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The growth process of the PEO films under escalating voltage waveform

WANG Li[1,a], FU Wen[1,b*], CHEN Li[2,c]

[1.] College of Chemical and Environmental Engineering, Guangdong Univ. of Petrochem. Tech., Maoming 525000, Guangdong, China;

[2.] School of Chemistry & Chemical Engineering, South China Univ. of Tech. Guangzhou 510640, Guangdong China

[b*]a449192213@163.com

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Abstract: In order to get a clear picture for describing the growth process of plasma electrolytic oxidation coatings under escalating voltage waveform, the characteristics of PEO coatings formed at different reaction stages were systemically investigated. The morphology and corrosion resistance of the films were studied by scanning electron microscope and potentiodynamic polarization curves. The uniform, semi-transparent and better corrosion resistance of the oxide films on the magnesium electrode surface were formed owe to the extended anodizing time at the initial stage under escalating voltage mode. After sparking occurred, generated ceramic coatings were brokedown, melted, cooled and solidified continuously, so the ceramic coatings were uniform and dense. It also exhibited superior corrosion resistance.

Introduction

Plasma electrolytic oxidation (PEO), also known as micro-arc oxidation, developed on the conventional anodic oxidation[1-3]. It can grow ceramic oxide films on the light metals or its alloys in situ such as aluminum, magnesium and titanium. The micro-region discharge sparks can generate on the anode surface, so the uniform ceramic films will be formed on the surface of the light metal. Magnesium is one of the lightest structural metals, which makes it one of the favoured materials to minimize vehicle weight and therefore to reduce exhaust gas emissions in transport fields. But its application is limited because of its poor corrosion resistance. The corrosion resistance of the magnesium can be reduced by alloying with aluminium, manganese or zinc, but its process is complex. PEO provides a new means of surface modification of metallic materials. The formed films adhered to the substrate well and exhibit good corrosion resistance[4-8].

In the paper, the escalating voltage waveform was used during the PEO process in the Na_2SiO_3 electrolyte. AZ31 magnesium alloy was the substrate. The growth characteristics of the PEO films under escalating voltage waveform were investigated through the films' surface morphologies and corrosion resistance at different reaction stages.

Experiment

PEO equipment and electrolyte

AZ31 magnesium alloy and the stainless steel were used as the anode (Al 3.1074 wt.%, Zn 0.9075 wt.%, Mn 0.4219 wt.%, Si <0.0104 wt.%, others <0.01 wt.%) and the cathod, respectively. The power supply was a home-made DC power supply with voltage 0~1400 V and current 0~2.5 A. The samples were polished up to 2000 grit and degreased ultrasonically with acetone and washed with distilled water. The composition of the electrolyte is 20 g/L Na_2SiO_3 and 4 g/L KOH.

Experiment method

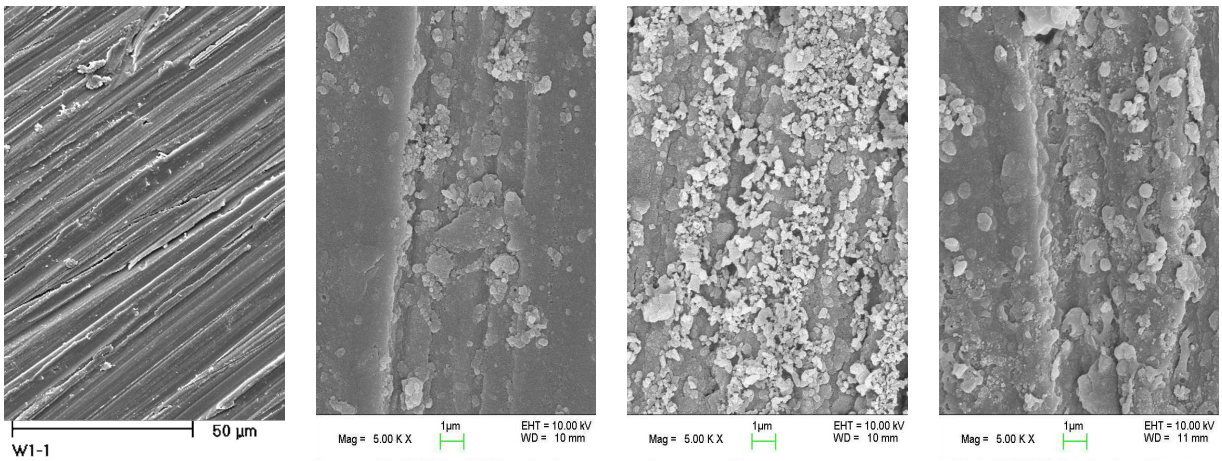
The escalating voltage waveforms were used in the experiment. The samples were treated with the voltage escalated 10 V for every 5 minutes, 300 V was the terminal voltage. The surface morphology and microstructure of the PEO films were observed with scanning electron microscope (SEM, LEO 1530 VP). Corrosion resistance of the oxide films was assessed by potentiodynamic polarization tests using Autolab system in 3.5 wt.% NaCl solution. The details have been reported elsewhere[9-12].

Results and discussions

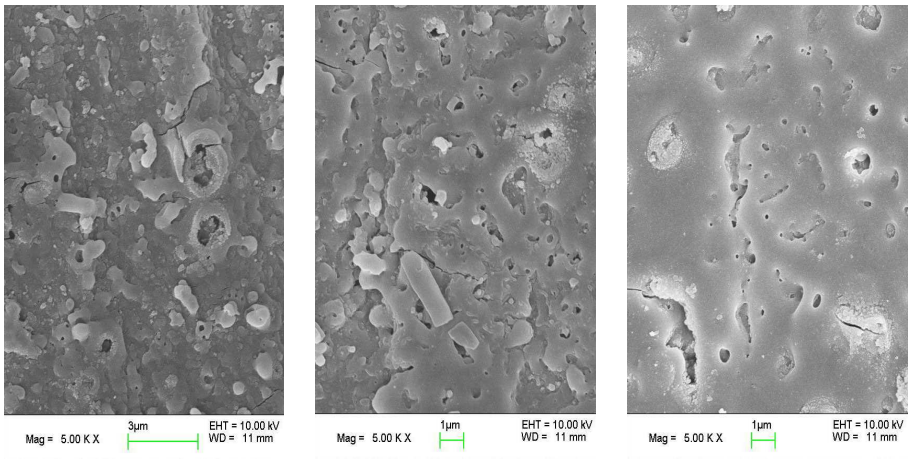
The surface morphologies of the PEO films at different reaction stages

The surface morphologies of the PEO films formed under escalating voltage mode at different reaction stages were shown in Fig.1. Fig.1 (a) shows the morphologies of the AZ31 magnesium alloy. It can be seen that the polished trace was still visible. When the conventional anodic oxidation happened (Fig 1b, 50 V), a few granular oxides were formed on the surface of the sample, some small gas bubbles occurred on the sample surface. With the increase of the voltage, more and more oxides were formed on the surface of the sample(Fig 1c and d, 100 and 150 V), what is more, more and more small gas bubbles were also produced aroud the surface of the sample. A thin oxide films were also formed on the surface of the sample (Fig 1d, 150 V). Since 150 V had not reached the breakdown voltage of the oxide films(also known as the dielectric barrier layer), so the period during 50-150 V still follows the conventional anodic oxidation stage.

After treated at 200 V for 5 min(Fig 1e), it reached the breakdown voltage of the dielectric barrier layer[9-12], so the discharge happened. A large amount of small sparks distributed on the surface of the samples. At the same time, a mass of bubbles companying with shrill sounds produced. Lots of discharge channels were visible on the micro-structrue of the films (as shown in Fig. 1e), what is more, some melting products were also distributed on the surface of the sample. As the voltage reached 250 V(Fig 1f), plasma sparks discharge became much bright with stronger intensity. So the films at the voltage melted heavily than that of 200 V. When the AZ31 magnesium alloy was treated at 300 V(Fig 1g), the PEO films exhibited uniform surface morphologies.



(a)AZ31 (b) 50 V (c) 100 V (d) 150 V



(e) 200 V (f) 250 V (g) 300 V

Fig. 1. Surface morphologies of magnesium alloy AZ31 samples obtained at different PEO reaction stage

The electrochemical properties of the PEO films formed at different reaction stages

When the AZ31 magnesium alloy was treated at different time during the PEO process, the electrochemical properties of the PEO films were different. The polarization curves of the PEO films formed at different reaction stage (100 V, 200 V and 300 V) were investigated. It was shown in Fig. 2. The corrosion resistance R_p and corrosion current density were calculated by the Tafel curves' slopes of anode and cathod. The calcultated formula was as follow:

$$R_p = \frac{b_a b_c}{2.3 i_{corr}(b_a + b_c)} \quad (1)$$

Corrosion potential, corrosion current density and corrosion resistance of the filmed samples are often used to characterize the corrosion protective property of the films. The high corrosion potential or corrosion resistance and low corrosion current density of the films suggest a low corrosion rate and a high uniform corrosion resistance performance.

From Fig. 2, it can be seen that as the PEO process carried on, the corrosion resistance of the PEO films increased. The values of R_p at 100, 200 and 300 V were 9.496, 2.009e^{+4}, 1.35e^{+6} Ohm. That is to say, when the plasma spark discharge happened, the PEO films exhibited better corrosion resistance with lower current density and higher corrosion resistance.

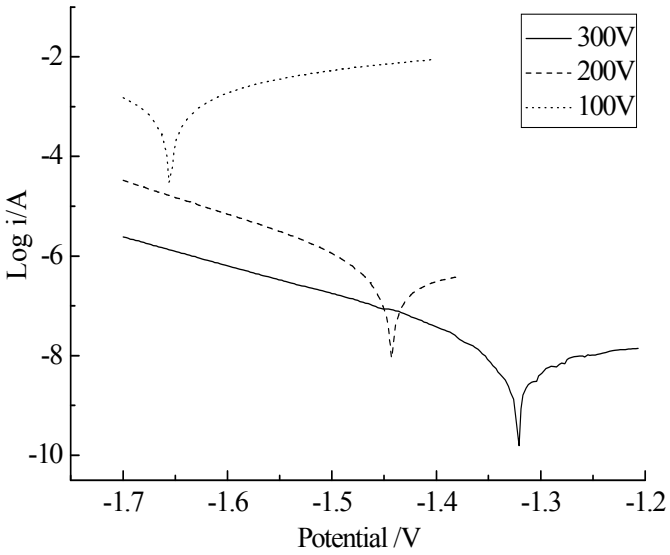


Fig. 2. Potentiodynamic polarization curves of PEO ceramic coatings formed at different PEO reaction stage

Conclusions

(1) The PEO films' growth characteristics were discussed according to their surface morphologies at different reaction stages. At the conventional anodic oxidation stage, the oxide films formed, which was also known as the dielectric barrier layer. After the barrier layer breakdown, the discharge happened, the oxide films were melted and showed ceramic surface morphologies.

(2) As the PEO process carried on, the corrosion resistance of the PEO films increased. The values of R_p at 100, 200 and 300 V were 9.496, $2.009e^{+4}$, $1.35e^{+6}$ Ohm.

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