



ELSEVIER

Contents lists available at ScienceDirect

Materials Letters

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

Influence of the cathodic activity of magnesium alloys on the electrochemical deposition of calcium phosphate

R. Walter^{a,b}, M. Bobby Kannan^{a,b,*}, Y. He^b, A. Sandham^c

^a Biomaterials and Engineering Materials (BEM) Laboratory, James Cook University, Townsville, Queensland 4811, Australia

^b School of Engineering and Physical Sciences, James Cook University, Townsville, Queensland 4811, Australia

^c School of Medicine and Dentistry, James Cook University, Cairns, Queensland 4870, Australia

ARTICLE INFO

Article history:

Received 7 March 2014

Accepted 17 May 2014

Available online 27 May 2014

Keywords:

Magnesium alloy

Biomaterials

Calcium phosphate

Degradation

ABSTRACT

The aim of this study was to investigate whether the cathodic activity of magnesium alloys plays a significant role on the electrochemical deposition of calcium phosphate (CaP). CaP was deposited electrochemically on two magnesium alloys, i.e., magnesium–calcium (Mg–Ca) and magnesium–aluminium–zinc (AZ91), with different electrochemical degradation behaviour. The in vitro degradation behaviour of the CaP coated samples was evaluated using electrochemical impedance spectroscopy (EIS) in simulated body fluid (SBF). The polarisation resistance (R_p) of the CaP coated Mg–Ca alloy was ~85% lower than that of the CaP coated AZ91 alloy. Fourier transform infrared (FTIR) analysis showed no difference in the chemical nature of the coatings. However, scanning electron microscopy (SEM) analysis revealed that the coating particles on Mg–Ca alloy were less densely packed than those on the AZ91 alloy. This can be attributed to the higher dissolution rate of Mg–Ca alloy as compared to AZ91 alloy. As a result, the former exhibited higher cathodic charge density which produced higher hydrogen evolution, thereby affecting the coating process.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Calcium phosphate (CaP) has gained interest as a potential coating material for magnesium alloys to tailor the degradation rate of these materials for biodegradable implant applications [1–6]. Electrochemical deposition technique is attractive for CaP coating due to its capability of coating rapidly at room temperature and also the most intricately shaped implants. There has been a significant amount of research on galvanostatic [7,8] and potentiostatic [1,9] electrochemical deposition of CaP on magnesium and its alloys. However, a widely reported limitation of these methods is the high rate of hydrogen evolution during the coating process, which affects the uniformity of the coating.

A pulse-potential method has shown to produce CaP coating on magnesium and its alloys with improved performance [4,10]. In principle, the OFF time in the pulse-potential method dissipates the charge build up on the surface, and thereby allow ions to freely diffuse towards the substrate [11]. A recent study by one of the authors has shown that addition of ethanol to the coating

electrolyte improves the packing of CaP on a magnesium–aluminium–zinc alloy (AZ91) [5]. A synergistic effect of pulsed-potential and ethanol addition has also been reported by the author, which produced high performance CaP coating on AZ91 alloy [3].

Since the diffusion of the coating ions is critical for better coating, the degradation behaviour of the substrate may also play an important role on the coating morphology and performance. It is expected that the mass transfer resistance due to substrate dissolution would impact the cathodic deposition of CaP on the surface. To the best of authors' knowledge, there has been no study on correlating the substrate dissolution or cathodic activity behaviour with CaP coating and its performance. In order to investigate the relationship, Mg–Ca alloy which exhibits lower degradation resistance than AZ91 alloy was taken as a substrate material for CaP coating. CaP was coated on the alloy using the pulse-potential method and the in vitro performance of the coating was compared against the CaP coating on AZ91 alloy.

2. Materials and methods

A typical three-electrode cell, i.e., Ag/AgCl reference electrode, graphite counter electrode and sample as working electrode, was used to coat CaP on Mg–Ca alloy (1 wt% Ca). For comparison, the coating conditions used in this study were kept similar to those

* Corresponding author at: School of Engineering and Physical Sciences, James Cook University, Townsville, Queensland 4811, Australia. Tel.: +61 7 47815080; fax: +61 7 47816788.

E-mail address: bobby.mathan@jcu.edu.au (M. Bobby Kannan).

used previously for AZ91 alloy [3]. The coating solution contained $\text{Ca}(\text{NO}_3)_2$, 0.06 M $\text{NH}_4\text{H}_2\text{PO}_4$ and 30% v/v ethanol. Prior to the coating, the alloy was incrementally ground from 120 to 1200 grit SiC paper and then ultrasonically cleaned in ethanol and dried. Coating was carried out under a pulsed-potential of $-3/0$ V with 35% duty cycle (10 mS ON and 18.5 mS OFF) for 60 min. The coating morphology was examined using a Jeol JSM5410L scanning electron microscope (SEM). The functional groups of the coating were determined using Fourier transform infrared (FTIR) spectroscopy analysis (Perkin Elmer spectrum 100 FTIR spectrometer).

in vitro evaluation of the coating was done using an ACM Gill AC potentiostat. The electrolyte was simulated body fluid (SBF) buffered with tris(hydroxymethyl)aminomethane (TRIS) buffer at 37 °C and pH 7.40, the composition of which can be found elsewhere [12]. Samples were immersed in SBF for 2 h prior to testing to establish a relatively stable open circuit potential. Electrochemical impedance spectroscopy (EIS) was performed over the frequency range of 10^5 – 10^{-2} Hz at 5 mV AC amplitude. Equivalent circuit modelling of the EIS results was done using ZSimpWin V. 3.21 software to determine the polarisation resistance (R_p).

3. Results and discussion

SEM analysis revealed that the coating morphology was significantly different between the coatings on Mg–Ca and AZ91 alloys (Fig. 1(a–d)). A low magnification micrograph (Fig. 1a) of the coating on Mg–Ca alloy showed visible protruding particles distributed evenly across the entire surface. On the AZ91 alloy, however, the particles were relatively flat, with a much lower number of protruding particles (Fig. 1c). Higher magnification micrographs of the coatings showed that the particles were of a slightly smaller size on the Mg–Ca alloy than those on the AZ91 alloy (Fig. 1b and d). The packing of the particles were relatively denser on the AZ91 alloy. The FTIR spectra of the two coatings suggest that the coatings are similar in composition (Fig. 2). The strong bands at 1122, 1052 and 984 cm^{-1} correspond to phosphate

[13,14], and the bands at 1631 cm^{-1} and 874 cm^{-1} correspond to hydroxide and carbonate groups, respectively.

The in vitro degradation behaviour of the bare alloys was evaluated in SBF. Fig. 3a shows the EIS plots of bare Mg–Ca and AZ91 alloys. Both alloys showed similar characteristics, i.e., high and mid frequency capacitive loops. The AZ91 alloy also showed a low frequency inductive loop, which has been shown to be indicative of pitting corrosion [12]. The Nyquist plot of Mg–Ca alloy was modelled using the equivalent circuit $R_s(Q_f(R_f(Q_{dl}R_{ct})))$, where R represents resistors and Q represents constant phase elements. R_s is the solution resistance, R_f and Q_f represent film effects, Q_{dl} represents double layer capacitance and R_{ct} represents charge transfer resistance. The AZ91 alloy used a similar model with added inductive elements: $R_s(Q_f(R_f(Q_{dl}R_{ct}))(R_iL))$. This model has been used for magnesium in chloride containing environments [15]. The bare

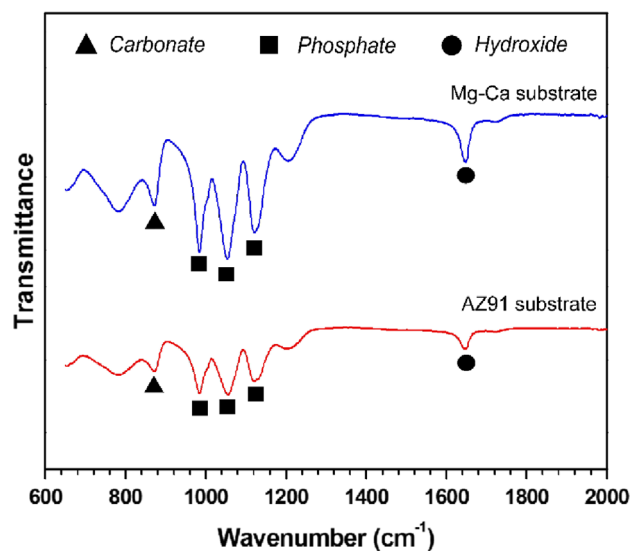


Fig. 2. FTIR spectra of the calcium phosphate coating on Mg–Ca and AZ91 alloys.

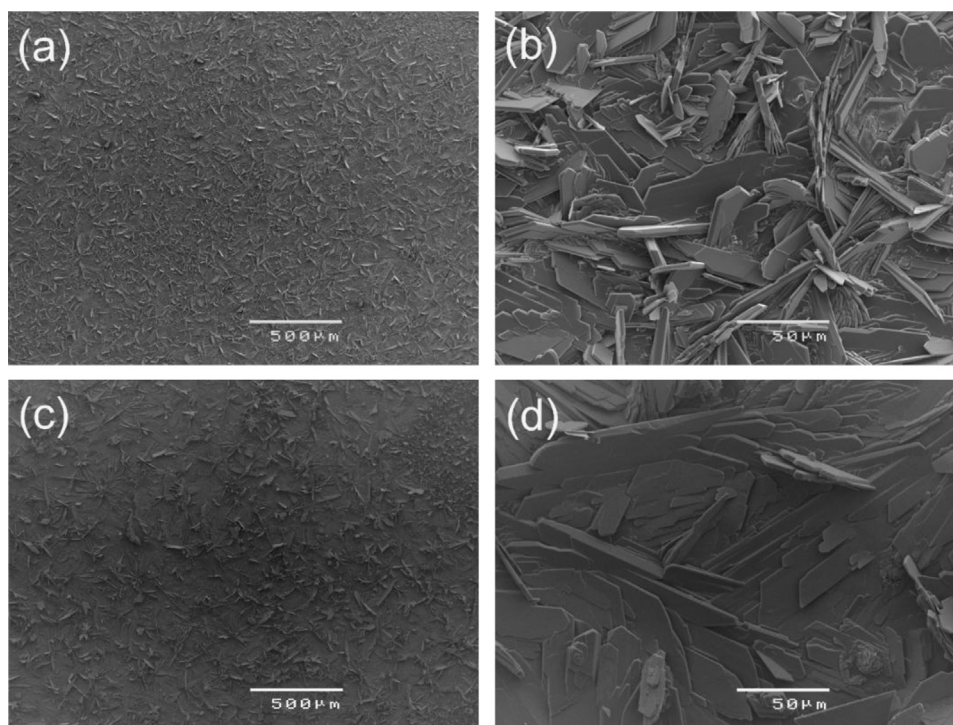


Fig. 1. SEM micrographs of the calcium phosphate coating on: (a, b) Mg–Ca alloy, and (c, d) AZ91 alloy.

Download English Version:

<https://daneshyari.com/en/article/1643842>

Download Persian Version:

<https://daneshyari.com/article/1643842>

[Daneshyari.com](https://daneshyari.com)