



Probing local corrosion performance of sol-gel/MAO composite coating on Mg alloy



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ABSTRACT

In this study, sol-gel technique was used to prepare $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ (HA) coating on Micro arc oxidation (MAO) coated degradable Mg matrix composites to reduce their primary degradation and enhance biocompatibility in simulated body fluid (SBF). The microstructure and phase composition were analyzed using Scanning electron microscopy (SEM) and X-ray diffraction (XRD). Potentiodynamic polarization (PDP) and electrochemical impedance spectroscopy (EIS) were used to examine their global corrosion behavior. Scanning vibrating electrode technique (SVET) and local electrochemical impedance spectroscopy (LEIS) were used to evaluate the potential distribution and impedance differences among the different zones. The global measurements show that the sol-gel/MAO coating has much better corrosion resistance than MAO coating, since the sol-gel coating sealed the pores produced in the MAO process. The post-corrosion microstructures of sol-gel/MAO composite coating on magnesium alloy are in agreement with the results of local corrosion performances. The corrosion mechanism is explained by proposing an empirical model.

1. Introduction

Recently, there has been a proliferation in demand of temporary implants for bone fracture in the fields of orthopedics, dentistry and surgery. Magnesium (Mg) alloys are considered as potential new kind of degradable biomaterial in the field of hard-tissue engineering owing to their low-specific gravity, biocompatibility and mechanical characteristics such as high strength and elastic modulus [1–3] close to that of natural bone [4]. Bone scaffolds like plates, screws, and stents made of such biomaterial are expected to have a fast degradation rate after bone restoration to avoid future inflammations [1,2]. However, Mg, having a low electrode potential (−2.37 V), when coupled to other materials, is highly susceptible to galvanic corrosion [3–5] especially in moist conditions. There could also be pitting corrosion and other localized corrosion processes occurring on the surface of the metals, and sometimes it is more severe than global corrosion [17]. Micro-arc oxidation (MAO) is an effective method to protect them [6–8] from corrosion as MAO coating demonstrates excellent adhesion to metallic substrate [9–11]. However, the porous microstructure of the MAO coating [12] leads to percolation of the fluid into the substrate causing damage to the Mg substrate. Sol-gel technology is a commonly used technique to seal the

micropores in such functional coatings to ensure good corrosion resistance [13–16]. Global electrochemical tests measure the average corrosion signal of such materials [7] while in-situ experiments are sensitive to the local differences in electrochemical reactivity on the metal surface [17], and thus contributing to a better description of corrosion behavior. Among these analytical techniques, scanning vibrating electrode technique (SVET) [18,19] and local electrochemical impedance spectroscopy (LEIS) [20] have shown greater applicability for the investigation of localized [21,22], galvanic [23], and microbiological corrosion [24]. SVET employs a vibrating reference micro-electrode to detect the potential gradients produced in the proximity of a reacting surface [18,25] and corrosion current density of the material surface can be effectively measured in-situ. Local impedance can be monitored using LEIS technology, which can accurately measure the localized corrosion resistance of each specific part of metal corrosion [26]. Therefore, the difference in the corrosion degree between the scratch and the coating can be evaluated analytically [27,28], thus enabling understanding the mechanism of corrosion in coatings with defects.

It is noted that the local damage (e.g., scratch) of the surface coating on Mg alloy may have a big influence on its corrosion behavior in

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human body. Ma. et al. has studied the influence of the scratch on the local corrosion behavior of MAO coated Mg alloy [29]. However, so far, for sol-gel/MAO composite coating on Mg alloy, most studies are focused on investigating the global corrosion behavior [2,9,10,16,30], and the local corrosion behavior is rarely reported. Therefore, our work will fill this knowledge gap by studying the local corrosion behavior of the sol-gel/MAO composite coating with artificial scratch using SVET and LEIS, by which the distribution of corrosion current density and electrochemical impedance in different zones (scratch and coating) of the samples will be measured. Global electrochemical tests, including potentiodynamic polarization (PDP) and electrochemical impedance spectroscopy (EIS) are also used for the evaluation of general corrosion resistance of the samples. Finally, a phenomenological model is proposed to explain the localized corrosion mechanism of sol-gel/MAO coated AZ31 magnesium alloy.

2. Materials and experimental methods

2.1. Coating preparation

AZ31B magnesium alloy sheets with the size of $50 \times 50 \times 3 \text{ mm}^3$ were prepared. The chemical composition of AZ31B is given in Table 1. The sample surface was ground by sand papers, rinsed in deionized water, polished using Al_2O_3 particles for 10 min, cleaned in an ultrasonic cleaner in ethyl alcohol for another 10 min, and finally dried in the air.

MAO coatings were processed using the HNMAO-20 equipment (produced by Xi'an HaoNing electronic technology co, LTD). In the MAO coating process, AZ31 alloy sample and stainless steel container with electrolyte inside were used as anode and cathode, respectively. The electrolyte was prepared by adding 15 g NaAlO_2 , 2.0 g NaOH, 4 g EDTA-Ca and 1.5 g $(\text{NaPO}_3)_6$ into 1 L of distilled water, and kept at room temperature. Finally, the MAO coatings were deposited on AZ31 alloy under the applied voltage of 425 V for 3 min. HA sol-gel solution was prepared by mixing alcohol solution of $\text{Ca}(\text{NO}_3)_2$ and P_2O_5 . Firstly, 9.85 g $\text{Ca}(\text{NO}_3)_2$ and 1.78 g P_2O_5 were dissolved into 25 mL ethanol, respectively, then $\text{Ca}(\text{NO}_3)_2$ ethanol solution was added into P_2O_5 ethanol solution slowly, and the pH of solution was adjusted to about 7.2 with ammonia solution. Finally, the mixed solution was stirred at room temperature for 30 min and then was sealed and kept still for 24 h. The sol-gel coatings were prepared using dip-coating method. The MAO coated sample was immersed in the sol-gel solution vertically for 2 min and withdrawn with a speed of 1 cm/min. The operation was repeated three times in order to increase the thickness of the sol-gel coatings. The coating was dried at 80°C in a drying box (DH-201) for 30 min between the subsequent sol-gel layers. Finally, the coated samples were heated at 500°C for 3 h in a muffle furnace and the sol-gel layer was effectively deposited on the MAO coated samples.

2.2. Coating characterization

To examine the surface morphologies of the MAO and sol-gel/MAO coated samples, scanning electron microscope (SEM, QUANTA400F, FEI) was employed to observe the surface and cross-sectional morphologies of the coated samples before and after corrosion. X-ray diffraction (XRD, Smart Lab, Japan) with Cu-K radiation was used to analyze the phase components of the samples at a scanning speed of $5^\circ/\text{min}$ over a scan range of $20\text{--}80^\circ$ and a glancing angle (2θ) of 2° . Scratch tester (REVETEST Scratch Tester, CSM) was used to measure the

Table 1
Chemical composition of AZ31B magnesium alloy (wt%).

Al	Zn	Mn	Si	Cu	Ni	Fe	Mg
3.1	0.8	0.15	0.06	0.03	0.02	0.01	Bal.

adhesion strengths of the MAO and sol-gel/MAO coatings on the substrate.

2.3. Global electrochemical test

PDP and EIS were used to test the global electrochemical behavior using an electrochemical workstation (IM6, Germany). Measurements were carried out in a conventional three-electrode cell, where the sample acted as the working electrode ($10 \times 10 \text{ mm}^2$ exposed area), the saturated calomel was used as the reference electrode (SCE), and the platinum electrode was the counter electrode. The electrolyte was prepared by dissolving 7.996 g NaCl, 0.350 g NaHCO_3 , 0.224 g KCl, 0.228 g $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$, 40 ml HCl (1 mol/L), 0.305 g $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, 0.278 g CaCl_2 , 0.071 g Na_2SO_4 and 4.00–6.057 g $\text{NHC}(\text{CH}_2\text{OH})_3$ into 1 L of distilled water, and kept at the temperature of 37°C in the process. The pH value was adjusted to 7.25 using HCl (1 mol/L). In the PDP tests, the sweep rate was 10 mV/s in the range of -500 mV and $+1 \text{ V}$ (relative to open circuit potential), respectively. The EIS tests were conducted in the frequency range of 0.01 Hz–10 kHz with the voltage amplitude of 10 mV.

2.4. Local electrochemical test

SVET and LEIS measurements were performed using AMETEK equipment (VersaSCAN, USA). It can be considered as a semi-quantitative tool, where it allows the visualization of corrosion processes but the precise data for determining corrosion rates cannot be obtained [18]. The sample with the size of $10 \times 10 \text{ mm}^2$ was embedded in epoxy resin with a diameter of 30 mm. An artificial scratch with the size of $0.3 \times 2 \text{ mm}^2$ was made using the scalpel. The scan areas of SVET and LEIS tests were set as $(1\text{--}2) \times 3 \text{ mm}^2$ in which the artificial scratch was included. The step sizes of X and Y directions are $100 \mu\text{m}$. The electrolyte is the same as the corrosion media used in the global electrochemical test. The specific parameters of SVET experiment are as follows: the tip is an insulated Pt-Ir wire with a diameter of about $10 \mu\text{m}$. The probe was placed above the sample surface at a height of $80 \mu\text{m}$. The vibration amplitude of probe is about $30 \mu\text{m}$ and the frequency is 80 Hz. Three-electrode system for SVET and LEIS tests is shown in Fig. 1. The difference between the SVET and LEIS tests is the shape of the probe. LEIS probe consists of a platinum micro-disk and a platinum ring that has the same tip diameter and material with SVET. In addition, the vibration amplitude of probe is 10 Hz in the scanning process.

3. Results and discussions

3.1. Coating characterization

3.1.1. SEM morphology of the coatings

The surface and cross-section morphologies of the MAO and sol-gel/MAO coatings are shown in Fig. 2. Fig. 2(a₁) shows that a dense coating with micro-pores was produced using the MAO technology. Fig. 2(b₁) shows the microstructure of sol-gel/MAO coating with a smoother surface than that of the MAO coating, since the micro-pores were sealed by sol-gel coating [15]. However, the crack appeared on the surface. Cracking is common in sol-gel coating and could be attributed to a large number of causes which lead to building up of stresses [14,31]. The quality of the sol-gel coating can be affected by the sol-gel process, however, it is also dependent on other factors, such as the chemical composition, coating thickness and heat treatment process of the coating prepared, etc. The cross-section morphologies of the MAO and sol-gel/MAO coatings are shown in Fig. 2(a₂) and Fig. 2(b₂), respectively. It shows that the thickness of the MAO coating and sol-gel/MAO coating is about $3 \mu\text{m}$ and $8 \mu\text{m}$, respectively, and the compactness of the sol-gel/MAO coating is better than that of the MAO coating. The sol-gel coating acts as a barrier layer that effectively sealed micro-pores in MAO coating, therefore, the sol-gel/MAO coating is expected to exhibit

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