Effects of current output modes on the growth kinetics and corrosion resistance of micro-arc oxidation coatings on magnesium alloy

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Abstracts
Micro-arc oxidation (MAO) coatings were prepared on the AZ31 Mg alloy under the constant/gradient current control modes. The effects of current output modes on the growth rate, energy consumption, microstructure, and corrosion resistance of MAO coatings were studied. The results show that the current step-down mode (G852) exhibited a lower unit energy consumption than the constant current mode (C5) and the current step-up mode (G258), even though the same average current density current was used during MAO process. Meanwhile, the G852 is conducive to a thick and dense coating, resulting in a better corrosion resistance. The method of energy saving preparation of corrosion resistant MAO coating by adjusting the current mode is of great significance for practical production.

1. Introduction

The magnesium (Mg) alloys, as lightweight structural materials, have have been widely concerned for many future applications. Nevertheless, the low corrosion and poor wear resistance of Mg alloys usually restrict their practical application [1]. Micro-arc oxidation (MAO), also known as plasma electrolytic oxidation (PEO), is an environmentally friendly and economic surface treatment technology [2]. In the MAO process, under the influence of terminal voltage, the micro-arc discharge is generated on the surface of Mg alloys. The resulting high temperature and pressure conditions causes the Mg atoms in the substrate micro-zone bond with the oxygen plasma to produce a ceramic oxide coating [3]. These oxide coatings, showing high hardness and excellent resistance to bimetallic corrosion, are capable of enhancing effectively the mechanical and corrosion resistance of Mg alloys [4–6].

Many works have indicated that the microstructure and properties of the MAO coatings on Mg alloys mainly depend on the electrolyte, electrical parameters and substrate composition in MAO process [7–9]. The growth mechanism of the MAO coatings on Mg alloys has also been studied [10–12]. It has been verified that the anions from electrolyte and the other alloying atoms in Mg substrates would be involved in the process of micro-arc discharge, and thus affects the coating properties, such as breakdown voltage, microstructure, composition and growth rate of the coating [13, 14]. Liang et al. [15] and Huo et al. [16] proved that the silicate electrolyte was conducive to the growth of dense MAO coatings, while the electrolyte containing phosphate facilitated a relatively porous structure and increased the growth rate of the MAO coating. Meanwhile, Muhaeffel et al. [17], Cakmak et al. [18] and Liu et al. [19] indicated that the microstructure and alloying elements in Mg substrate had great influence on the corrosion resistance of the MAO coatings.

Electrical parameters in MAO process include working voltage, current, frequency, pulse width and duty cycle [20]. Among these, the working voltage and current are the most important electrical parameters, which directly influence the thickness and morphology of the MAO coatings. Most studies paid much attention to optimizing the magnitude of current [21–23], whereas relatively neglected the effect of current mode on the MAO coating. In this work, the MAO coatings were grown on AZ31 Mg alloy under the same average current density but different current output modes. The effects of current output mode on the thickness, micro-pore
size and corrosion behavior of the MAO coatings were evaluated. Besides, the relationship between the current mode and energy efficiency during the MAO process was analysed.

2. Materials and methods

2.1. Micro-arc oxidation treatment
AZ31 Mg alloy plates, with a composition of 2.59% Al, 0.93% Zn, 0.31% Mn and balance Mg, were purchased from Dongguan Feitai Metal Products Co., Ltd (China). The alloy plates were cut out to small blocks (dimensions of 30 × 20 × 8 mm).

The MAO coatings were prepared using a unipolar pulse power supply under the constant and gradient current control modes for 30 min. The MAO process was divided into three 10 min steps. The current densities applied in each step for different modes are listed in Table 1. During the MAO process, Mg substrate was used as anode and a stainless-steel plate was used as cathode. The electrolyte was composed of 7 g l⁻¹ sodium metasilicate (Na₂SiO₃), 2 g l⁻¹ potassium hydroxide (KOH), and 5 g l⁻¹ potassium fluoride (KF). The temperature of the electrolyte during the micro-arc oxidation process was kept below 30 °C by the stirring and cooling system. The pulse width and frequency were fixed at 300 μm and 500 Hz. After the MAO treatment, the specimens were rinsed under running deionized water for 5 min and dried in the air immediately.

2.2. Coating characterization
The thickness of MAO coating was measured using an FMP20 eddy current thickness meter. The average value was employed from 12-point measurements except for the maximum and minimum. The surface and cross-section morphologies of the MAO coatings were observed through a scanning electron microscope (SEM, JSM-6510, Japan). Image J software was employed to statistically analyse the pore size and porosity. Three SEM images, with the 300× magnification (427 × 290 μm²), were chosen from each specimen to compute porosity.

2.3. Corrosion test
The electrochemical behaviours of the MAO coatings were tested on an electrochemical workstation (Autolab PGSTAT302 N), using a typical three-electrode cell system. The specimens were set as the working electrode, the reference electrode was the Ag/AgCl electrode and the platinum electrode was used as the counter electrode. The corrosion medium was 3.5 wt.% NaCl solution which the specimens (exposed area of 1 cm²) were immersed in at room temperature of 25 °C. After certain immersion periods (1 h, 5 h and 10 h), electrochemical impedance spectroscopy (EIS) test was conducted with a signal amplitude of 10 mV over the open circuit potential (OCP) in a frequency range of 10⁵ Hz to 0.01 Hz. Then, the potentiodynamic polarization test was performed at a sweep rate of 10 mV s⁻¹. To ensure the reproducibility of results, each specimen was carried out triplicate.

3. Results and discussion

3.1. Effect of the current output mode on the growth kinetic of the MAO coating
Figure 1 demonstrated the voltage-time responses in the different current output modes. In the constant current mode (C5), the voltage rise process could be divided into three stages [5, 24, 25]. Before the breakdown voltage (Uₜ₅), the voltage increased sharply, and this process was named as the general anodic oxidation stage. Subsequently, the rising rate of voltage slowed down, and the reactions went through the white spark discharge stage. When the voltage exceeded the critical voltage (Uₜ₅), it turned into the orange arc discharge stage, and the voltage increased very slowly. For the current step-up mode (G258), the operating voltage showed two rising nodes, when the current density increased from 2 to 5 A dm⁻² and 5 to 8 A dm⁻², respectively. On the contrary, the decrease of the operating voltage occurred at the nodes where the current density lowered in the current step-down mode (G852). Besides, because of the larger current density in the initial phase, the G852 took less time to

| Step | Time (min) | C5 | G258 | G852 |
|------|------------|----|------|------|
| I    | 0–10       | 5  | 2    | 8    |
| II   | 10–20      | 5  | 5    | 5    |
| III  | 20–30      | 5  | 8    | 2    |
reach the $U_b$ and $U_c$ than the other two current modes. It was worth pointing out that the $U_I$ values during the C5, G258, and G852 were similar, due to the same average current density ($5 \text{ A dm}^{-2}$).

The thickness and average growth rate of the MAO coatings at each step under different current output modes are given in figure 2. With regard to the C5, the coating growth rates gradually decreased with the treatments time (figure 2(b)). This trend would be reversed by raising current density step-by-step (G258). Conversely, the trend would be boosted during the current step-down mode (G852). Since the average current density of the three modes was the same, the thickness and total growth rate of the coatings that prepared by C5 and G258 mode were similar. However, the thickness and growth rate of the coatings prepared in the G852 mode was slightly higher.

The MAO coating growth is a process that high-energy discharge occurs, that leads to partial fusion of coating material and the deposition of an oxide coating on the substrate [12]. Discharge energy was a critical factor in the growth of MAO coating. To discuss its effect, the energy consumption during MAO process was calculated according to figure 1 and equation (1).

$$W = I \int U(t) \, dt$$

$W$ is electrical energy consumption (kW·h), $U$ is voltage (V), $I$ is current density (A dm$^{-2}$), and $t$ is time for treatment (h). From figure 3, the higher the current density at each stage, the greater the energy consumption. In addition, the ratio of energy consumption ($\Delta W$) and thickness variation ($\Delta d$) in each step is defined as unit energy consumption ($W_{\text{unit}}$). Since the average current density was the same in all three modes, their total energy consumption was almost the same. Figure 3(b) indicated that the larger current density led to the higher $W_{\text{unit}}$ in the Step I. With the coating thickening, the $W_{\text{unit}}$ of coating growth increased gradually for the C5 and G258.
However, the $W_{\text{unit}}$ of the coating fluctuated slightly in G852. Among them, the total $W_{\text{unit}}$ of C5, G258 and G852 were $0.01847$ kW·h/(dm$^2$·μm), $0.01767$ kW·h/(dm$^2$·μm) and $0.01616$ kW·h/(dm$^2$·μm), respectively. In other words, the G852 uses about 10% less energy than the C5 when growing the same thickness of coatings. In summary, the current step-down mode (G852) was beneficial to slightly reduce energy consumption.

### 3.2. Effects of the current output modes on the microstructures of the MAO coating

Figure 4 shows the surface morphologies of the MAO coatings prepared under different current control modes. Abundant micro-pores and sintered grains unevenly distributed on the surface. Generally, the micro-pores are regarded as the discharge channels during MAO process, while the sintered grains are the deposition of melt oxide erupted from the discharge channel unevenly distributed on the surface [4, 26].

To further analyse the coating morphology, Image J software was used to measure the diameter and number of micro-pores from SEM images, and their histograms (figure 5) was obtained. The pore sizes were mainly distributed between 4–20 μm, and a small number of micro-pores above 20 μm appeared on the G258. The average pore diameter of the coating in G852 was the smallest, 9.77 μm. The G258 was the largest, 11.19 μm.
The evolution of the surface morphology for the MAO coatings treated under the C5, G258 and G852, is given in figure 6. The statistical analyses for their pore size and porosity are exhibited in figures 7 and 8, respectively. From figure 6, the surface morphology shifted significantly. For the C5, with the increase of reaction time, the average micro-pore diameter increased from 6.27 \( \mu \text{m} \) to 10.52 \( \mu \text{m} \). For the G258, the average diameter of micro-pores increased greatly, that increased from 2.24 \( \mu \text{m} \) to 11.19 \( \mu \text{m} \) with the processing time. Concerning G852, the pore diameter was kept between the range of 8–10 \( \mu \text{m} \) during the whole MAO process, even if the protrusions gradually increased. Moreover, some micro-pores are sealed in the step III of the G852, which results in the coating having minimal porosity (figure 8). Therefore, the G852 mode could make the coatings denser to some extent.

Based on the microstructure characteristics of the three coatings, it could be inferred that the current output modes had marked impact on the spark discharges status on anode surface. For the C5, as the processing time prolonged, the operating voltage increased (figure 1), but the number of discharge reduced. In other words, the intensity and size of a single discharge would be improved significantly with processing time. Meanwhile, in the later stage of the MAO, the strong discharge is more likely to cause the type B discharges [10]. Hence, the diameter of the micro-pores increased with processing time, and the MAO coating formed in the C5 had a relatively large roughness. This phenomenon was magnified in the G258, as shown in figure 6, because there existed a two-stage rise in current density. However, in the case of the G852, the intensity of discharge dropped evidently with the current density decreasing twice. Accordingly, the type A & C discharges were more likely to occur in the later stage of the MAO [10], which resulted in sealing the originally formed large micro-pores (figure 6).

Figures 9(a)–(c) show the cross-section morphologies of the MAO coatings prepared. Each coating consisted of a dense inner layer and a porous outer layer. The thickness of the dense inner layer for each sample was given in figure 9(d). In three samples, the dense layer of C5 was thicker than G258, but thinner than G852. The layer-by-layer growth pattern of MAO coating suggested that the highest current density of step I results in the G852 having the thickest inner dense layer.

3.3. Effects of the current output modes on the corrosion resistance of the MAO coatings

Figures 10(a)–(c) are the Nyquist plots of the MAO coatings obtained by EIS tests after immersion for different immersion periods. At initial 5 h immersion, the Nyquist plots of the three specimens were composed of two
arcs. The arc in the high frequency was related to the porous outer layer, while the arc in the low frequency represented the barrier property of the dense inner layer. After immersing for 10 h, an obvious inductive arc appeared in the Nyquist plots of G258 and C5 (figure 10(c)), indicating that the oxide coatings had been locally damaged, and caused the corrosion of the substrate. The radius of capacitive loop in the Nyquist plot and modulus of impedance at low frequency ($|Z|_{f=0.01 \text{ Hz}}$) in the Bode plot are often considered as an indication of the corrosion resistance of the samples.

As shown in figure 10, the G852 exhibited the best corrosion resistance at each period of EIS tests, because of its the highest thickness and lowest porosity (figures 2 and 5). Up to 5 h immersion, the corrosion resistances of
Figure 9. Cross-section micrographs of the MAO coatings: (a) C5, (b) G258, (c) G852, and (d) the thicknesses of the dense layers.

Figure 10. EIS testing results of the MAO coatings immersed for different time: (a) 1 h, (b) 5 h, (c) 10 h and (d) modulus of impedance in the low frequency band.
the three samples were observed to improve, which was probably caused by the hydrolysis of MgO [19]. Moreover, after immersion for 5 h, the corrosion resistance of G258 was better than that of C5, which was mainly attributed to the higher thickness of G258 (figure 2). However, the corrosion resistance of G258 was worse than that of C5 again after 10 h. This was most likely related to the lower thickness of the dense layer under the G258 mode (figure 9) [27].

The samples immersed for 10 h were carried out potentiodynamic polarization tests to further evaluate their corrosion resistance (figure 11). Tafel extrapolation method [28, 29] was used to analyze their corrosion potentials ($E_{corr}$) and corrosion current densities ($i_{corr}$), and the results were summarized in table 2. Furthermore, the polarization resistance ($R_p$) was calculated based on the Stern-Geary formula given by equation (2) [6, 30], where $\beta_a$ and $\beta_c$ are the anodic and cathodic Tafel slopes, respectively. The corresponding values are listed in table 2.

$$R_p = \frac{\beta_a \beta_c}{2.303 i_{corr} (\beta_a + \beta_c)}$$

According to the values of $R_p$ and $i_{corr}$, after immersion for 10 h, the C5 revealed better corrosion resistant than the G258, and the corrosion resistance of G852 was higher than that of the other two samples slightly, which was consistent with the results of EIS tests.

According to the results of EIS test, the G852 always keep a higher corrosion resistance, especially after 5 h of corrosion, its value of $|Z|_{1000 \text{ Hz}}$ was about 40 times that of C5. After 10 h of corrosion, the corrosion resistance of each coating decreased rapidly, the difference of corrosion resistance of the coatings was smaller and smaller. However, since the thickness of the inner dense layer of G852 is slightly higher than that of C5 and G258, its value of $|Z|_{1000 \text{ Hz}}$ was still higher than that of C5 and G258. And from the polarization curve, the $i_{corr}$ of G852 was slightly lower than that of C5 and G258. Therefore, it could be inferred that the G852 mode could slow down the corrosion process of coatings to a certain extent.

4. Conclusions

(1) The growth of MAO coating in the constant current mode was non-linear, and the average growth rate gradually decreases in the three steps. This trend could be boosted by the current step-down mode (G852) and be reversed by raising current density step-by-step (G258). With the influence of different coatings

![Figure 11. The potentiodynamic polarization curves of the MAO coatings immersed in 3.5 wt.% NaCl solution for 10 h.](image)

| Samples  | $\beta_a$(mV dec$^{-1}$) | $\beta_c$(mV dec$^{-1}$) | $E_{corr}$(V versus Ag/AgCl) | $i_{corr}$(A cm$^{-2}$) | $R_p$(Ω·cm$^2$) |
|----------|-------------------------|-------------------------|----------------------------|------------------------|-----------------|
| 5–10 h   | 282.1                   | 124.3                   | -1.42                      | 4.79 x 10$^{-9}$       | 7.81 x 10$^6$   |
| G258–10 h| 312.5                   | 133.1                   | -1.34                      | 6.91 x 10$^{-9}$       | 5.84 x 10$^6$   |
| G852–10 h| 195.7                   | 109.7                   | -1.38                      | 3.20 x 10$^{-9}$       | 9.54 x 10$^6$   |
growth process, compared with C5 and G258, the thickness of coatings prepared in G852 mode increased slightly, and unit energy consumption decreased slightly.

(2) In the current step-down mode, the discharge intensity on the coatings surface decreased, which made the pore size and porosity of the coatings decrease and it is beneficial to slow down the corrosion process of the coating.

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