Corrosion Science 79 (2014) 206–214

Contents lists available at ScienceDirect

Corrosion Science

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

Self-adjustment of calcium phosphate coating on micro-arc oxidized magnesium and its influence on the corrosion behaviour in simulated body fluids

GuangYi Liu [a,b], Shawei Tang [a], Dechao Li [c], Jin Hu [a,*]

[a] School of Materials Science and Engineering, Harbin Institute of Technology, Harbin 150001, China
[b] State Key Laboratory for Marine Corrosion and Protection, Luoyang Ship Material Research Institute, Qingdao 266071, China
[c] College of Stomatology, Jiamusi University, Jiamusi 154004, China

ARTICLE INFO

Article history:
Received 19 January 2013
Accepted 14 November 2013
Available online 21 November 2013

Keywords:
A. Magnesium
B. EIS
B. SEM

ABSTRACT

A calcium phosphate (Ca-Ph) coating was prepared on micro-arc oxidized magnesium using deposition method. The microstructure of the Ca-Ph coated sample and corrosion behaviour in simulated body fluid (SBF) were investigated. The results showed that the coating consisted of hydroxyapatite (HA) and dicalcium phosphate dihydrate (DCPD). Temperature significantly affected the microstructure of the coating. Increased temperature promoted HA formation but inhibited DCPD deposition. The microstructure of the Ca-Ph coating underwent self-adjustment in SBF. Bonelike apatites were formed on the coated sample, which not only increased the thickness of coating, but also improved corrosion performance of the coated sample in SBF.

1. Introduction

As potential biodegradable implants, magnesium and its alloys have received more and more attentions [1–5]. Mg^{2+} is one of the most abundant cation in the human body, which plays an important role in human metabolism [6]. The density, yielding strength and elastic modulus of magnesium are very close to natural human bone [7]. It is important to mention that the application of magnesium implant could relieve the patient from secondary operation and diminish costs [8]. Moreover, Magnesium alloys can help to improve the bone healing [9,10]. Magnesium alloy cardiovascular stent is also expected to be a good choice as long-term implant [11]. However, rapid corrosion of magnesium in physiological media inhibits its clinical application [12].

Alloying [12–20] and surface treatments [21–26] are effective ways to protect magnesium against corrosion. Of those, calcium phosphate coating is known to improve corrosion performance of magnesium alloys in SBF [27,28], and could be used as a barrier for corrosion [29–31]. Biomimetic calcium phosphate coated magnesium showed lower corrosion rate than the uncoated magnesium [32]. Hu et al. prepared DCPD coating on AZ91D magnesium alloy, and the corrosion rate of the coated AZ91D alloy in SBF was retarded [33]. Song et al. prepared HA layer on AZ91D alloy by means of electrodepositing to improve its biodegradation behaviour in the human body [34]. Besides that, calcium phosphate coating is also known to improve biocompatibility and bone growth at the site of magnesium implantation [35]. Xu et al. prepared a calcium phosphate coating on the surface of Mg–Mn–Zn magnesium alloy by phosphating process, the calcium phosphate coating obviously promoted surface bioactivity of magnesium alloy [36]. Cell culture results also showed that the calcium phosphate coated magnesium alloy behaved better cytocompatibility than the uncoated one [37].

Most studies focused on the improvement of biocompatibility or corrosion resistance of magnesium alloys with calcium phosphate coating. However, few report examined the adjustment of the calcium phosphate coating itself in simulated physiology solutions. Theoretical analysis indicated that different solution environments affected the nucleation and growth of calcium phosphate [38,39]. In fact, the corrosion performance of calcium phosphate coated magnesium in SBF varies with the adjustment of the coating. Therefore, it is necessary to investigate the change of calcium phosphate coating in SBF, especially the self-adaptive growth of the coating and its effect on the corrosion behaviour in SBF.

In this study, a Ca-Ph coating was prepared on the surface of micro-arc oxidized magnesium by deposition method. The effect of temperature on the microstructure of the Ca-Ph coating before and after immersion in SBF was investigated. The evolution of the Ca-Ph coating in SBF and its effect on the corrosion resistance of the coated magnesium were also studied in detail.

---

* Corresponding author. Address: School of Materials Science and Engineering, Harbin Institute of Technology, BOX 433, Harbin 150001, China. Tel.: +86 451 86415894; fax: +86 451 86413922.
E-mail address: hujin@hit.edu.cn (J. Hu).

0010-938X/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.corsci.2013.11.011

2. Experimental

Commercial pure magnesium (99.99%) was used in this study. The specimens (ϕ15 mm × 4 mm) were ground with 1500 grit SiC paper. Firstly, a micro-arc oxidation (MAO) layer was fabricated on the surface of magnesium as a substrate. The electrolyte of alkaline silicate contained 15 g/L $Na_2SiO_3{\cdot}9H_2O$, 8 g/L NaOH and 8 g/L KF. The working voltage was 400 V in the first 10 min and 450 V in the following 10 min. The substrates were then washed in deionized water and dried in air. After that, 500 mL 0.17 mol/L $Ca(NO_3)_2$ and 500 mL 0.10 mol/L K_2HPO_4 were selected as calcification solution. The solution temperature was set to 27 °C, 47 °C and 67 °C, respectively. The substrates were put into $Ca(NO_3)_2$ solution, followed by K_2HPO_4 being immediately dribbled into the $Ca(NO_3)_2$ solution. The dribbling process spent about 4 h and the coated substrates were retained in the calcification solution for 3 h after dribbling. Finally, a calcification coating was formed on the substrate surface [40].

Surface morphologies of the prepared coating were examined using scanning electron microscopy (Quanta 200FEG, USA). Elemental analysis of the coating was identified by EDX (EDAX, USA). Phase composition of the calcification coating was investigated by an X-ray diffraction (X'Pert, Philips, Netherlands) with a Cu Kα radiation source at 40 kV and 40 mA. The data was collected by grazing incidence method with 3° of incident beam angle, and the scanning range was from 10° to 90° with a scanning speed of 0.05 °/min. Surface functional group of the coating was detected by fourier transform infrared spectroscopy (FT-IR) (Avatar 370, Nicolet, USA). Transmission mode was used at room temperature with KBr pellet.

Electrochemical measurements including potentiodynamic polarization and electrochemical impedance spectroscopy were carried out in Kokubo SBF [41] at 37 °C using Gamry Reference 3000. The SBF consisted of 8.035 g/L NaCl, 0.355 g/L $NaHCO_3$, 0.225 g/L KCl, 0.231 g/L $K_2HPO_4{\cdot}3H_2O$, 0.311 g/L $MgCl_2{\cdot}6H_2O$, and 0.292 g/L $CaCl_2$. Solution pH value was adjusted to 7.4 with 1.0 mol/L HCl and tris(hydroxymethyl)aminomethane ($(CH_2OH)_3$-CNH_2). A classic three-electrode cell was used in the electrochemical experiments. The working electrode was the measured sample with an exposure area of 1 cm^2. Saturated calomel electrode (SCE) and platinum plate were used as reference and counter electrode, respectively. Before starting the potentiodynamic polarization test, the sample was kept at open circuit potential (OCP) for 300 s. Then the measurement started from −200 mV with respect to OCP with a sweep rate of 0.5 mV/s. The corrosion currents were calculated by Tafel extrapolating. For the electrochemical impedance spectroscopy (EIS) measurement, the frequency was ranged from 10^5 to 10^{-2} Hz. The AC amplitude was 10 mV around the open circuit potential. The EIS results were fitted and analysed using ZsimpWin 3.20 Echem software. Each test was repeated three times in order to verify the results.

Immersion test was performed in SBF at 37 °C for 4 weeks. The SBF was updated every two days during immersion. Hydrogen gas was collected by means of inverse measuring cylinder. The pH value of SBF solution was monitored with a pH meter.

3. Results

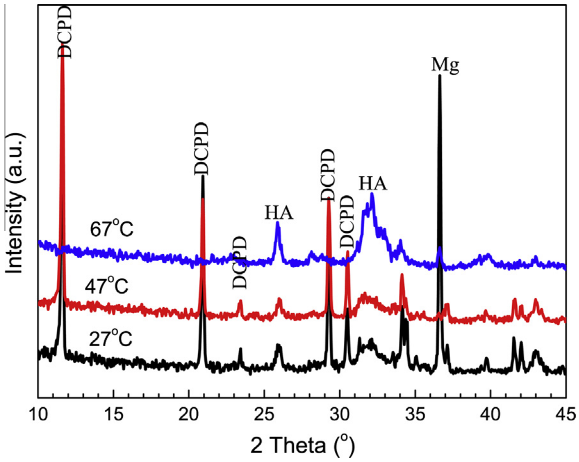

Fig. 1. X-ray diffraction patterns of the Ca-Ph coated substrate at different temperatures.

Fig. 1 shows the X-ray diffraction spectra of the coated substrates prepared at different temperatures. It was found that the calcification coating was composed of HA and DCPD. With an increase of temperature, the intensity of DCPD diffraction peaks decreased, while the diffraction peaks of HA increased gradually. The diffraction peaks of DCPD were not detected at 67 °C, only HA was observed in the pattern. This indicated that higher temperature inhibited DCPD deposition but improved HA formation. Furthermore, a distinct diffraction peak of magnesium was found in the 27 °C sample, which was invisible in the other samples. These phenomena suggested that increasing temperature improved the formation of thick Ca-Ph coating on the substrate, which resulted in magnesium peaks not being detected in the 47 °C and 67 °C samples.

Fig. 2 shows the morphologies of the calcification coatings obtained at various temperatures. When the temperature was 27 °C and 47 °C, two kinds of crystal characteristics, flake-like and spherical-shaped morphologies were observed on the substrate surfaces (Fig. 2(a and b)). According to the XRD analysis, they were confirmed as DCPD and HA, respectively. With an increase of temperature, the microstructures of the Ca-Ph coating changed dramatically. Although DCPD flakes were still situated on the substrate surface at 27 °C and 47 °C, they were larger and less at 47 °C than that of at 27 °C. Moreover, DCPD flake was not found on the substrate surface at 67 °C, only spherical-shaped HA existed on the substrate surface (Fig. 2(c)). Thus, an increase of temperature promoted the growth of DCPD flake itself, but the deposition of DCPD on the substrate surface was restrained. The morphology of HA on the substrate was strongly relative to the temperature. From the insert pictures of Fig. 2, it was found that spherical HA presented a porous network structure at 27 °C (insert in Fig. 2(a)), which then changed into band structure (insert in Fig. 2(b)) and string structure (insert in Fig. 2(c)) as temperature increased.

Fig. 3 illustrates potentiodynamic polarization curves of the Ca-Ph coated substrates in SBF. The polarization curve of micro-arc oxidized magnesium was put as control. The E_{corr} of all the Ca-Ph coated samples were nobler compared to uncoated substrate (Table 1). However, the increase of E_{corr} was slight, and there was a little difference in current density. The introduction of Ca-Ph coating did not distinctly change the polarization curves.

AC impedance spectra of the Ca-Ph coated samples in SBF are shown in Fig. 4 (scatter points). All the Bode spectra of the coated samples were similar. Modulus of the coated substrates dropped to 10^4 ohms cm^2 after 48 h of immersion, and then remained relatively constant. Three time constants distributed among high, medium and low frequency zones. It was considered that there were two protective layers on pure magnesium: the outside Ca-Ph coating and the inside MAO layer. At the beginning of immersion (less than 12 h), penetration of active chloride ions in the MAO layer led to its partial destruction. For the 47 °C and 67 °C samples, there were two time constants in the high frequency and middle frequency region, respectively. With an increase of