

# Structure and mechanical properties of magnesium alloy treated by micro-arc discharge oxidation using direct current and high-frequency bipolar pulsing modes

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## Abstract

AZ91D magnesium alloy samples were treated by micro-arc discharge oxidation (MDO) using two different voltage modes: direct current (dc) and high-frequency bipolar pulsing (BP) to improve the surface properties. The structure, composition, and mechanical characteristics of the oxide films prepared using the same average current density were investigated by scanning electron microscopy (SEM), energy-dispersive X-ray spectrometry (EDS), X-ray diffraction (XRD), optical microscopy, profilometry, as well as microhardness and pin-on-disk tests. Both the dc and BP oxide films have mainly the MgO phases and improved microhardness and lower wear rates compared to the untreated Mg alloy. However, the oxidation rate, composition, and structure are different for the two voltage modes. For the same treatment time, the BP mode gives a higher oxidation rate. The BP film is denser and has higher micro-hardness, lower friction coefficient, and smaller weight loss against steel in the scratch test. Our results thus indicate that high-frequency, bipolar pulsing MDO yields a better coating on the Mg alloy.

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## 1. Introduction

Magnesium (Mg) and its alloys are one of the lightest metals used in the construction, automotive, aerospace, and communications industries. Owing to its low-density, high-specific strength, and good cast and welding ability, interests in Mg and Mg alloys are proliferating rapidly [1]. However, there are some inherent problems arising from their chemically active nature, such as poor corrosion resistance, friction, and wear characteristics [2]. In order to improve these properties, surface modification is a viable approach and techniques such as electrochemical plating, anodization, physical vapor deposition (PVD), and chemical vapor deposition (CVD) have been proposed [3–6].

Micro-arc discharge oxidation (MDO), also called plasma electrolytic oxidation (PEO), is derived from the conventional

anodic oxidation technology and has attracted increasing interests in the surface treatment of lightweight metals to enhance their wear and corrosion resistance [7]. For example, MDO has successfully been utilized to produce ceramic coatings on magnesium and its alloys to enhance corrosion protection [8–11]. However, some adverse results such as non-uniformity of the coating thickness and high-porosity have also been reported [12]. Therefore, in order to realize the full potential of MDO, more detailed studies are needed. In particular, the treatment parameters must be optimized in order to further enhance the corrosion resistance and wear resistance of Mg and Mg alloys. In MDO, direct current (dc) or alternating current (ac) is typically used [7,13]. Recently, the use of pulsed bipolar current has been proposed [14], but a systematic investigation of the efficacy of these different modes on the mechanical properties of Mg and its alloys has not been conducted. In this work, AZ91D magnesium alloy samples are treated by MDO using the direct current (dc) or bipolar pulsing (BP) mode. The structure, composition and mechanical characteristics of the two types of samples are compared.

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## 2. Experimental details

Rectangular coupons (20 mm × 10 mm × 3 mm) of AZ91D Mg alloy (Al 8.5–9.5 wt.%, Zn 0.5–0.9 wt.%, Mn 0.17–0.04 wt.%, Si ≤ 0.05 wt.%, Fe ≤ 0.04 wt.%, Cu ≤ 0.015 wt.%, Ni ≤ 0.001 wt.%) were mechanically polished with waterproof abrasive paper up to 800 grits prior to micro-arc discharge oxidation. The aqueous solution consists of 5 g/l sodium silicate and 2 g/l sodium hydroxide electrolytes, and a detailed description of the apparatus can be found elsewhere [15]. The output of the power supply was connected on one side to the bath and on the other side to the samples immersed in the electrolyte. Two different MDO modes, namely direct current (dc) and bipolar pulsing (BP), were used in our experiments. An average current density of 3 A/dm<sup>2</sup> was maintained on the surface by controlling the voltage amplitude in both cases. In the bipolar pulsing (BP) mode, the rectangular pulse with a frequency of 800 Hz has four stages: 250 μs for the positive pulse, 500 μs for the negative pulse, 400 μs between the positive pulse and the next negative pulse, and 100 μs between the negative pulse and the following positive pulse. Each oxidation process was conducted for 20 min at an electrolyte temperature of less than 40 °C. To maintain a stable average electric density, the voltage was varied between 120 and 198 V in the dc mode, and 180 and 470 V for the positive voltage in the BP mode, whereas the negative voltage was maintained at 50 V during the process.

The surface and cross-sectional morphologies of the oxide coatings were characterized by optical microscopy and scanning electron microscopy (SEM, JEOL JSM-820). X-ray diffraction (XRD, D/max 2550, Japan) was conducted using the Cu Kα line between 2θ values of 30° and 80° with a step of 0.05° to analyze the phase composition, with the acceleration voltage and current being 30 kV and 30 mA, respectively. Energy-dispersive spectrometry (EDS, JEOL JSM-820) was employed to determine the elemental composition. Surface roughness measurements were carried out using a Taylor-Hobson/Form Talysurf PGI surface texture tester along a set distance of 4 mm. The coating hardness was evaluated by means of Vickers indentation under a load of

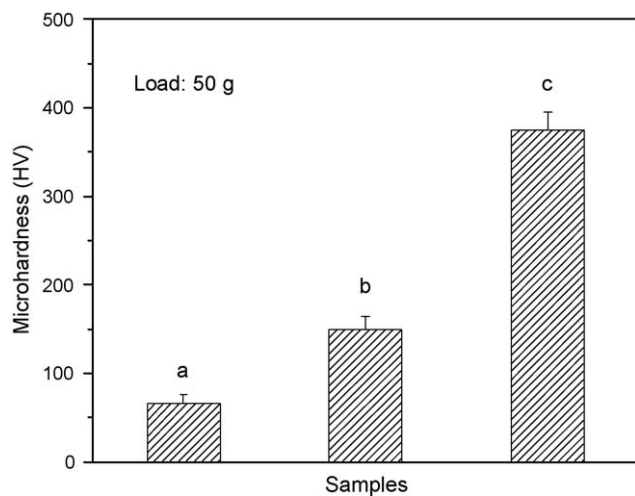


Fig. 1. Microhardness values measured using a load of 50 g from: (a) untreated Mg sample; (b) dc MDO sample; (c) BP MDO sample.

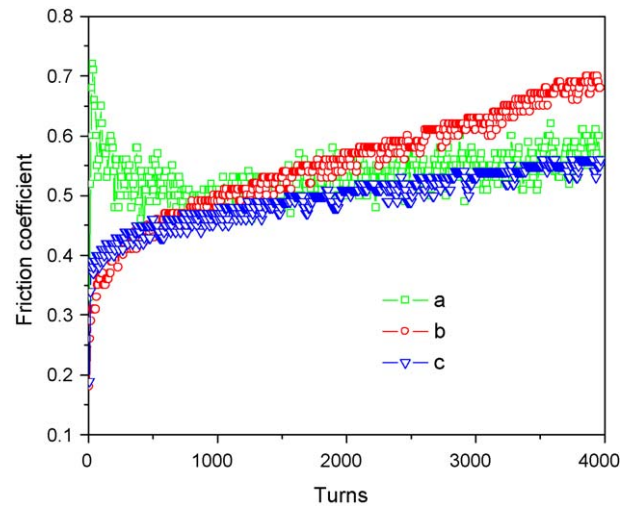


Fig. 2. Friction coefficients as a function of sliding turns measured from: (a) untreated Mg alloy; (b) dc MDO sample; (c) BP MDO sample.

50 g with a dwell time of 10 s. The friction coefficients were measured using a computer-controlled oscillating ball-on-disk scratch tester equipped with a 5 mm WC ball. The wear tests were conducted in air under a load of 4 N with a rotation diameter of 5 mm and sliding speed of 200 rpm.

## 3. Results and discussion

To evaluate the mechanical properties of the MDO samples, the micro-hardness values determined from the untreated and MDO samples are shown in Fig. 1. It is obvious that the untreated Mg alloy is relatively soft and MDO improves the surface hardness. For example, the best hardness value of 374.9 kg/mm<sup>2</sup> is achieved on the BP sample.

The results obtained from the pin-on-disk friction and wear tests are displayed in Fig. 2. The friction coefficient of the untreated Mg-AZ91D sample is initially high and diminishes from 0.73 to 0.5 after about 500 turns. This reduction can be attributed to the tribo-mechanism changes that improve the

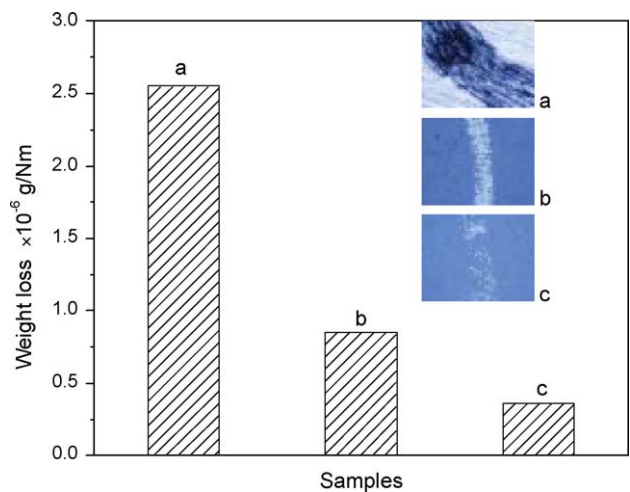


Fig. 3. Wear weight loss and wear tracks obtained from: (a) untreated Mg alloy; (b) dc MDO sample; (c) BP MDO sample.

lubricity of the surfaces. Oxidation of magnesium causes a hard thin oxide layer to be formed thereby transforming the friction/wear mechanism from ploughing into the soft bulk material into microfracture of the thin hard oxide films on the soft substrate [16]. The friction coefficients of both MDO samples show variations and a more detailed inspection reveals that the friction coefficient of the BP sample is 0.35–0.5 compared to 0.3–0.7 determined from the dc sample. In both cases, the friction coefficients are higher than or similar to that observed for the steady-state wear of the untreated substrate. Both MDO films have excellent dry wear resistance as characterized by the weight loss and the wear tracks observed by optical microscopy (50×)

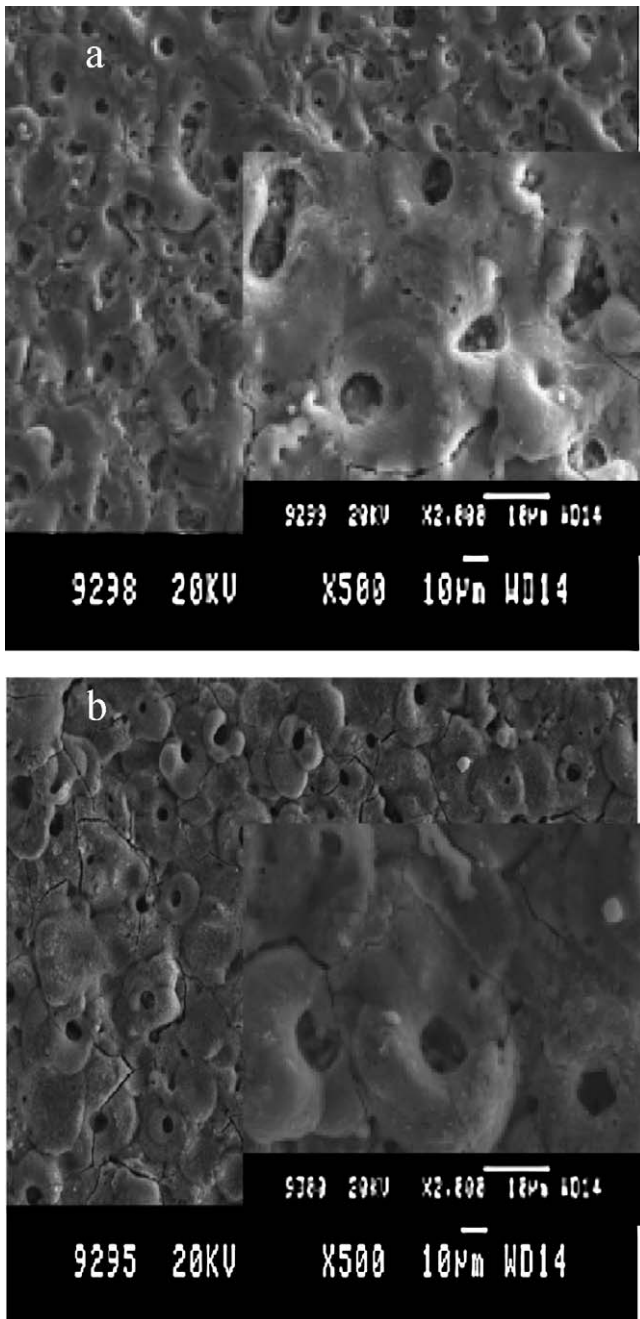


Fig. 4. SEM images showing the surface morphology of: (a) dc MDO sample and (b) BP MDO sample.

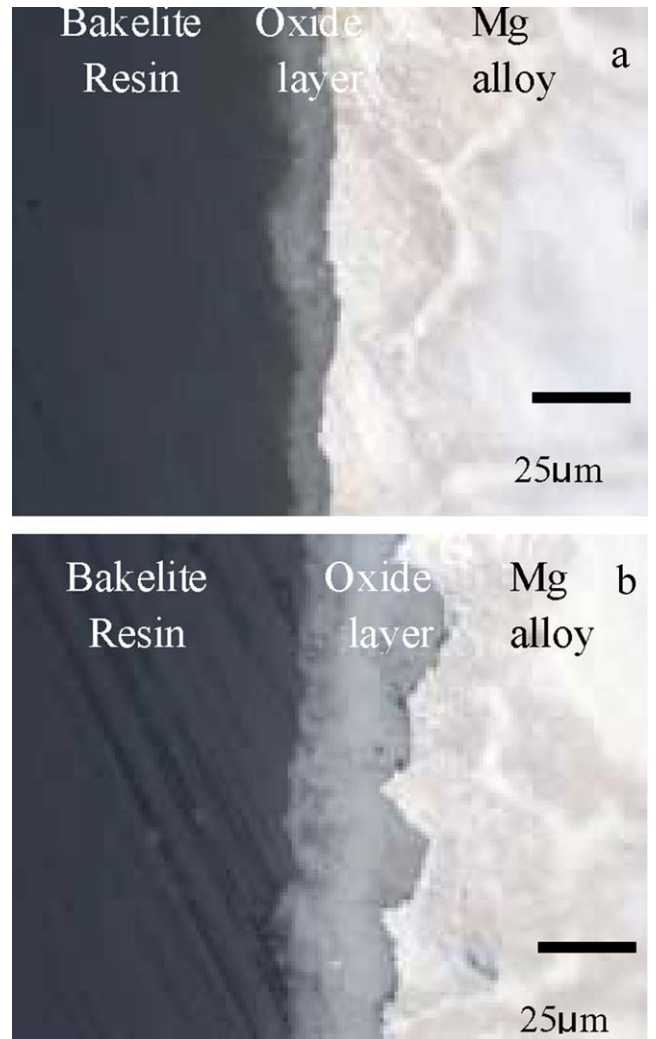


Fig. 5. Cross-sectional images obtained optical microscopy from: (a) dc MDO sample and (b) BP MDO sample.

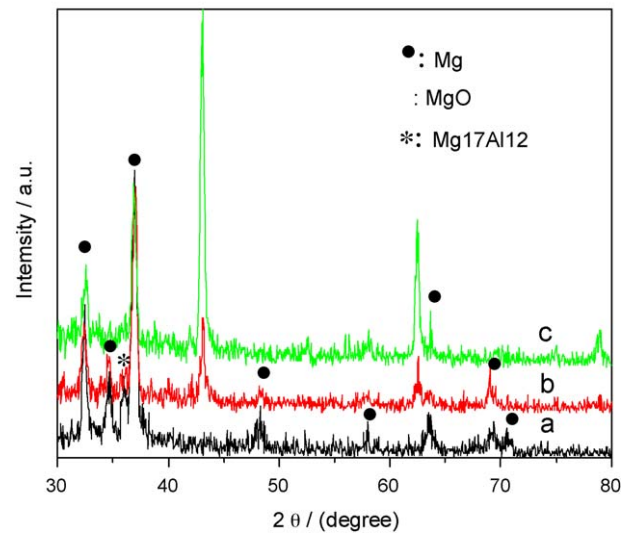


Fig. 6. XRD patterns obtained from: (a) untreated Mg specimen; (b) dc MDO sample; (c) BP MDO sample.

shown in Fig. 3. The results indicate that the BP sample has the best performance as illustrated by the narrower and more compact wear cracks.

Fig. 4 illustrates the surface morphology of the films formed on the magnesium alloys by micro-arc discharge oxidation using the same average current density but different voltage modes of dc and BP. It can be seen that both surfaces show the typical porous and coarse features, but a closer look reveals a small difference. Compared to the dc sample, the BP sample has relatively less pores in the same area and the surface layer is thus denser. For oxidation at the same current density, the BP mode provides a larger current pulse in the working range compared to the dc mode, thus enabling the creation of shorter but more energetic micro discharge events. Simultaneously, the lifetime of one micro-arc or spark is less than 1 ms, and so the micro-arc discharge is constant in the dc mode. Consequently, there is a better balance between oxidation and fusing/recrystallization during the film formation in the BP mode with a positive pulse width of 250  $\mu$ s. The oxidation or oxide formation rate can be determined by studying the cross-section of the samples. As shown in Fig. 5, the thickness of the BP oxide is about 30  $\mu$ m whereas that of the dc oxide layer is only about 15  $\mu$ m thick. The difference is about a factor of 2. Fig. 6 displays the XRD patterns acquired from the untreated Mg alloy and the two types of MDO samples. The results indicate that the main phase is MgO in all the treated samples. Based on the peak intensities, it can be inferred that the BP mode is the most efficient means to form the MgO phase.

There are four main factors that influence the micro-mechanical and tribological behavior. They are the hardness of the film and substrate, thickness of the film, roughness of the surface, and size and hardness of any debris in the contact area [17]. Compared to the dc sample, the BP sample has a thicker, denser, and harder oxide layer, which is primarily responsible for the more stable and smaller friction coefficients.

#### 4. Conclusion

In this work, the treatment efficacy of two MDO techniques, direct current (dc) and bipolar pulsing (BP), on AZ91D magnesium alloys are studied and compared. Both films are composed

mainly of the MgO phase that yields improved micro-hardness and lower wear rates compared to the untreated Mg alloy. The enhancement effects are more substantial using the BP mode. In addition to a larger oxidation rate, the BP sample is denser and has higher micro-hardness and lower friction coefficients compared to the dc sample. The significantly better properties of the BP sample can be attributed to the higher frequency current pulses, which enable the creation of shorter and more energetic micro discharge events. Our results indicate that high-frequency, bipolar (positive and negative) pulsing MDO is the technique of choice for the enhancement of surface properties of Mg alloys.

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