Surface & Coatings Technology xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

Hydrothermal biomimetic modification of microarc oxidized magnesium alloy for enhanced corrosion resistance and deposition behaviors in SBF

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ARTICLE INFO

Available online xxxx

Keywords:
Microarc oxidation
Hydrothermal
Coating
Biocorrosion
Bioactivity

ABSTRACT

Bioactive composite coatings with a microarc oxidation (MAO) bottom layer and a biomimetic top hydrothermal layer were developed on an AZ31B magnesium alloy by combined MAO and hydrothermal treatment. The composition and microstructure of the coatings were analyzed by X-ray diffraction (XRD) and scanning electron microscopy (SEM). Potentiodynamic polarization and soaking test in simulated body fluid (SBF) were used to evaluate the biodegradation and bioactivity of coated magnesium. The results show that the bioactive top hydrothermal layer containing $CaHPO_4$, HA and $Ca_3(PO_4)_2$ grows on a 10 μm thick MAO bottom layer. The corrosion current of samples with MAO-hydrothermal duplex layers is reduced to 4.780×10^{-6} A cm^{-2}, the corrosion potential is increased to −0.92 V. The sealing pore effect of the top hydrothermal layer enabled the MAO bottom layer to obtain a significantly improved corrosion resistance property. The MAO-hydrothermal sample had a weight increase of 14.52 mg cm^{-2} compared to 24.7 mg cm^{-2} weight loss for the MAO bottom layer after 28 days, due to the CaP compound deposition induced by the top hydrothermal surface.

1. Introduction

Magnesium and its alloys have attracted great attention as temporary bone implant materials [1–4] due to the mechanical properties close to natural bone [5–7], perfect biocompatibility [8–10] and gradual degradation in the human physiological environment [11–13]. However, the rapid corrosion, generation of a large volume of hydrogen gas, accumulation of the hydrogen bubbles in gas pockets adjacent to the implant, and increase in local pH of the body fluid, are the major impediments in using them as an implant material.

Strategies such as alloying [14–16], protective coatings [17–19] and surface treatments [20–22] have been developed to improve corrosion resistance, mechanical properties and bioactivity of magnesium alloys. Among the various processing methods, microarc oxidation (MAO) has received considerable attention. The MAO coating usually contains an inner dense part and an outer porous part, in which the inner dense part is commonly called as a barrier layer. The barrier layer would delay the rate of corrosion attack during the initial period of implantation, and the decrease in the extent of hydrogen evolution would enhance the primary neo-formation of bone around the implant.

Increasing the thickness of the inner dense layer is a useful strategy to increase the long-term corrosion resistance of MAO coated magnesium samples and it can be achieved by an appropriate choice of electrolytes and process parameters [23–25]. However, the more numbers of micropores and cracks tend to appear on the surface of MAO coatings with the increasing coating thickness, which can be considered as a severe limitation [26]. The presence of micropores and cracks on and through the MAO coatings increases the tendency of the corrosive medium to adsorb and concentrate into these defects. This would accelerate the infiltration of the corrosive medium through the coating and subsequently down to the substrate. To seal the defects of micropores and cracks by multi-functional approaches seems to be logical in terms of achieving an acceptable corrosion protection and biocompatibility [26]. Recently, the duplex coatings combining MAO bottom layer with a bioactive top layer, such as MAO/electrochemical deposited nanostructured akermanite ($Ca_2MgSi_2O_7$) [27], MAO/chemical deposited HA-DCPD [28], and MAO/sol–gel TiO_2 duplex coatings [29], have been developed. Exactly the bioactive top layer can both enhance the biocompatibility and improve the corrosion resistance by sealing the remained micropores present on the MAO coating surface.

In this work, we propose a simple strategy of combing MAO and hydrothermal treatment to design duplex layers with an anti-corrosion MAO bottom layer and a bioactive top hydrothermal layer on an AZ31B magnesium alloy. The bioactive top hydrothermal layer can seal the micropores and cracks of MAO bottom layer surface. More importantly, the bioactive calcium phosphate compounds can be synthesized during hydrothermal process to promote bone healing and regeneration. A mixing electrolyte of Na_2SiO_3–NaOH–Ca $(H_2PO_4)_2$ was designed to form a MAO bottom layer containing MgO, $Mg(OH)_2$, Mg_2SiO_4, and $CaSiO_3$. A solution of $Ca(NO_3)_2$–KH_2PO_4 was used to grow a bioactive top hydrothermal layer with CaP containing compounds. The composition and microstructure of the coatings were analyzed by X-ray diffraction (XRD) and scanning electron microscopy (SEM). Potentiodynamic

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http://dx.doi.org/10.1016/j.surfcoat.2015.02.010
0257-8972/

polarization and soaking tests in simulated body fluid (SBF) were used to evaluate the biodegradation and bioactivity of coated magnesium.

2. Experimental

2.1. Coating preparation

An AZ31B alloy was used as the primary substrate material, whose chemical composition (wt.%) is 2.5–3.0% Al, 0.70–1.3% Zn, 0.2% Mn and balance Mg. Samples of magnesium alloy for MAO treatment were machined into round plates with a diameter of 10 mm and thickness of 2 mm. The plates were degreased with acetone in ultrasonic bath, mechanically polished with 400, 800 and 1200 grit emery papers, rinsed with distilled water and dried in warm air. The mixing solution of 10 g L^{-1} NaOH, 15 g L^{-1} Na_2SiO_3 and 10 g L^{-1} $Ca(H_2PO_4)_2$ was used as the electrolyte for MAO treatment. The magnesium alloy samples and the stainless steel were used as the anode and cathode, respectively. Pulse frequency and duty cycle were fixed at 600 Hz and 8%. The temperature of the electrolyte was kept nearly at 30 °C using a stirring and cooling system. The MAO bottom ceramic layers were produced at a constant voltage of 450 V for 10 min. The coated samples were rinsed in water and dried in hot air for the subsequent preparation of a top hydrothermal layer.

The additives of $Ca(NO_3)_2 \cdot 4H_2O$ and $KH_2PO_4 \cdot 3H_2O$ were dissolved in a 20 mL distilled water in the desired proportions and the pH was controlled to 3 by dilute nitric acid. The ratio of Ca/P in the hydrothermal solution was 1.67 with P concentration of 0.1 mol L^{-1}. Subsequently, the magnesium alloy samples with MAO bottom ceramic layers were put into the autoclave (volume 40 ml), and heated to 150 °C for different time periods of 1, 3, 5, 10 and 15 h. Using the combined MAO and hydrothermal processes, the magnesium samples with MAO bottom layer and a biomimetic top hydrothermal layer were obtained.

2.2. Coating characterization

The phase composition of the MAO bottom layer and MAO-hydrothermal duplex layer was examined by Philips X'Pert X-ray diffraction (XRD) with a Cu-K_α source. Surface morphology of the produced layers was observed with a scanning electron microscope (SEM, S-3400N, Hitachi Co.), and an eddy current thickness gauge (Minitest 600B, Germany EPK.) was used to measure the thickness of the layers.

2.3. Corrosion and apatite-forming ability studies

Acellular simulated body fluid (SBF) was synthesized as a test medium to evaluate the bioactivity and bio-corrosion behavior of the coated AZ31B alloy samples. The detailed chemical composition of SBF was listed in Table 1, which was prepared by dissolving reagent-grade chemicals of NaCl, $NaHCO_3$, KCl, $K_2HPO_4 \cdot 3H_2O$, $MgCl_2 \cdot 6H_2O$, $CaCl_2$ and Na_2SO_4 into distilled water and buffering at pH 7.4 with trishydroxymethyl aminomethane ($(HOCH_2)_3CNH_2$) and 1.0 mol L^{-1} HCl at 37 °C [30]. For potentiodynamic measurements, a CHI604C electrochemistry workstation was used. All electrochemical measurements were conducted using a conventional three-electrode electrochemical cell with the samples as the working electrodes, a platinum plate as the auxiliary electrode and a saturated calomel electrode (SCE) as the reference. The exposed area of the sample surface limited by the inner wall of the cylinder was 1.0 cm^2. And the samples were allowed to stabilize at their open circuit potential for 30 min before the measurements were started. Potentiodynamic polarization was measured at 25 °C with a scan rate of 0.01 V s^{-1} from −2.0 V to 0 V respect to the corrosion potential value, E_{corr}. Potentiodynamic polarization curves were thus acquired and the corrosion potential (E_{corr}) and corrosion current density (i_{corr}) were determined using the Tafel extrapolation method.

The corrosion degradation and bio-activating behaviors of MAO layer and MAO-hydrothermal duplex layer samples were evaluated by total soaking in SBF solution at 37.4 °C. The sample without any surface treatment was used as reference. Each sample was soaked in SBF for 2, 7, 14, 28 and 56 days. The corrosion rate was evaluated by a weight loss method, the weight loss (Δ) is determined by the following equations:

$$\Delta = (m - m_0)/S_0 \quad (1)$$

$$S_0 = \pi D_0^2 \quad (2)$$

where m_0, S_0 and D_0 represents original mass, surface area and diameter of Mg alloy, MAO layer and MAO-hydrothermal duplex layer samples. m represents the mass after soaking for different time periods.

Meanwhile, the surface macromorphologies after soaking test were caught by the digital camera, which were used to indicate the corrosion damage degree. The biomimetic apatite-forming ability of coated samples during SBF soaking was evaluated by analyzing the surface morphologies by SEM and phase composition by XRD method.

Table 1
Chemical compositions of simulated body fluid (SBF).

Composition	Concentration
NaCl	8.035 g L^{-1}
$NaHCO_3$	0.355 g L^{-1}
KCl	0.225 g L^{-1}
$K_2HPO_4 \cdot 3H_2O$	0.231 g L^{-1}
$MgCl \cdot 6H_2O$	0.311 g L^{-1}
10 mol/L HCl	3.9 ml L^{-1}
$CaCl_2$	0.292 g L^{-1}
Na_2SO_4	0.072 g L^{-1}
Tris	6.118 g L^{-1}

3. Results and discussion

3.1. Surface characterization of MAO bottom layer

Fig. 1 shows the microstructure of MAO layer formed on AZ31B magnesium alloy. The MAO layer is mainly composed of MgO phase, and incorporated with a small amount of Mg_2SiO_4, $Mg(OH)_2$ and $CaSiO_3$ phases (Fig. 1a). The appearance of Mg_2SiO_4 and $CaSiO_3$ phases will be helpful to enhance the biocompatibility of the layer [31]. Due to the quick-cooling effect of the electrolyte during sparing discharge process, Ca and P can bond to oxygen and exist in MAO layer as amorphous components containing Ca^{2+}, HPO_4^{2-} and PO_4^{3-} ions [32]. The existence of the amorphous state [33] can promote the deposition of CaP compounds during the subsequent hydrothermal treatment. The MAO layer produced on the magnesium alloy by the following possible reactions:

$$Mg^{2+} + 2OH^- \rightarrow Mg(OH)_2$$

$$Mg(OH)_2 \rightarrow MgO + H_2O$$

$$2Mg^{2+} + SiO_3^{2-} + 2OH^- \rightarrow Mg_2SiO_4 + H_2O$$

$$Ca^{2+} + SiO_3^{2-} \rightarrow CaSiO_3.$$

The oxide products form on the magnesium surface by the complex chemical reactions occurring in the sparking discharge channels. Depending on the sparking discharging essence of MAO process, it is inevitable to produce some micropores on and through the MAO layer. Fig. 1b indicates that there appear many typical micropores of medium diameter size 2 ± 0.5 μm on the MAO layer surface. At the same time, the over accumulation of reaction products causes excessive

Please cite this article as: J.W. Guo, et al., Surf. Coat. Technol. (2015), http://dx.doi.org/10.1016/j.surfcoat.2015.02.010