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ScienceDirect
Journal of Bionic Engineering 10 (2013) 156–161

In Vivo Corrosion Resistance of Ca-P Coating on AZ60 Magnesium Alloy

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Abstract

Magnesium-based alloys are frequently reported as potential biodegradable orthopedic implant materials. Controlling the degradation rate and mechanical integrity of magnesium alloys in the physiological environment is the key to their applications. In this study, calcium phosphate (Ca-P) coating was prepared on AZ60 magnesium alloy using phosphating technology. AZ60 samples were immersed in a phosphating solution at 37 ± 2 ˚C for 30 min, and the solution pH was adjusted to 2.6 to 2.8 by adding NaOH solution. Then, the samples were dried in an attemperator at 60 ˚C. The degradation behavior was studied in vivo using Ca-P coated and uncoated magnesium alloys. Samples of these two different materials were implanted into rabbit femora, and the corrosion resistances were evaluated after 1, 2, and 3 months. The Ca-P coated samples corroded slower than the uncoated samples with prolonged time. Significant differences ($p < 0.05$) in mass losses and corrosion rates between uncoated samples and Ca-P coated samples were observed by micro-computed tomography. The results indicate that the Ca-P coating could slow down the degradation of magnesium alloy in vivo.

Keywords: Ca-P coating, mass loss, micro-computed tomography, corrosion resistance, magnesium alloy

doi: 10.1016/S1672-6529(13)60210-3

1 Introduction

Magnesium alloys have been recently proven as effective biodegradable orthopedic implant materials[1,2]. However, the in vivo corrosion of magnesium alloys critically hinders their use as biodegradable implant materials. During corrosion, the rapid degradation of magnesium alloys leads to subcutaneous bubbles from hydrogen evolution and an increase in the pH of body fluids and blood by local alkalization[3,4]. Therefore, controlling the degradation rate and mechanical integrity of these alloys in the physiological environment is the key to their applications.

Several strategies have been reported to overcome the low corrosion resistance and regulate the biocorrosion rate of magnesium alloys. One strategy is the addition of other elements[5,6] such as Mn, Zn, and Al as alloying elements to develop different alloys in the past decades. In recent years, Ca and rare-earth elements have been used to produce binary magnesium alloys that show good corrosion resistance but limited bone response[7]. Another strategy for effectively reducing the corrosion of magnesium alloys is surface modification[8]. Calcium phosphate (Ca-P) coating is recognized as one of the most biocompatible materials for bone replacement and regeneration and is widely used as a bioactive coating in clinical orthopedic implants such as titanium (Ti) alloys[9]. Recently, Ca-P coating has been used to protect magnesium alloys from fast corrosion. For example, Ca-P coating on AZ30 and Mg-Mn-Zn alloys was reported to improve corrosion resistance[10,11].

In the present study, Ca-P coating was prepared on an Mg-Al alloy (AZ60) by a two-step chemical process without pretreatment. Then, the samples were implanted into the femoral shafts of rabbits. Analysis and evaluation of the degradation in vivo were conducted based on corrosion measurements and micro-computed tomography (Micro-CT) technology.

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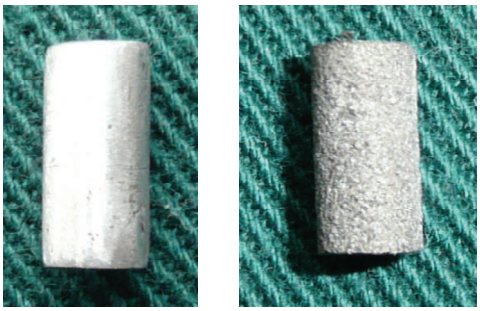
2 Materials and methods

2.1 Preparation of materials

Die-cast AZ60 magnesium alloy supplied by the Research Institute of Composite Materials of Tianjin University was used as the substrate material. The magnesium alloy composition is listed in Table 1. The sample (diameter of 3 mm and length of 8 mm) surface was polished using silicon cardite (SiC) paper with up to 2000 grit. The sample was then cleaned by sonication in acetone. Ca-P coating was prepared on the samples by a two-step chemical process without pretreatment. The cleaned samples were immersed in a phosphating solution at 37 ± 2 ˚C for 30 min, and the solution pH was adjusted to 2.6 to 2.8 by adding NaOH. After drying the samples at 60 ˚C, the coated layer with an average thickness of approximately 6 μm was found to be mainly composed of dicalcium phosphate dihydrate ($CaHPO_4•2H_2O$) and a small quantity of magnesium phosphate ($Mg_3(PO_4)_2$)[12]. Fig. 1 shows photographs of the coated and uncoated samples and Fig. 2 shows the SEM surface morphology and Energy Dispersive X ray Spectroscopy (EDS) result of the coated samples.

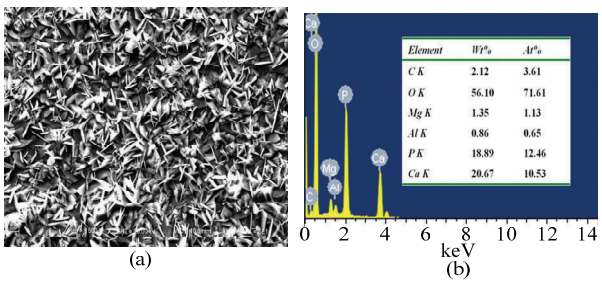
Table 1 Composition of AZ60 magnesium alloy

Element	Al	Zn	Mn	Si	Cu	Ni	Fe	Mg
wt. %	5.8–7.2	<1.0	0.15–0.5	≤0.1	≤0.05	≤0.005	≤0.005	Balance



(a) (b)

Fig. 1 Photographs of uncoated (a) and Ca-P coated (b) samples.



(a) (b)

Fig. 2 Surface morphology (a) and EDS result (b) of Ca-P coated sample.

The Ca-P coated and uncoated samples were cleaned by ultrasonication in ethanol for 20 min. Prior to the surgery experiments, all samples were sterilized with 29 kGy of gamma radiation[13].

2.2 In vivo degradation

2.2.1 Surgery

All animal experiments were conducted based on the animal welfare requirements of ISO 10993-2:2006. A total of 24 adult New Zealand rabbits with a body weight of 2.5 kg to 3.0 kg were used. The rabbits were randomly divided into two groups. All rabbits were anesthetized with 0.5 pentobarbital sodium solution for surgery. After predrilling with a 2.8 mm hand-operated drill, the Ca-P coated samples were implanted into both femoral shafts of the rabbits in the experimental group. Meanwhile, the uncoated samples were implanted into both femoral shafts of the rabbits in the control group. Afterwards, all rabbits were injected subcutaneously with penicillin as antibiotic prophylaxis. The experimental and control groups were separately fed for 3 months.

2.2.2 General observation

After surgery, the rabbits' behavior, eating, activity, healing, and body weight change were observed. The rabbits were then sacrificed, and the soft tissue reaction of the surgical site was observed.

2.2.3 Corrosion mass loss

The mass of the sample (M1) was obtained before implanting into the bodies of the rabbits. After sacrificing the rabbits, the corroded samples were removed from the specimens, cleaned with distilled water, dried, and weighed (M2) again. The difference in the weights of the test samples before and after the experiment represented the mass loss after 3 months of corrosion in vivo (M1 – M2).

2.2.4 Micro-CT measurements

After 1, 2, and 3 months of implantation, eight rabbits (four of each group) were euthanized at each time, and the femora containing the coated and uncoated samples were fixed in 75% absolute alcohol. These samples were individually scanned using a micro-CT system (GE, healthcare, USA) to examine their in vivo degradation. The CT settings were 20 μm slice thickness and 1024 × 1024 pixel matrix. After scanning, 3D im-