



# Corrosion behavior of porous ZrO<sub>2</sub> ceramic coating on AZ31B magnesium alloy



Yue'e Gao, Lianfu Zhao, Xiaohong Yao\*, Ruiqiang Hang, Xiangyu Zhang, Bin Tang

Research Institute of Surface Engineering, Taiyuan University of Technology, Taiyuan 030024, China

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## ABSTRACT

Magnesium alloys have been recognized as promising implant materials because of their biodegradability. However, rapid degradation due to electrochemical corrosion compromises their cytocompatibility and mechanical integrity. In the present work, a porous ZrO<sub>2</sub> ceramic coating was constructed on the surface of AZ31B magnesium alloy (ZrO<sub>2</sub>-AZ31B) to improve its corrosion resistance. The corrosion resistance of the coating was evaluated in simulated body fluid solution by electrochemical techniques. Higher open circuit potential, impedance and polarization resistance of ZrO<sub>2</sub>-AZ31B indicate it has a better corrosion resistance than that of AZ31B substrate in simulated body fluid solution. The results suggest that fabricating a ZrO<sub>2</sub> ceramic coating on magnesium alloys is an effective method to decrease the degradation rate of magnesium alloys thereby better matching clinical requirements.

## 1. Introduction

Over the past 10 years, magnesium and its alloys have been considered as promising implant materials due to their favorable mechanical properties, biodegradability and good biocompatibility [1–6]. In detail, the Young's modulus of magnesium alloys is very close to that of natural bone, and similar Young's modulus can reduce the stress shielding effect in orthopedic applications [1]. Magnesium-based implants can avoid the second surgery because of the biodegradability in the physiological environment. Furthermore, magnesium is the fourth element of the human body and is an essential element of the body's daily metabolism. However, their rapid degradation rate results in evolution of large amounts of hydrogen and alkaline environment around the implants, which may cause severe cytotoxicity and even implant failure [1]. More importantly, the rapid degradation does not match the surrounding tissue healing and growth, finally causing safety concerns such as secondary fracture for bone fixation implants. Therefore, it is necessary and significant to mitigate the degradation rate of magnesium-based materials in the physiological environment. Actually, many technologies have been reported to enhance the corrosion resistance of magnesium-based materials while maintain the good biocompatibility, such as alloying, composition purification, surface modification, etc. [1,7–10]. Among the various modified methods, surface modification is one of the most effective approaches to protect the magnesium-based materials from rapid degradation [11].

In the process of surface modification, adopting proper coating

material is critical. Zirconium (Zr) and zirconium oxide possess good corrosion resistance, cytocompatibility and antibacterial properties, thus have been regarded as promising coating materials to improve the corrosion resistance of magnesium alloys [12–19]. As reported, ZrO<sub>2</sub>-containing coating formed on magnesium alloy can enhance its corrosion resistance [20]. Zhao et al. [14] obtained a ZrO<sub>2</sub>-containing film on magnesium alloys by dual zirconium and oxygen ion implantation. The corrosion rate of substrates had reduced after the treatment, proved by electrochemical test and weight loss measurements. Einkhah et al. [15] fabricated an oxide layer with Zr compounds on AZ31B magnesium alloy via sequential two-step PEO, electrochemical test showed the corrosion resistance of AZ31B has been improved. Accordingly, it can be evidence-based speculated that producing a pure ZrO<sub>2</sub> coating on the surface of magnesium-based biomaterials is a more effective way to improve their corrosion resistance.

Although previous works showed the ZrO<sub>2</sub> coating on magnesium alloys can enhance their corrosion behavior as discussed above, few have reported the coating was prepared by combining magnetron sputtering with micro-arc oxidation methods. In this paper, a porous ZrO<sub>2</sub> coating was fabricated on AZ31B magnesium alloy by a two-step method. First, a flat Zr film was deposited on the substrate by magnetron sputtering, then the Zr film was transformed to ZrO<sub>2</sub> coating through micro-arc oxidation (MAO). Afterwards, the corrosion behavior of the coating was assessed by electrochemical test.

\* Corresponding author at: Taiyuan University of Technology, Research Institute of Surface Engineering, YingZe, West Street, Taiyuan, China.  
E-mail address: [xhyao@tyut.edu.cn](mailto:xhyao@tyut.edu.cn) (X. Yao).

## 2. Material and methods

### 2.1. Sample preparation

Commercial AZ31B magnesium alloy was cut into small sheets (10 mm × 10 mm × 5 mm) and used as substrates in this study. Prior to surface treatment, the samples were polished with SiC abrasive papers mechanically, and then cleaned by alcohol and deionized water, finally dried in air for used. The Zr film was deposited on AZ31B surface by magnetron sputtering, before the deposition, the substrates were pre-sputtered at a negative pulse bias of  $-600$  V for 30 min. Then the pure Zr film was deposited at a voltage of 300 V, current of 5 A, while the bias voltage of substrate is  $-60$  V, deposition time is 100 min. After deposition of Zr film, the ZrO<sub>2</sub> ceramic coating was fabricated by MAO with a stainless steel sheet as the cathode while the sample as the anode. The samples were oxidized in an aqueous electrolyte containing 10 g/L Na<sub>3</sub>PO<sub>4</sub>·12H<sub>2</sub>O, 10 g/L (NaPO<sub>3</sub>)<sub>6</sub> and 2 g/L NaOH for 6 min at a constant current density of 0.2 A/cm<sup>2</sup>. The duty cycle and frequency were 20% and 800 Hz, respectively. To obtain a constant electrolyte temperature during MAO, the electrolyte bath was cooled by recycled water during the whole process.

### 2.2. Sample characterization

The cross-sectional and surface morphologies of deposited Zr film and ZrO<sub>2</sub> ceramic coating were observed by scanning electron microscopy (SEM, JSM-7001F, JEOL), and the element compositions were examined by energy-dispersive X-ray spectroscopy (EDS, Bruker) attached to the SEM mentioned above. The phase compositions of the specimens were analyzed by an X-ray diffractometer (XRD; DX-2700, Haoyuan) with Cu K $\alpha$  radiation between 2 $\theta$  values of 25° and 75°. The bonding strength between the coating and substrate was evaluated by an automatic scratch tester (HT-3002, China) with a diamond indenter (200  $\mu$ m radius). Loading force from 5 N to 20 N with a loading rate of 15 N/min, scratch speed was 2 mm/min. The acoustic emission signals of the surfaces were recorded during the test, and observed morphologies of scratching tracks by SEM.

### 2.3. Electrochemical test

To evaluate the corrosion behavior of the different samples, electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization tests were carried out on an electrochemical workstation (CS350, China) in simulated body fluid (SBF) with a pH of 7.40 at 37 °C. The SBF was prepared according to the literature [21]. The standard three-electrode system was used for electrochemical experiments, with platinum electrode as the auxiliary electrode, saturated calomel electrode (SCE) as the reference electrode (which had been calibrated by a standard hydrogen electrode before every test), and the sample as the working electrode. Before EIS and potentiodynamic polarization tests, open circuit potential ( $E_{\text{OCP}}$ ) were monitored in SBF for 30 min to acquire a stable value. EIS tests were carried out over a frequency range of 10<sup>4</sup> Hz to 10<sup>-2</sup> Hz with AC signal amplitude of 10 mV. Potentiodynamic polarization curves were measured from  $-0.5$  V to 1.0 V (vs.  $E_{\text{OCP}}$ ) at a scanning rate of 1 mV/s after the EIS test. The surface morphologies of the samples after electrochemical test were observed by SEM. The samples were isolated with epoxy resin to avoid the exposure of substrates while taking the electrochemical test. In order to guarantee the reliability and reproducibility, the corrosion tests of each sample were repeated at least three times.

## 3. Results and discussions

### 3.1. Zr film deposited by magnetron sputtering

Fig. 1(a) shows the cross-sectional morphology of Zr film deposited

by magnetron sputtering. It can be seen that Zr film deposited on the AZ31B matrix flatly and uniformly, and the thickness of the film is about 3.8  $\mu$ m. Fig. 1(b) shows the curve of elements distribution, which is obtained by EDS line-scanning along the direction of the arrow in Fig. 1(a). It can be seen at the interface between the Zr layer and the substrate, the content of Zr decreases gradually while the Mg content increases, and the thickness of the film coincides with the result in Fig. 1(a).

### 3.2. ZrO<sub>2</sub> coating by MAO

Fig. 2 shows the cross-sectional morphology and the surface microstructure of the ZrO<sub>2</sub> coating. As can be seen in Fig. 2(a), the thickness of the coating is about 20  $\mu$ m. The coating surface exhibits a typical porous structure with pore diameters ranging from 2 to 8  $\mu$ m. Some micro-cracks on the coating surface are also observed. As reported [20,22–24], these pores are generated by the molten oxide and gas bubbles released from the micro-arc discharge channels during MAO process, while the micro-cracks are originated from great thermal stress resulting from the rapid solidification of molten oxide in the electrolyte.

Fig. 3 shows the voltage-time response curve measured during the MAO process. It can be seen that the voltage rises rapidly at the initial stage, and there are many bubbles generate around the surface of the specimens as the voltage increasing. Then small and dense spark points appear on the specimen surface after the voltage reaches the breakdown value. With the appearance of spark, the ZrO<sub>2</sub> coating begins to produce on the surface of the samples. About 1 min later, the voltage rising rate decreases and gradually tends to 0.1 V/s, finally the voltage reaches at 532 V. Fig. 4 shows the XRD patterns of different samples. For the AZ31B substrate, there is mainly Mg phase in its XRD pattern. For the Zr-deposited sample, the main phase is hexagonal Zr, and also some weak diffraction peaks of Mg. As can be seen from the XRD patterns of AZ31B and Zr-AZ31B samples, the diffraction peaks of Zr and Mg are so close, indicating they have a similar crystal structure. Tetragonal ZrO<sub>2</sub> (t-ZrO<sub>2</sub>) phase has appeared after MAO, and also some diffraction peaks of Zr, MgO and Mg are detected. This suggests that X-ray can penetrate through the ZrO<sub>2</sub> ceramic coating [25].

### 3.3. Scratch test

Fig. 5 shows the results of scratch test. Fig. 5(a) and (c) are the acoustic emission signal intensity during the scratch tests of deposited Zr film and ZrO<sub>2</sub> ceramic coating respectively. When the coating is broken, the intensity of the acoustic emission signal increases suddenly, so can analyze the damage of the coating according to the critical load value. As can be seen, the critical loads of Zr film and ZrO<sub>2</sub> ceramic coating are 9.36 N and 18.83 N respectively, indicating better bonding strength between the ZrO<sub>2</sub> ceramic coating and substrate.

Fig. 5(b) and (d) is the morphologies of scratch tracks of deposited Zr film and ZrO<sub>2</sub> ceramic coating respectively. It can be seen that the Zr film begins to peel off at the position pointed by the arrow in Fig. 5(b), and can be clearly observed the film have dropped off at the end of scratch track. For the ZrO<sub>2</sub> ceramic coating, there is no obvious fall of the coating, only slight damage of the coating at the position pointed by the arrow at the end of scratch track in Fig. 5(d). Therefore, it can be shown that the bonding strength of the coating after micro-arc oxidation has been improved effectively.

### 3.4. Electrochemical test

#### 3.4.1. Open circuit potential (OCP)

Fig. 6 shows the  $E_{\text{OCP}}$ -time (vs. SCE) response curves of different samples, which are monitored for 30 min in SBF solution. For bare AZ31B, the  $E_{\text{OCP}}$  increases rapidly at the beginning, finally reaches a stable value of  $-1.75$  V. The curves of Zr-AZ31B and ZrO<sub>2</sub>-AZ31B are

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