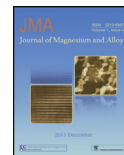


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Full length article

# The effect of pulse frequency on the electrochemical properties of micro arc oxidation coatings formed on magnesium alloy

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## Abstract

Micro arc oxidation (MAO) coatings were formed on magnesium alloy AZ31B to improve the corrosion resistance using environmental friendly electrolyte solution under single-polar pulse power supply. The effect of electrical parameters of pulse frequency on the coating performance was studied at frequencies of 2.5 Hz, 25 Hz and 250 Hz. The coating performance at different frequencies was characterized by scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS) and potentiodynamic polarization testing method. It was found that the corrosion resistance of the MAO coatings was improved when increasing the pulse frequencies from 2.5 Hz to 250 Hz. The corrosion current in 250 Hz case decreased by three orders of magnitude as compared with bare Mg alloy and the corrosion impedance also increased remarkably, means significantly enhanced corrosion resistance than bare Mg alloy. The results give us more insight in the optimization of electrical parameters to improve the MAO coating performance. The MAO technology is attractive for application on magnesium and other light alloys for surface protection in automotive and space industries.

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**Keywords:** Micro arc oxidation; Magnesium alloys; Pulse frequency; Corrosion resistance; Potentiodynamic polarization

## 1. Introduction

Magnesium and its alloys with attractive properties of low density, high strength-to-weight ratio, high stiffness, good electrical conductivity and good thermal conductivity, are promising materials for applications in automotive, aerospace,

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and communications industries [1,2]. However, the wide application of magnesium alloy in industries has been restricted by the poor corrosion resistance. Coating techniques have often been applied to magnesium alloy surface to improve the corrosion resistance, including electro-deposition [3], vapour deposition [4], conversion coating [5], and anodizing [6]. All these technologies are less effectiveness and have limitations such as poor adhesion, low coating hardness or environmental toxicity. Micro arc oxidation (MAO), also called plasma electrolytic oxidation, is an environmental friendly process of plasma-assisted electrochemical conversion of the metal surface to form oxide coating layer on particularly light alloy, such as aluminium, magnesium and titanium [7]. The formed MAO coatings usually present high corrosion resistance, thermal stability, and strong adhesion to the substrate [8,9].

The coating performance formed by micro arc oxidation is mainly controlled by substrate material, the properties of the

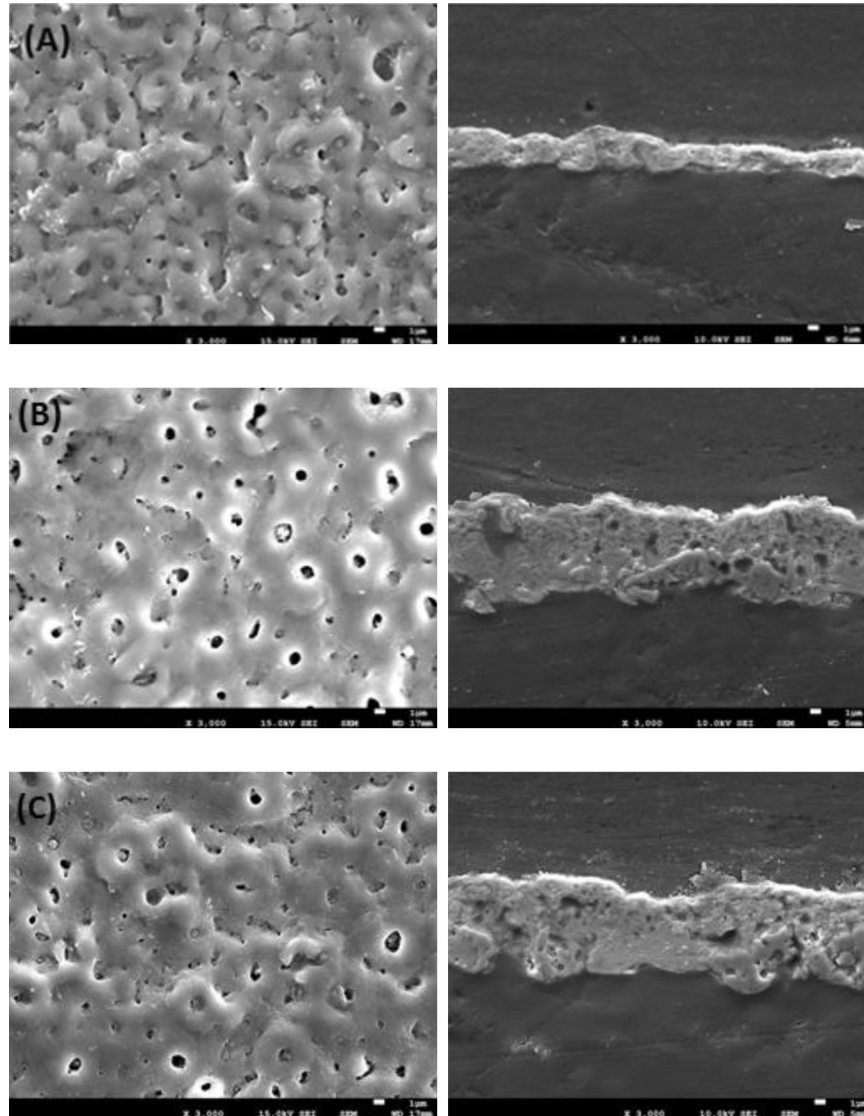


Fig. 1. FESEM of the surface morphology and cross-sectional morphology of MAO coatings at (A) 250 Hz, (B) 25 Hz and (C) 2.5 Hz pulse frequencies.

electrolyte (electrolyte composition and concentration), and the operation power parameters [9]. Many research works have been conducted to study the effect of electrical parameters on the coating performance, such as the effect of power mode [10], current density [11,12], and current frequency [13,14]. In the previous work of the authors [15] the effect of electrical parameters of applied voltage on the MAO coating performance was studied under single-polar pulse supply. Montazeri et al. [16] and Zhang et al. [17] has also studied the effect of applied voltage on the MAO coating performance for Ti alloys. Frequency is known to have strong effects on the MAO process under pulse power supply. In current study, the effect of pulse frequency on the MAO coating performance was studied at constant voltage. The surface morphology and the elemental composition of the coating were characterized using scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS), respectively. The method of potentiodynamic polarization and EIS were also adopted to study the coating corrosion resistance.

## 2. Material and methods

### 2.1. Preparation of micro arc oxidation coatings

Magnesium alloy test pieces (AZ31B) with dimension of (50 mm × 20 mm × 3 mm) were used as the substrate materials. The chemical composition of the AZ31 is Bal. Mg, 2.8% Al, 0.83% Zn, 0.59% Mn, 0.0023% Fe. The surface of the samples were polished with silicon carbide papers up to 1200 grits and then washed with acetone and DI water.

PC units used in this work mainly consist of electrolyte bath with stirring and cooling system and a power supply. Electrolyte solution was composed of 6 g/L KOH, 20 g/L Na<sub>2</sub>SiO<sub>3</sub>, 15 g/L triethanolamine. The temperature of the electrolyte was controlled at 15 °C. The Mg alloy sample immersed in the electrolyte was used as an anode, and the wall of the stainless steel bath was used as a cathode, by connected with the output of power supply. During the MAO treatment process, a fixed final voltage of 340 V was applied

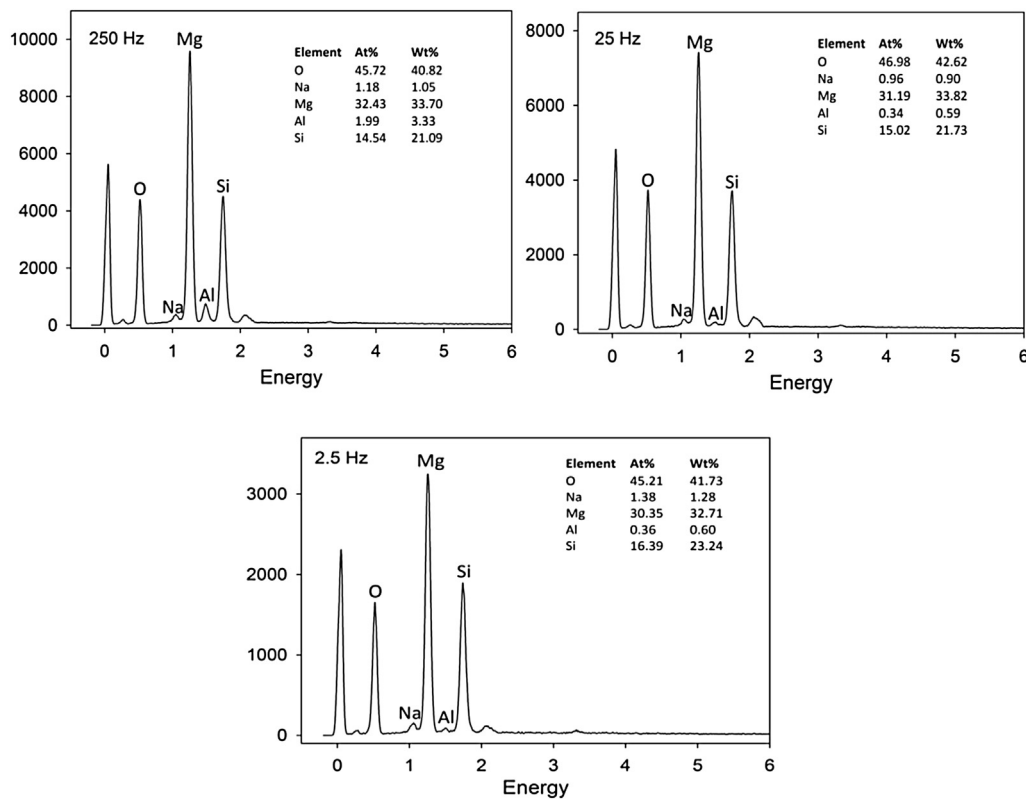


Fig. 2. Energy-dispersive X-ray spectroscopy (EDS) analysis of the MAO coatings at different frequencies.

with a fixed on-off pulse-time ratio of  $t_{\text{on}}/t_{\text{off}} = 3:1$  (i.e. 3 ms:1 ms, 30 ms:10 ms, 300 ms:100 ms). Each MAO process was conducted for 20 min in the electrolyte solution at temperature of 15 °C. Coated samples were rinsed with DI water and dried in air at room temperature.

## 2.2. Characterization

The surface morphology and cross-section of the PEO coatings were characterized by a scanning electron microscope (SEM, JEOL JSM-7001F Scanning Electron Microscope). The corrosion resistance of Mg alloy substrate and the coatings was evaluated using an AUTOLAB-POTENTIOSTAT electrochemical corrosion test system, in which a 3.5 wt. % NaCl solution was used as corrosion medium; and an area of 1 cm<sup>2</sup> of the sample was in contact with the corrosion solution. The reference electrode was a saturated Ag/AgCl electrode and the counter electrode was Pt. The scan was conducted with a constant rate of 1 mV/s. The electrochemical impedance spectroscopy (EIS) test was conducted from 10<sup>5</sup> to 0.1 Hz at amplitude of 5 mV using 3.5 wt. % NaCl solution.

## 3. Results and discussion

### 3.1. Surface morphology of MAO coatings

Fig. 1 presents the surface morphology of the MAO coatings as observed using FESEM. The coating surface is

typical micro-porous structure. As observed from the FESEM morphology of the MAO coatings obtained at different pulse frequencies, the pore size is smaller and the surface is more compact at frequency of 250 Hz as compared with coating at other frequencies. The smaller micropore size and the compact coating surface may facilitate the corrosion resistance of the MAO coatings. The differences in the micro-pore sizes in the three coatings can be attributed to the differences in the intensity of energy at these processing conditions. Even though the pulse ratio was the same in all the three cases, the discrete pulse-on-time was only 3 ms at 250 Hz frequency, which are one or two orders of magnitude lower than other frequency cases of 25 Hz and 2.5 Hz. This means the energy per pulse at 250 Hz case is much lower than that of 25 Hz and 2.5 Hz cases, which leads to the smaller pore size at 250 Hz.

The cross-sectional morphology of the MAO coatings at three pulse frequencies was also shown in Fig. 1. All the coatings contained a number of discharge pores filled with coating compounds. The coating thickness was found to be high at low frequency of 2.5 Hz. It is evident that the high energy per pulse facilitates growth rate of the coating to form higher thickness of the coating. Similar finding has also been found in other researches. Lv et al. has reported that the MAO coating growth rate was significantly dropped when the operating frequencies was increased from 100 Hz to 800 Hz for a magnesium alloy. And the coating produced by them presents a fine pore size at higher frequencies, which is consistent with the observations of this study.

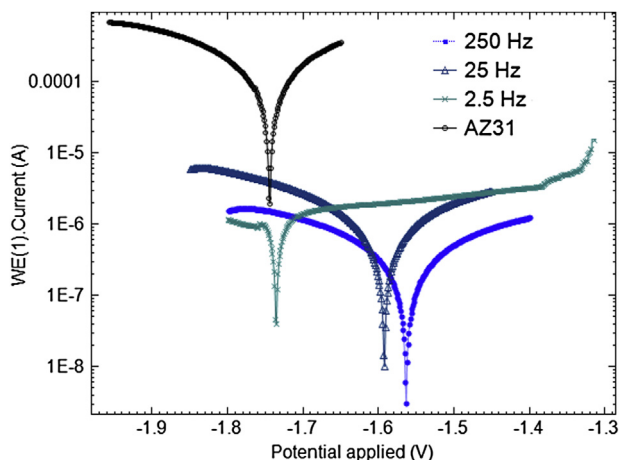


Fig. 3. Polarization testing results for MAO coating at pulse frequencies of 2.5 Hz, 25 Hz and 250 Hz.

### 3.2. Coating composition

In order to determine the silicate content in the coatings, EDS analysis was performed using energy-dispersive X-ray spectroscopy (EDS) on the surface of all the coatings and the results are presented in Fig. 2. It was found that the silicate content was decreasing with increasing the pulse frequency. The MAO coatings have a silicate content of 21.09, 21.73 and 23.34% in the 250 Hz, 25 Hz and 2.5 Hz conditions, respectively. The concentration of sodium was also found roughly in the decreasing order in the coatings as a function of increasing frequency. This confirms the effective participation of  $\text{Na}^+$  and  $\text{SiO}_4^{2-}$  ions in the MAO process at the lower frequency conditions, which again is attributed to the relative longer pulse-on-time, providing a higher energy per pulse in the 2.5 Hz condition.

### 3.3. Corrosion resistance property

The corrosion resistance properties of the MAO coatings prepared at three different pulse frequencies were measured by potentiodynamic polarization test in a 3.5 wt.% NaCl solution, as shown in Fig. 3. The parameters related to the corrosion resistance property such as corrosion potential ( $E_{\text{corr}}$ ) and corrosion current density ( $I_{\text{corr}}$ ) were measured from the potentiodynamic polarization curves using the Tafel fitting method. The polarization tests were listed in Table 1. The high corrosion potential and/or low corrosion current indicates good corrosion resistance. It was shown in Table 1 that with the pulse frequency increase from 2.5 Hz to 250 Hz, the corrosion current density decreased by one order of

Table 1  
Results of potentiodynamic polarization tests for MAO coatings at pulse frequencies of 2.5 Hz, 25 Hz and 250 Hz.

	$E_{\text{corr}}$ calc (V)	$E_{\text{corr}}$ obs (V)	$j_{\text{corr}}$ ( $\text{A}/\text{cm}^2$ )	$I_{\text{corr}}$ (A)	Corrosion rate (mm/year)
AZ31	-1.76	-1.76	3.6E-04	3.6E-04	8.0309
250 Hz	-1.56	-1.56	4.8E-07	4.8E-07	0.0106
25 Hz	-1.63	-1.63	1.6E-06	1.6E-06	0.0374
2.5 Hz	-1.71	-1.71	4.3E-06	4.3E-06	0.0956

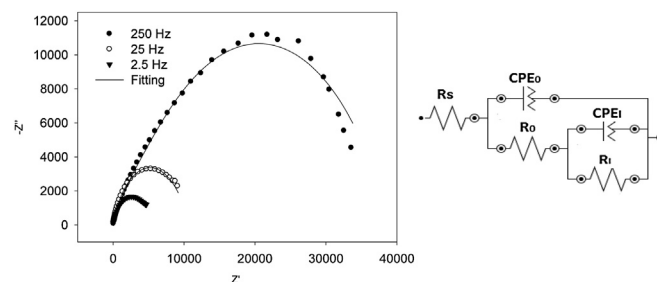


Fig. 4. EIS plot for MAO coatings at pulse frequencies of 250 Hz, 25 Hz and 2.5 Hz.

magnitude, from  $4.8\text{E}-07 \text{ A}/\text{cm}^2$  to  $4.31\text{E}-06 \text{ A}/\text{cm}^2$ . The corrosion potential is higher in the higher pulse frequency of 250 Hz case. The corrosion resistance parameters indicating that the corrosion resistance of MAO coatings decreased when the pulse frequency increased. Therefore, under constant voltage mode and pulse power mode, the higher pulse frequency e.g. at 250 Hz is beneficial for the coating anti-corrosion performance, when compared with the lower pulse frequencies case.

The electrochemical impedance tests were carried out in order to investigate the electrochemical response of the MAO coatings at the four different pulse frequencies and the results of Nyquist plots are displayed in Fig. 4. The impedance value increased as the pulse frequency value increased from 2.5 Hz to 250 Hz. The impedance of the MAO coating at 250 Hz presents the highest impedance value, which is in consistent with the potentiodynamic polarization results.

In order to quantitatively analyse the impedance value, an electrical equivalent circuit model is proposed as shown in Fig. 4. The EIS data for coated layers are fitted with the model, and the corresponding fitting results are represented as a solid line in Fig. 4. The equivalent circuit model consists of solution resistance ( $R_S$ ), resistance associated with outer layer ( $R_O$ ), which is in parallel with the constant phase element ( $\text{CPE}_O$ ); and resistance associated with the inner layer ( $R_I$ ) of the coating layer, which is in parallel with  $\text{CPE}_I$ . All fitting data derived from the model are summarized in Table 2. It was shown that there is a good correlation between the experimental data in Fig. 4 and the data calculated from the model in Table 2. As shown in Table 2, the impedance resistance of the inner layer ( $R_I$ ) was significantly higher than that of the outer layer ( $R_O$ ), indicating the corrosion resistance of the MAO coating layers are more dependent on the inner layer. When pulse frequency increased from 250 Hz to 2.5 Hz, the inner impedance  $R_I$  decreased remarkably, indicating the higher energy per pulse at low frequency value may damage inner compact resistance layer, and cause the deterioration of the corrosion resistance of the MAO coating layer at lower pulse frequencies.

Table 2  
The values of electrical element of equivalent data.

Sample	$R_S$ ( $\Omega \text{ cm}^2$ )	$\text{CPE}_O$ -P	$R_O$ ( $\Omega \text{ cm}^2$ )	$\text{CPE}_I$ -P	$R_I$ ( $\Omega \text{ cm}^2$ )
250 Hz	15.0	0.68	10,800	0.676	27,900
25 Hz	25.0	1.1	248	0.679	10,400
2.5 Hz	18.0	1.1	175	0.684	5220

#### 4. Conclusions

The pulse frequency has significant impact on the coating performance at constant voltage and pulse power supply mode when the pulse frequencies decrease from 250 Hz to 2.5 Hz. At higher frequency of 250 Hz, the coating surface is more compact and the corrosion resistance is better with corrosion current one order of magnitude lower than coatings at other lower frequencies, and lower corrosion resistance impedance. At lower pulse frequency of 25 Hz and 2.5 Hz, the coating surface is distributed with larger micropores which are not beneficial for the corrosion resistance of the coating. The higher energy per pulse at lower pulse frequency such as 2.5 Hz caused micropores with larger size, thicker MAO coating and more effective participation of the electrolyte with the mg alloy, however the higher energy per pulse may also cause the damage of the internal layer of the MAO coatings and the deterioration of the corrosion resistance as observed by the polarization testing and the EIS testing results.

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