygen arrives at the surface of matrix alloy through diffusion and electrochemical reaction rate of  $\text{Mg}^{2+}$  ion and  $\text{O}^{2-}$  ion is higher than the diffusion rate of ions, the interface reaction is never the controlling step and the oxidation rate is slower than that of the anodic oxidation. With the ceramic coating thickening, the diffusion rate decreases.

With the elapse of oxidization time, the membrane thickness is continuously increased and it will be even difficult for breakdown and thus the reaction path is shortened. The reaction can be carried out on locally damaged areas, and this will also increase the surface roughness of membrane. At the same time, with the prolongation of processing time, the voltage needed for breakdown is continuously increased so that the porosity of membrane enlarges and the thickness of tectorium increases. The higher the energy density is, the longer the gas escape path is, so that migration rate of ion increases and the growth manner of ceramic coating diverges that of micro-arc oxidation stage. The growth process of ceramic coating still accords with parabolic regularity with data fitting software CurveExpert1.3 in the arc light stage. The formula of linear regularity can be described as  $Y=9.8-0.43X+0.06X^2$ .

Fig.2 shows the growth manner of ceramic coating in the different stages. It is apparent that the longer the time of MAO process, the thicker the inner layer and outer layer of membrane are. However, the growth rule is different. In the initial stage of oxidation, the ceramic coating grows mainly outward. Because the surface of matrix alloy has no oxide film or has half-baked oxide film in the initial stage of oxidation, magnesium can contact with oxygen fully. As a result, the growth of membrane accords with the manner of outward growth, which leads to the formation of tensile stress in the inner oxide film so that the membrane is loose comparatively. When the surface of matrix alloy is covered with intact

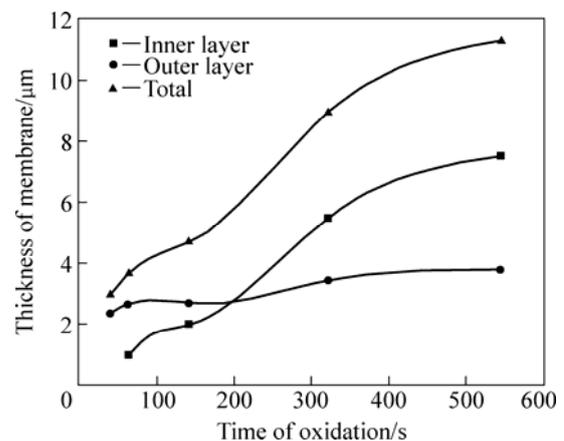


Fig.2 Growth manner of ceramic coating in different stages

oxide film, the high voltage can break down locally damaged areas and then  $O^{2-}$  ions reach to the matrix along discharge path, which makes the growth manner of ceramic coating change to inward growth. As electric breakdown always locates in locally damaged areas of membrane, it can accelerate the formation of dense layer in micro-arc oxidation stage.

### 3.2 Growth mechanics of ceramic coating on Mg-Zn-Gd magnesium alloys

Fig.3 shows the surface morphologies of ceramic coating in the different stages. It is apparent that fog deposition and flocculent deposition begin to appear on the surface of the samples in anodic oxidation stage at 18 s. Then, these deposits gather, diffuse and form initial ceramic coating of MAO. When the time of oxidation is 2 min and 15 min, the deposits on the samples surface have disappeared and are replaced by microporosity formed by micro-arc discharge (diameter of about 1–2  $\mu\text{m}$ ). The local umbilicate areas are composed of electric breakdown holes. At 45 min, on the surface of samples relatively big spurting holes appear (diameter of about 4–5  $\mu\text{m}$ ) and big molten particle generates around the holes. At this time, the surface is irregular, which is related with the larger local arc light in the process of MAO.

### 3.3 Structure and phase composition of ceramic coating

Fig.4 shows line scanning electronic microscope photographs of ceramic coating cross-section. It is apparent that the membrane consists of the loose layer and the dense layer. In the initial MAO stage, relatively low arc starting voltage breaks down uniformly the oxide

film naturally developed on the samples surface and generates molten magnesium oxide and other oxides through metallurgical bonding on electrolyte cooling. Because transient temperature of micro-area discharge is up to 2 000  $^{\circ}\text{C}$  and discharge process only occurs on the surface of the samples in the initial stage, the coating is relatively compact. With the prolongation of processing time, the voltage needed for breakdown is continuously increased so that at this time, the continuous thickening of membrane depends upon repeating breakdown of the original ceramic coating, which generates the oxidization in inner layer. The gas generated in the cooling process must have corresponding escape path. Because of the difference in the cooling condition, outer layer is first frozen so that the inner gas escape generates volcano spurting structure. So, the thicker the ceramic coating is, the looser the layer is.

Fig.4 shows that the contents of Mg and Si element are relatively low in the loose layer, on the contrary, the contents continuously increase in the dense layer. The distribution of oxygen element is opposite to that of Mg and Si element in the loose layer and dense layer and Si element concentrates obviously in the dense layer. Fig.5 shows various elements distribution of coating. It is apparent that the component of ceramic coating is mainly MgO in the initial stage of MAO, called anodic oxidation stage. In the micro-arc oxidation stage, the loose layer is composed of MgO and chemical compound generated in the ionic reaction of solution and the content of MgO is low in superficial coating. The content of Si decreases continuously in the dense layer and the contents of chemical compound generated in the ionic reaction are reduced continuously. On the contrary, the contents of MgO and F increase gradually. As the radius of  $F^{-}$  ion is

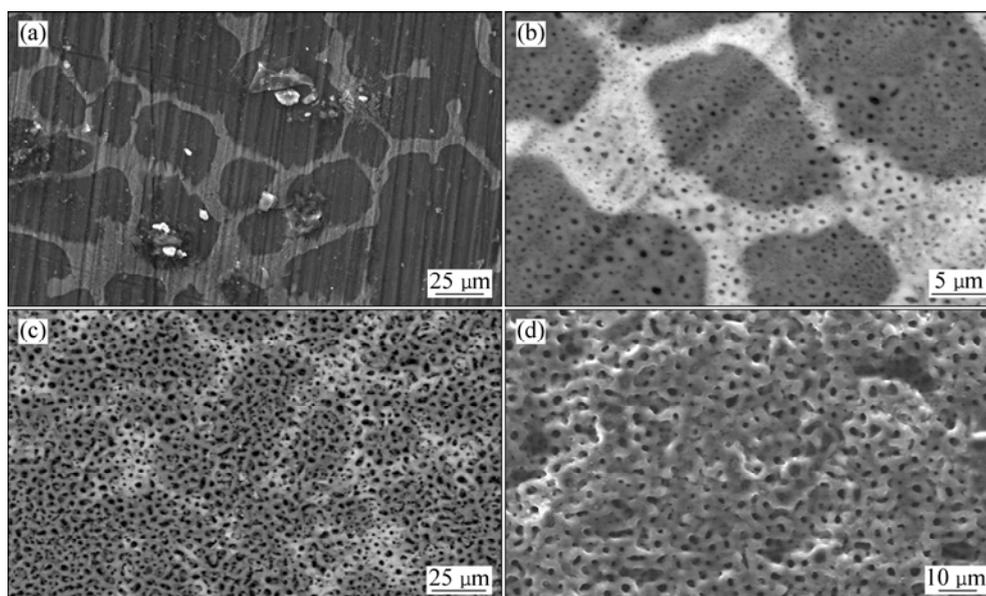
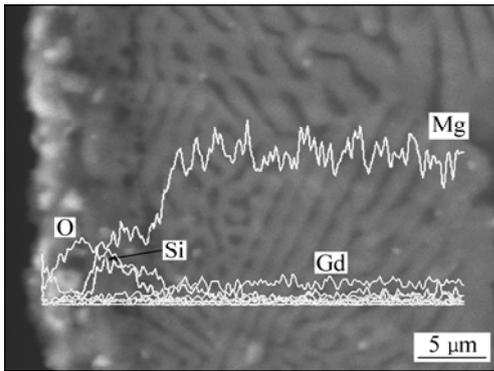
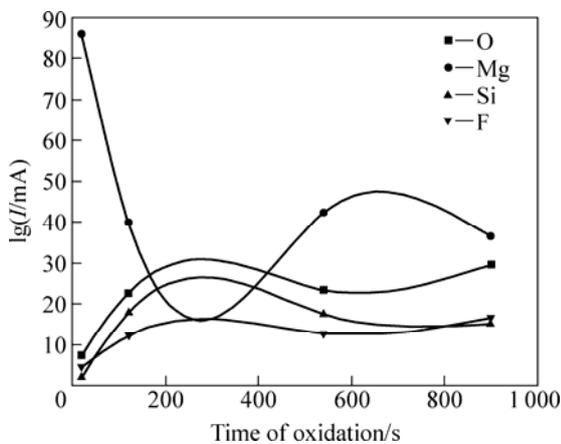


Fig.3 Surface morphologies of ceramic coating in different stages: (a) 18 s; (b) 2 min; (c) 15 min; (d) 45 min



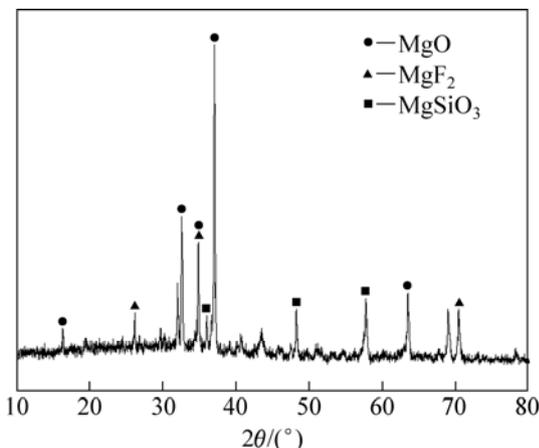
**Fig.4** Line scanning electronic microscope photograph of ceramic coating cross-section



**Fig.5** Elements distribution of coating

small, it has strong force of penetration.

Fig.6 shows XRD pattern of ceramic coating. It is apparent that the main phase of ceramic coating is the cubic lattice MgO and there is a small amount of MgSiO<sub>3</sub>. According to elements distribution in Fig.5, the loose layer is composed of MgO, MgF<sub>2</sub> and MgSiO<sub>3</sub>, and the dense layer is mainly composed of MgO. The contents of MgF<sub>2</sub> and MgSiO<sub>3</sub> decrease gradually.

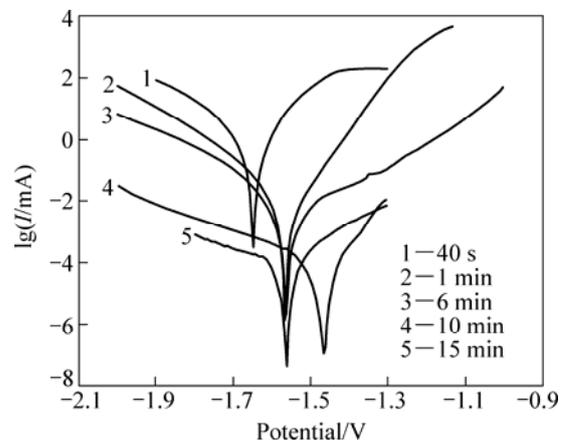


**Fig.6** XRD pattern of ceramic coating

### 3.4 Corrosion resistance of ceramic coating in different stages

Fig.7 shows the Tafel polarization curves of ceramic coating in different stages. It is apparent that corrosion rate firstly decreases and then increases with the prolongation of processing time. In other words, corrosion resistance of coating firstly increases and then decreases. The corrosion resistance is better from 6 min to 10 min. The reason is mainly the different formation mechanisms in the different stages so that microstructure and structure are different. The anodic oxidation film generated in the early micro-arc oxidation stage is the necessary condition of micro-arc discharge. When the voltage acts on the anode and cathode, the anions containing oxygen ion form a anion coacervate of hydrate containing magnesium ion under the anodic voltage in the solution interface between magnesium and electrolyte. The more the voltage and anodic current increase, the thicker the coacervate coating is, and then the coacervate coating appears supersaturated to deposit in the solution interface between magnesium and electrolyte. At the same time, due to great Joule heat generated under the high voltage and great current at the interface, the sedimentary deposits continuously condense, dehydrate and cool rapidly so that the oxide film can be formed at the interface, and then the sedimentary deposits form a barrier layer block for electron migration at the anodic interface under electric field condition, which leads to the formation of high electric field in barrier layer. With the electric potential increasing, the electric field enlarges gradually to reach breakdown voltage, which gives rise to spark discharge and then micro-arc oxidation occurs. In this stage, the membrane is common anodic oxide film that is relatively thin, deficiency and has low corrosion resistance.

When the controlling voltage exceeds a certain critical value, some isolated vulnerable area of coating is firstly broken down and spark discharge phenomenon



**Fig.7** Tafel polarization curves of ceramic coating in different stages

takes place at the same time because of electrolyte destabilizing. Above all, a lot of discharge paths are formed in the inner ceramic coating, which produces electron snowflake that gives rise to the temperature increasing of the oxide in the inner discharge paths. In the high electric field condition, the component of anion, such as  $O^{2-}$  ion, enters paths through electrophoresis manner. At the same time, the plasma reaches the high temperature and the high pressure in short time of  $10^{-6}$  s, which gives rise to meltability of matrix and alloy element and then they enter paths through diffusion and subsequently generate oxidation. Once again, the oxide of magnesium and the other component jet out from discharge paths, get to the surface of coating contacting with electrolyte, and then freeze rapidly in quenching condition, which increases the thickness of coating around the discharge paths. Lastly, the discharge paths cool down and the reaction products deposit in the path wall. This process sustains the shorter time, so exothermic effect occurs and volume increases.

With the prolongation of processing time, some isolated vulnerable areas on the whole surface of the coating repeat previous process so that the ceramic coating is thickened uniformly. In constant current oxidation condition, the growth rate of coating is approximately constant. The thicker the ceramic coating is, the larger the self impedance is. In order to maintain the constant current, the voltage increases gradually with the oxidation time increasing.

In the micro-arc oxidation stage, the surface of magnesium alloy produces great uniform minute spark discharge and the discharge paths generated by spark discharge are also very uniform and minute. After discharge is weakened, the surface of coating has many remaining discharge micropore and small aperture (Fig.3(c)). In this stage, the thickness of ceramic coating increases and the coating is very compact, which leads to the improved corrosion resistance of coating. With the time increasing continuously, the ceramic coating is thickened gradually and the quantities of the discharge paths decrease. When the voltage reaches the critical value, MAO begins to turn into arc light stage. In this stage, because of the high voltage and the large discharge energy, the mass of product increases, which enlarges the aperture of micropores formed by cooling and freezing in the discharge paths. At the same time, the longer the MAO time, the thicker the ceramic coating is. When micro-area is broken down and molten, the volume of molten pool enlarges, the fused mass increases and the molten particles are rather large after ejecting. In addition, multiple pulse gives birth to continuous discharge or multiple discharge paths merge into a great path in some vulnerable area of coating, which increases the aperture of micropores so that the porosity of ceramic

coating and thickness of the loose layer enhance and the corrosion resistance of ceramic coating declines gradually.

Fig.7 shows EIS patterns of ceramic coating in the different stages. As seen in Fig.7, with the thickness of coating increasing, the impedance value firstly increases and then decreases. Small capacitive impedance arc occurs in the high frequency stage. With the prolongation of processing time, micro-arc ceramic coating restrains the rate of electron charge movement so that big capacitive impedance arc appears on EIS pattern in the low frequency stage. At 9 min of micro-arc oxidation, the diameter of capacitive impedance arc is the biggest and the corrosion resistance is the best. The results of impedance accord with Tafel polarization curve and it is proved that the results are correct.

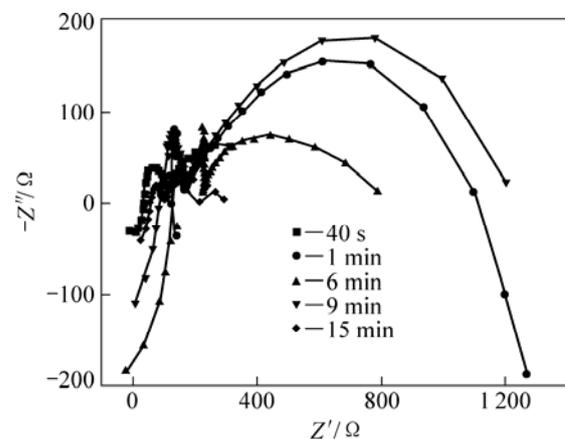


Fig.7 EIS patterns of ceramic coating in different stages

## 4 Conclusions

1) The kinetics law of micro-arc oxidation can be fitted by software CurveExpert1.3. The results show that the kinetics curve of anodic oxidation accords with linear law. The formula of linear regularity can be described as  $Y=4.1X$ . The kinetics curves of micro-arc oxidation and arc light belong to parabolic regularity. The expression of parabolic regularity can be described as  $Y=-4.9+4.38X-0.32X^2$  and  $Y=9.8-0.43X+0.06X^2$ , respectively.

2) The longer the MAO time, the thicker the inner layer and outer layer of membrane are. However, the growth rule is different. In the initial stage of oxidation, ceramic coating grows mainly outward. When the thickness of the membrane reaches a certain critical value, the growth manner of ceramic coating changes to inward growth.

3) The loose layer consists of  $MgO$ ,  $MgF_2$  and  $MgSiO_3$  phases and the dense layer mainly consists of  $MgO$ . The contents of  $MgF_2$  and  $MgSiO_3$  decrease gradually. The component of ceramic coating is mainly  $MgO$  in the anodic oxidation stage. In the micro-arc

oxidation stage, the loose layer consists of MgO and chemical compound generated in the ionic reaction of solution and the content of MgO is low in superficial coating. The content of Si decreases continuously in the dense layer. On the contrary, the contents of MgO and F increase gradually.

4) With the prolongation of oxidation time, the impedance and corrosion resistance firstly increase and then decrease. At 9 min of micro-arc oxidation, the ceramic coating has the better corrosion resistance.

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