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ScienceDirect
Trans. Nonferrous Met. Soc. China 20(2010) 2198−2203

Transactions of
Nonferrous Metals
Society of China

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

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Received 23 October 2009; accepted 30 August 2010

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 $MgSiO_3$ 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 to10 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^2. 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

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DOI: 10.1016/S1003-6326(09)60442-8

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

$$Mg^{2+}+O^{2-}\longrightarrow MgO \quad (1)$$

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.

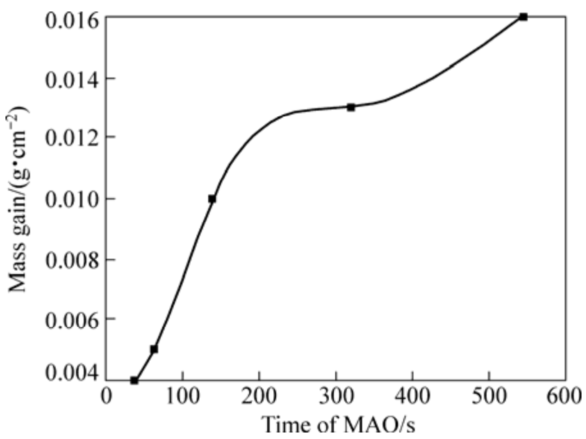

Fig.1 Growth process of ceramic coating in different stages

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 Mg^{2+} ion and 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

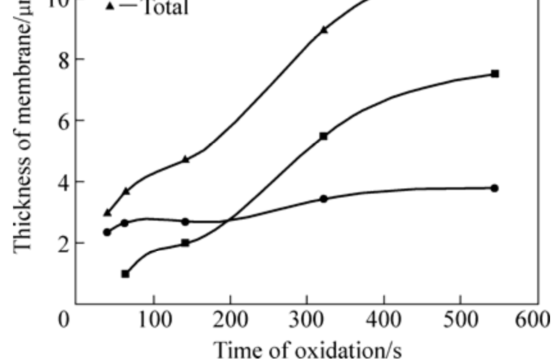

Fig.2 Growth manner of ceramic coating in different stages