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Trans. Nonferrous Met. Soc. China 25(2015) 1500−1505
Transactions of Nonferrous Metals Society of China
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# Effect of current frequency on properties of coating formed by microarc oxidation on AZ91D magnesium alloy

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Received 6 June 2014; accepted 9 October 2014

**Abstract:** The microarc oxidation (MAO) coatings produced at different current frequencies on AZ91D magnesium alloys were studied systematically. The morphologies, thickness, corrosion performances, and tribological properties of the coatings were investigated by the scanning electron microscopy, the electrochemical measurement system, and MS−T3000 friction test rig, respectively. The results show that the structure of the coatings becomes denser, and thickness becomes thinner with the increase of the current frequency. It is also found that the corrosion resistance of the coatings produced at higher frequency is improved greatly and the difference of the corrosion current density becomes small with increasing current frequency, which is similar to that of the coating thickness. The tribological test shows that the friction coefficient decreases with increasing the current frequency and the wear resistance of the coatings is influenced by both the thickness and structures. All these results were explained by analyzing the growing process of the MAO coating.

**Key words:** AZ91D magnesium alloy; microarc oxidation; current frequency; morphology; corrosion resistance; wear resistance

## 1 Introduction

Magnesium and its alloys have high specific strength, good cast and welding ability, good electromagnetic shielding and damping characteristics, which make them more and more important in automobile, aerospace and communication industries [1,2]. However, magnesium alloys are soft, active and highly susceptible to get corrosive in their practical applications. Surface treatment is an efficient way to improve the properties of magnesium alloys so that to extend their applications [3−5]. Microarc oxidation (MAO) is a relatively new surface treatment method to form function ceramic coatings on magnesium alloys [6]. After MAO process, the hardness, wear resistance, corrosion resistance, mechanical strength and electrical insulation of magnesium alloys can be greatly enhanced [7,8]. The characteristics of MAO coatings depend on many factors, such as the nature of the substrate, the components of the electrolyte, the electrical parameters, and treatment time [9−13].

Micro-discharges can be found flashing on the surface of the sample during the MAO process, and the coatings look uniform with fine small and frequently moving micro-discharges while they look coarse with large yellow and long lived micro-discharges [14,15]. The growing process of the MAO coating can be divided into three steps [16]. Firstly, discharge channel is formed, and the anionic components of the electrolyte and the melted alloy enter the channel. Then, the plasma chemical reactions take place in the channel. In the end, the discharge channel is cooled by the electrolyte and the reaction products are deposited onto the walls of the channels. Actually, the growing process of MAO coatings is a discharging (melted)/cooling (deposited) process. However, the formation of the discharge channel and the transfer of the electrolytic anions are greatly dependent on the electric field. The discharging and cooling time are dependent on the time of power on and off. Therefore, the electrical parameters, such as the current frequency, play a key role in the growing process of MAO coatings. In this work, different current frequencies were used to produce MAO coatings on

**Foundation item:** Project (11005151) supported by the Young Scientists Fund of the National Natural Science Foundation of China; Project (YETP1297) supported by the Beijing Higher Education Young Elite Teacher Project, China; Project (BEIJ2014110003) supported by the Undergraduate Research and Innovative Undertaking Program of Beijing, China
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DOI: 10.1016/S1003-6326(15)63751-7

AZ91D magnesium alloy. The surface morphologies, composition, corrosion resistance, and the tribological properties of the coatings were studied systematically. The correlations between applied current frequency and material characteristics were analyzed, and the growing mechanisms of MAO coatings were discussed.

## 2 Experimental

Rectangular coupons (20 mm × 10 mm × 2 mm) of AZ91D magnesium alloy (8.5%−9.5% Al, 0.50%−0.90% Zn, 0.17%−0.27% Mn and Mg balance) were used as the working electrodes in the experiment. Prior to the MAO treatment, the specimens were successively ground with a series of SiC abrasive paper (up to 1000 grid), then degreased in acetone, ethanol and distilled water using an ultrasonic bath. The stainless steel bar of the stirring system was used as the counter electrode. The distance between the working electrode and the counting was about 10 cm. An aqueous solution was prepared with a composition of 10 g/L $Na_2SiO_3$+8 g/L NaF+1 g/L NaOH and the temperature of the solution was remained below 30 °C. The current density was controlled constant at 5 A/$dm^2$ during the entire treatment. Different current frequencies of 200, 400, 800, 1000 and 1500 Hz were used during the oxidized process and all the samples were oxidized for 10 min.

The surface morphologies of MAO coatings were examined by the scanning electron microscopy (SEM, HITACH S−4200 and S−4800). All the samples detected by SEM were sputtered with a thin gold layer in order to prevent surface charging effects. The corrosion performances were carried out using an M283 electrochemical measurement system in 3.5% NaCl (mass fraction) solution with the saturated calomel electrode (SCE) used as the reference electrode. The friction properties of the coatings sliding against $Si_3N_4$ ball in a ball-on-disc configuration were measured on an MS−T3000 test rig. The testing diameter was 3 mm. The unlubricated sliding was performed at a load of 2 N and a sliding speed of 0.1 m/s. The sliding tests of all samples were kept for 10 min.

## 3 Results and discussion

### 3.1 Morphologies and thickness of coatings

The surface morphologies of MAO coatings fabricated at different current frequencies were observed by SEM (Hitach S−4200) (see Fig. 1). In Fig. 1, typical porous structures induced by the intensive sparking during the MAO process are observed. The diameter of the pores in the coatings decreases and the number increases with the increase of the current frequency. In addition, there are a few pores of very large size on the surface of coatings produced at 100 and 200 Hz, which make the coatings coarse. Coatings produced at 400, 800, 1000 and 1500 Hz look more uniform.

Three main steps lead to forming the MAO coatings, which are the formation of discharging channels, melting and oxidation of metal alloy, and cooling and deposition of the oxidized material. These three steps repeated all through the MAO process, leading to the increase of the coating thickness. The current frequency is the pulse number per second. More pulse numbers result in more micro-discharges and more discharge channels are left. Therefore, the number of pores on the surface of MAO coatings increases with increasing current frequency, which can be found from Fig. 1. During the pulse of one cycle, when the voltage reaches the break-down value, the dielectric breakdown takes place and discharges come into being. The lifetime of a single spark is about 0.17 ms [17], and the power-on time of one cycle for current frequencies at 100, 200, 400, 800, 1000, and 1500 Hz, is 5, 2.5, 1.25, 0.625, 0.5 and 0.335 ms, respectively. Therefore, only one or two discharges take place for 1000 and 1500 Hz in one pulse cycle, while tens of discharges take place at 100 and 200 Hz. It is easy to understand that in one pulse cycle, the discharges are opt to take place at the same site. At 1000 and 1500 Hz, one or two continuous discharges take place at one site, and the melted metal is oxidized, then the products are deposited and solidified around the channel. Since the discharging always takes place at the relative thin part of the layer, during the next pulse cycle, the discharge may take place at different places. However, for 100 and 200 Hz, tens of continuous discharges take place at one site, so the discharging is stronger, the temperature and pressure in the discharge channels are higher, and more metal materials are melted and sputtered out. Therefore, it can be found that larger size pores and more coarse surfaces in the coatings are produced at 100 and 200 Hz.

The morphologies of the cross sections of the MAO coatings are detected by SEM (HITACH S−4800), which are presented in Fig. 2. It can be found that the coating fabricated at 100 Hz is not consecutive, and there are large cracks and holes across the coating. With increasing the current frequency, the coatings produced at 200, 400, and 800 Hz become more uniform, but there are still cracks across the coating. When the current frequency increases to 1000 and 1500 Hz, respectively, the coatings are quite uniform and dense. Even there are still cracks in the coatings, they do not cross through the coating.

From the cross-sectional morphologies, we can obtain the thickness of the coating, for which we choose three different positions and get the mean value. The thickness of the coating is shown in Fig. 3. It can be

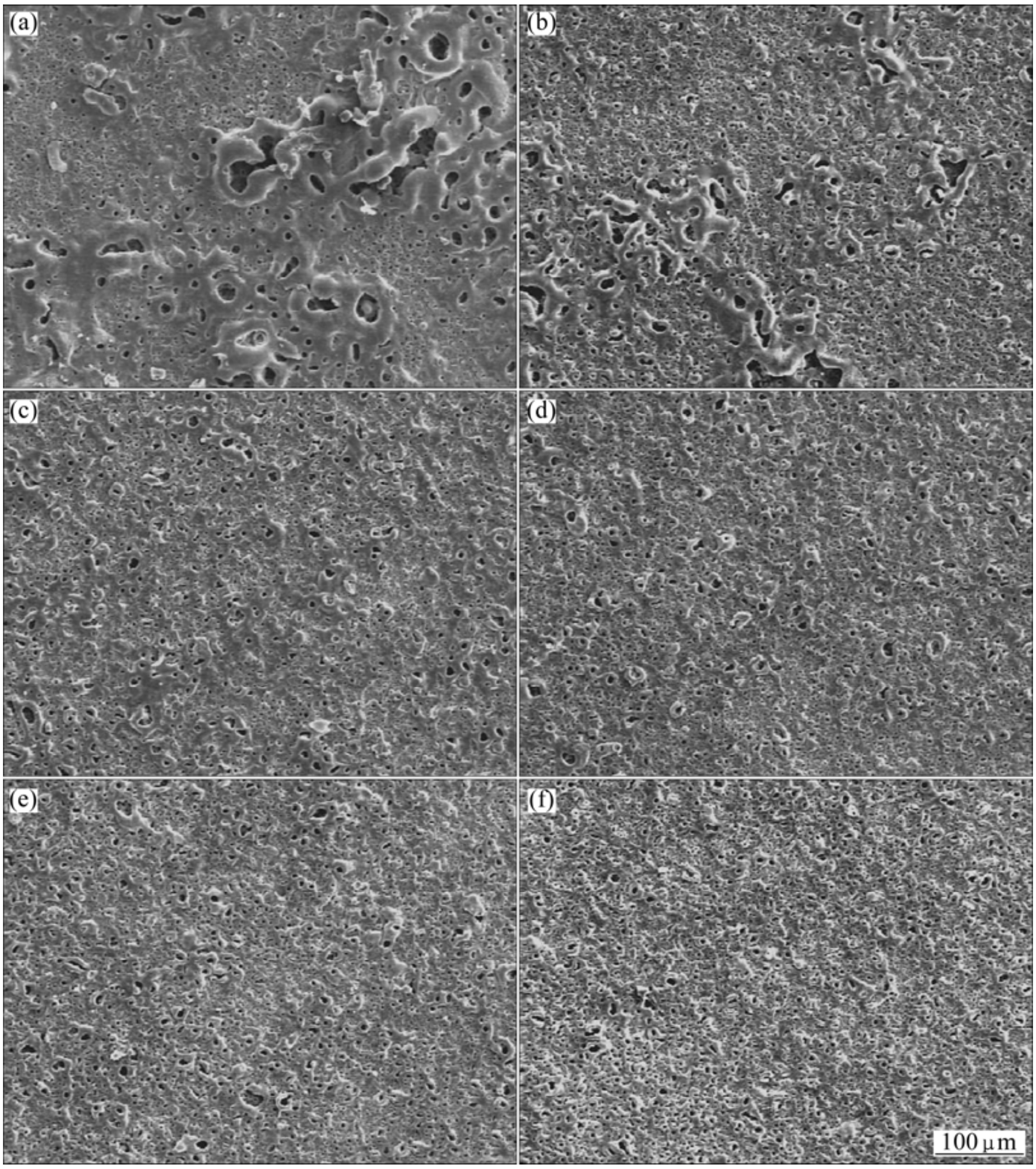


**Fig. 1** Surface morphologies of MAO coatings fabricated at different current frequencies with duty cycle of 50%: (a) 100 Hz; (b) 200 Hz; (c) 400 Hz; (d) 800 Hz; (e) 1000 Hz; (f) 1500 Hz

found that the coating thickness decreases with the increase of the applied current frequency. The thickness of the coating produced at 200 Hz is 28.20 μm, which is 16.75 μm thinner than that produced at 100 Hz, and the coating produced at 400 Hz is 7.9 μm thinner than that produced at 200 Hz. When the applied current frequencies are higher than 400 Hz, the difference between the coating thickness becomes smaller. The coating produced at 1500 Hz is only 1.50 μm thinner than that at 1000 Hz.

As discussed above, time becomes shorter in one cycle pulse with the increase of the current frequency. At higher frequency, less number of discharges take place at the same site and the discharging is weaker. Discharges always take place at the relatively thin place of the layer, which results in the uniform coatings. Besides, weak discharging contributes to lower temperature and lower pressure in the discharging channel, therefore not so much oxidized products are melted, sputtered and deposited. Therefore, the coating grows slowly under higher current frequency.

### 3.2 Corrosion resistance of coatings

The corrosion resistances of the coatings were evaluated through potentiodynamic polarization techniques in a 3.5% NaCl solution (mass fraction). Figure 4 shows the potentiodynamic polarization curves of the coatings produced at different current frequencies. The corrosion current density is an important parameter to evaluate the corrosion protective properties of the

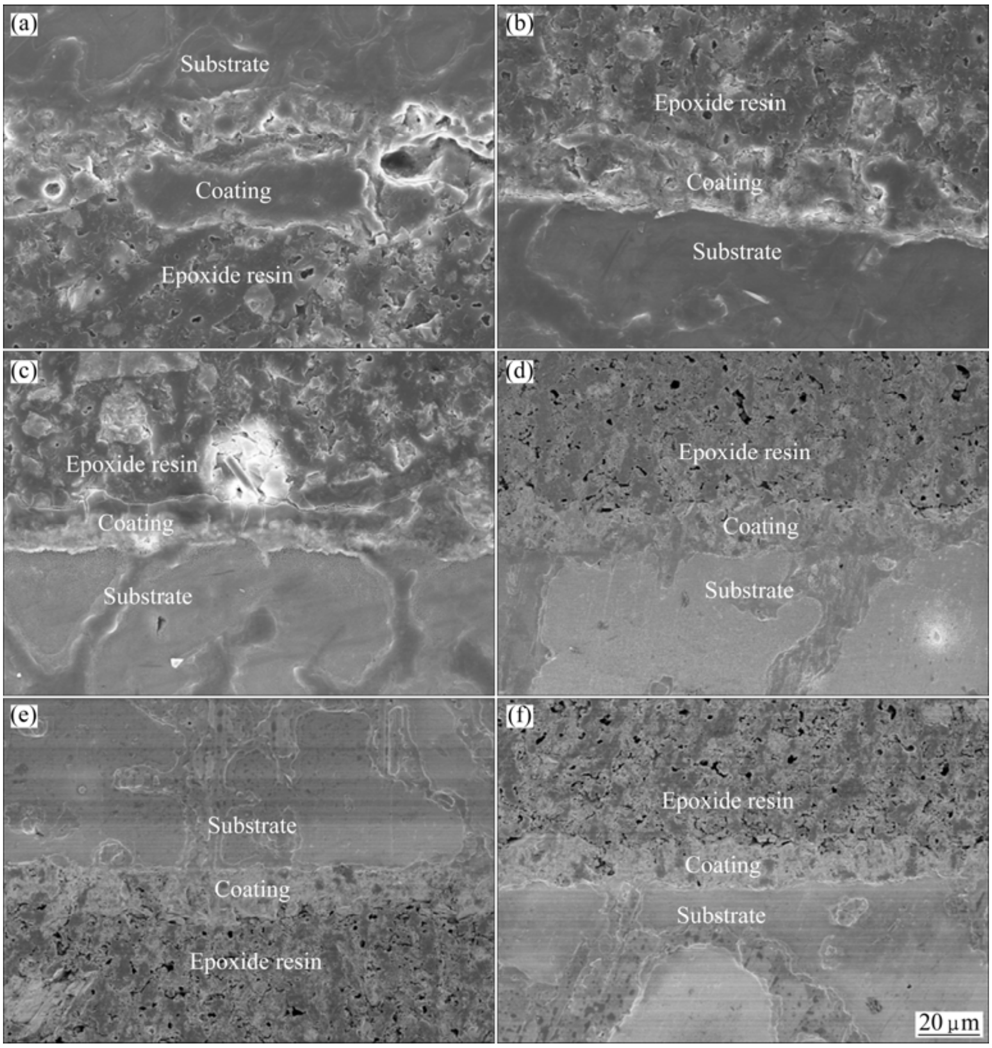


**Fig. 2** Cross-sectional morphologies of MAO coatings fabricated at different current frequencies with duty cycle of 50%: (a) 100 Hz; (b) 200 Hz; (c) 400 Hz; (d) 800 Hz; (e) 1000 Hz; (f) 1500 Hz

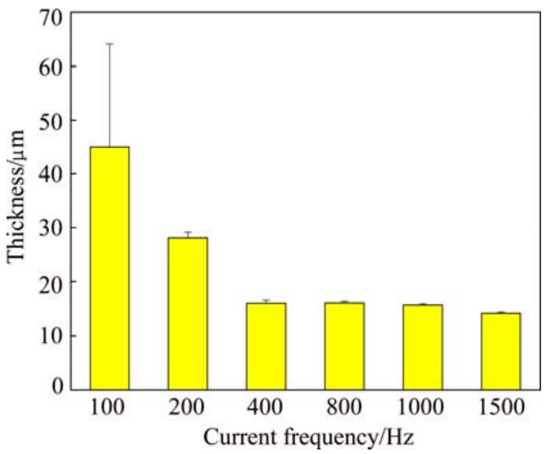


**Fig. 3** Thickness of coatings produced at different current frequencies

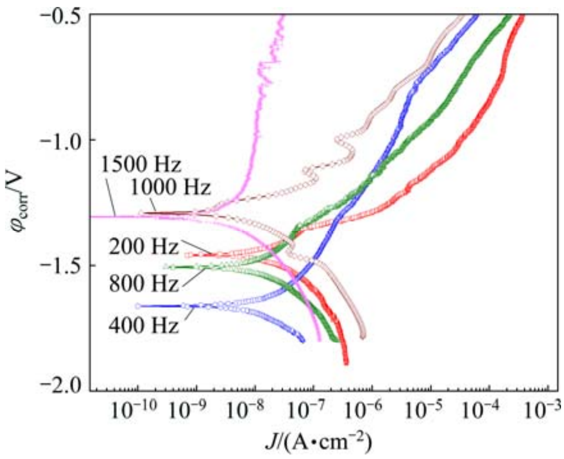


**Fig. 4** Potentiodynamic polarization curves of coatings produced at different current frequencies

coatings. It can be derived from the potentiodynamic polarization curves by the Corroview software and the results are shown in Fig. 5. The corrosion current density decreases with the increase of the current frequency of the power, which means that the anti-corrosion properties are better for coatings produced at higher frequencies than those at lower frequencies. In addition, the difference of the corrosion current density becomes little and little with the increase of the current frequency, which is similar to that of the coating thickness.

The corrosion current density is always influenced by the coating thickness and the coating denseness. According to our results, it is mainly dependent on the coating denseness. This is easy to understand. The coating produced at 200 Hz is much thicker than those at higher frequencies, but there are large size pores in the coating and perforative cracks across the whole coating thickness, through which the corrosion electrolyte is easier to pass through and get to the alloy substrate. Coatings produced at higher frequencies also have pores and cracks; however, their pore sizes are smaller and cracks do not go through the coating, which can effectively prevent the corrosion electrolyte from penetrating.

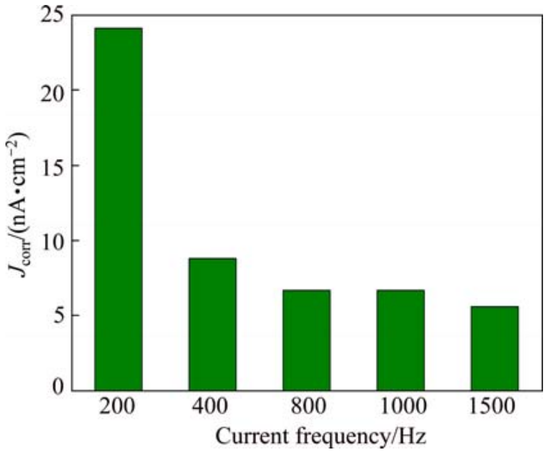


**Fig. 5** Corrosion current densities of coatings produced at different frequencies

### 3.3 Tribological properties of coatings

The friction coefficients of the coatings produced at different current frequencies against $Si_3N_4$ ceramic ball under dry friction condition were detected. Figure 6 shows the evolution of the friction coefficients versus sliding time. The coatings produced at 100 and 200 Hz have a similar friction coefficient of 0.6−0.7. The friction coefficients of the coatings produced at 400 and 800 Hz decrease sharply to 0.28−0.35, which is the same as that of the Mg substrate. This indicates that the coatings have been broken by sliding. The coatings produced at 1500 Hz have the friction coefficient of about 0.5, and they keep stable during the whole sliding time. As described above, the coatings produced at lower frequencies are coarser than those produced at higher frequencies, so the friction coefficients of the coatings are higher produced at 100 and 200 Hz. The coatings produced at 400 and 800 are smoother, but they are thin and have loose structure. So, they are easy to be broken when sliding with the $Si_3N_4$ ceramic ball. Although the coating produced at 1500 Hz has almost the same thickness with that of the coating produced at 400 and 800 Hz, its structure is much denser. Therefore, the coating produced at 1500 Hz exhibits stable low friction coefficient during the sliding time.

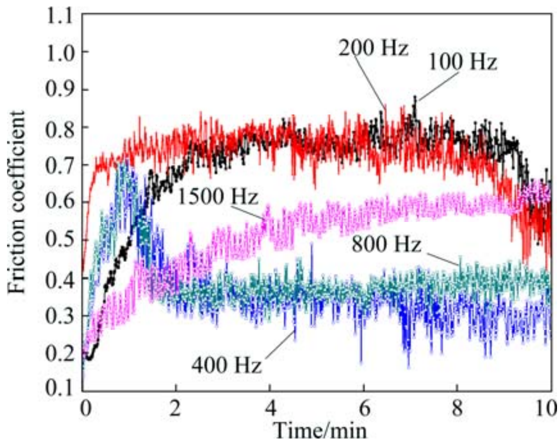


**Fig. 6** Friction coefficients of MAO coatings produced at different frequencies

## 4 Conclusions

1) The diameter of the pores in the coatings decreases and the number of the pores increases with the increase of the current frequency. At the same time, the structures become denser and thickness becomes thinner.

2) The corrosion current density decreases with the increase of the current frequency of the power, which means that the corrosion resistance is improved at higher current frequencies. In addition, the difference of the corrosion current density becomes little and little with the increase of the current frequency, which is similar to that of the coating thickness.

3) The friction coefficient decreases with increasing the current frequency. The fact that the wear resistance of coatings produced at 1500 Hz is better than those at 400 and 800 Hz can be explained by the denser structure of the coatings.

4) All the test results can be explained by analyzing the growing process of the MAO coating. At the higher frequencies, shorter time and less power are provided for discharging in one cycle, so, less number of discharges take place in the same site and the discharging is weaker. Therefore, the coating looks smooth and has less disfigurement.

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# 电源频率对微弧氧化 AZ91D 镁合金陶瓷层性能的影响

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**摘 要**：选取不同的电源频率，用微弧氧化方法在 AZ91D 镁合金表面制备一系列陶瓷层，并分别采用扫描电子显微镜、电化学工作站和 MS−T3000 摩擦磨损试验仪对陶瓷层的形貌、厚度、耐腐蚀性和耐磨性能进行系统研究。结果表明，随着电源频率的增大，生成的陶瓷层变致密，厚度变薄。随着电流频率的增加，陶瓷层的耐腐蚀性明显提高，与陶瓷层的厚度的影响相似，不同电流频率下得到的陶瓷层的腐蚀电流的差值均变小。陶瓷层的摩擦因数随着电流频率的增大而减小，其耐磨性能由膜层厚度及其结构致密性共同决定。通过微弧氧化陶瓷层的生长机理对得到的结果进行分析。

**关键词**：AZ91D 镁合金；微弧氧化；电源频率；形貌；耐腐蚀性；耐磨性

**(Edited by Wei-ping CHEN)**