Materials Science and Engineering C 29 (2009) 1311–1316

Contents lists available at ScienceDirect

Materials Science and Engineering C

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

Improve corrosion resistance of magnesium in simulated body fluid by dicalcium phosphate dihydrate coating

Yong Wang [a,b], Mei Wei [b,*], Jiacheng Gao [a]

[a] College of Materials Science & Engineering, Chongqing University, Chongqing, 400045, China
[b] The Institute of Materials Science, University of Connecticut, Storrs, CT 06269, USA

ARTICLE INFO

Article history:
Received 14 August 2007
Received in revised form 4 February 2008
Accepted 26 September 2008
Available online 11 October 2008

Keywords:
Magnesium
DCPD
Coating
SBF
Biodegradation

ABSTRACT

A dicalcium phosphate dihydrate (DCPD) coating composed of bar-shaped crystals was deposited on the surface of magnesium in order to slow down the corrosion rate of the substrate. The corrosion resistance of the DCPD-coated specimens was evaluated in a simulated body fluid (SBF) with uncoated specimens as a control. Time-dependent characteristics of specimens and the corresponding SBF were analyzed at 3, 5, 7, 14 and 21 days of immersion. Less weight loss and pH increase were observed for the coated group than the uncoated group. The coating was intact after 3 days of immersion although its dissolution was manifested by XRD examination. Noticeable DCPD dissolution occurred at the 5th day accompanied by a temporary increase in Ca and P concentrations in SBF which otherwise kept decreasing. Despite the dissolution of the coating, some DCPD particles were still observed on the surface of the substrate after 21 days of immersion. In contrast to the coated specimens, a porous layer of $Mg(OH)_2$ was formed on the surface of uncoated specimens at the 5th day of immersion. It was found that the corrosion rate of the coated group was substantially lower than that of the control.

1. Introduction

Metal materials, including titanium, stainless steel and cobalt chromium, are used extensively for hard tissue repair and replacement. They are suitable for load-bearing applications due to their superior mechanical strength and toughness. However, metal materials are generally bioinert *in vivo*, which may induce the formation of a fibrous tissue layer between the implant and surrounding tissue. Different techniques have been developed to apply bioactive coatings, such as calcium phosphates, onto the surface of metallic material to render the bioactivity of these materials [1–4]. Another major concern of metallic materials is their high elastic moduli, which can result in stress shielding of the surrounding bone and thereby decrease the stability of implants [5,6]. Hence, it is necessary to explore a more suitable metallic biomaterial for load bearing applications.

Magnesium is the fourth major cation in human blood plasma. It is essential to human metabolism and is naturally found in bone tissue. It is found that approximately 60–65% of total magnesium ions are in bone, 35% in tissue sections and only around 1–2% in extracellular fluid [7]. Magnesium deficiency could result in bone strength reduction and osteoporosis [8,9]. Therefore, it is believed that magnesium and its alloys are safe to be used as implants. Moreover, magnesium is the second most light metals used in engineering, only next to beryllium. The density of magnesium is 1.84 g/cm^3, which is closer to the density of natural bone (1.8–2.1 g/cm^3) than any other currently used metallic biomaterials. Furthermore, the elastic modulus of magnesium is 45 GPa, which is much lower than that of stainless steel (200 GPa), titanium (110 GPa) and cobalt chromium (210 GPa). As a result, stress shielding effect can be largely decreased or avoided if magnesium is used as an implant. In fact, magnesium alloy was applied to orthopaedic surgery in 1930s' [10]. Magnesium has been considered as an attractive novel biomaterial by a few research groups recently, [11,12]. Although magnesium has many attractive properties as an implant material, its rapid corrosion can result in the loss of mechanical integrity of the implant before tissue healing. Especially, the gas produced during the corrosion process could greatly hinder the tissue regeneration [10]. Many efforts have been made to improve the corrosion resistance of magnesium. Kuwahara et al. [13] applied a magnesium oxide layer on magnesium (99.9%) by heat-treating the metal at 803 K in air. After soaked in Hank's solution, the specimen's specific mass change was positive when the heat treatment time was longer than 9 h. A Mg-apatite, $(Ca_{0.86}Mg_{0.14})_{10}(PO_4)_6(OH)_2$, layer was formed on the surface of the specimen heat-treated for 25 h. Heat treatment was also performed by Lopez et al. [14], but the temperature used was much lower (345 °C) and the treatment time was much shorter (15 min) than those employed by Kuwahara et al. Compared to both untreated and HF solution-treated specimens, the heat-treated magnesium demonstrated better corrosion resistance in SBF. A combination of alkaline- and heat-treatment was attempted by Li et al. [15]. Such treated specimens induced calcium phosphate precipitation after soaked in

---

* Corresponding author. Tel.: +1 860 486 9253; fax: +1 860 486 4745.
E-mail address: m.wei@ims.uconn.edu (M. Wei).

0928-4931/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.msec.2008.09.051

SBF for 14 d. Al-Abdullat et al. [16] prepared a coating containing mainly $MgCO_3$ on the surface of pure magnesium, and they found that the specimens displayed no weight loss in Hank's solution for up to 75 days. A combination of coating and heat-treatment was carried out by Gao et al. [17], where a stearic acid film was formed on the surface of magnesium substrate. The coated specimens were then subjected to heat-treatment at 773 K for 10 h. No weight loss was detected in these specimens after soaked in SBF for up to 14 d. Moreover, a zero hemolysis ratio was demonstrated for the treated specimens, but it was 60% for the untreated magnesium.

To use magnesium as a biodegradable material, the coating applied should be biocompatible and ideally bioactive. Thus, the employment of an osteoconductive calcium phosphate coating can be a promising approach. In the present work, a dicalcium phosphate dihydrate coating was chemically deposited on the surface of magnesium and its effect on the corrosion behavior of the substrate was evaluated in SBF at the body temperature.

2. Materials and methods

2.1. Specimen preparation

Magnesium with a purity of 99.9% was used in this work. The as-cast ingot was annealed at 550 °C for 24 h to obtain a homogeneous composition and microstructure. It was then cut into rectangular specimens of $10 \times 28 \times 5$ mm^3. The specimens were ground using SiC papers ranging from 320 to 800 grits. They were cleaned in 5 wt.% potassium hydroxide solution followed by ultrasonically rinsing in acetone for 10 min. The weight of each specimen was recorded.

In order to form a calcium phosphate coating on the surface of the substrates, a group of specimens was chemically treated by soaking in an aqueous solution at 45 °C for 3 h. The solution was prepared by dissolving 6.2 g Na_2HPO_4 and 15.9 g $Ca(NO_3)_2$ into 300 ml de-ionized water and the resulting pH was 3.5. The treated specimens were weighted after ultrasonically rinsing in acetone for 10 min.

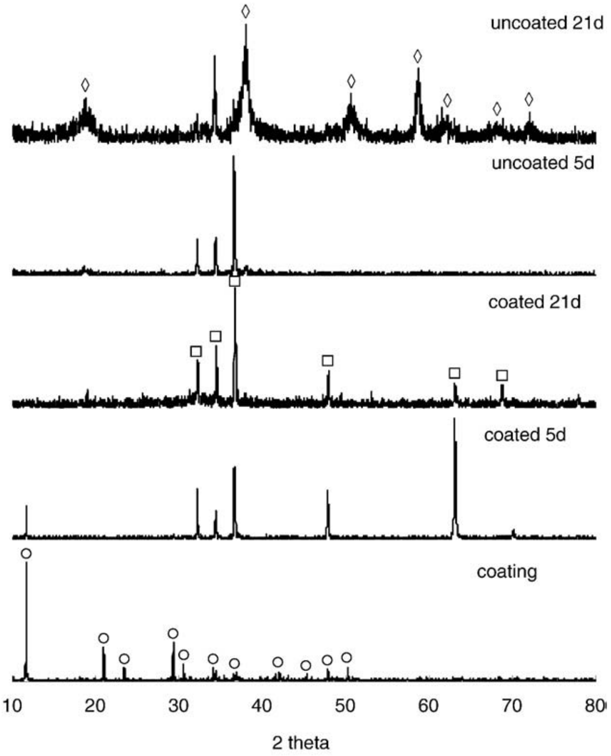

Fig. 1. XRD spectra of coating and samples after immersion for different time. o DPCD, ◇ $Mg(OH)_2$ □ Mg.

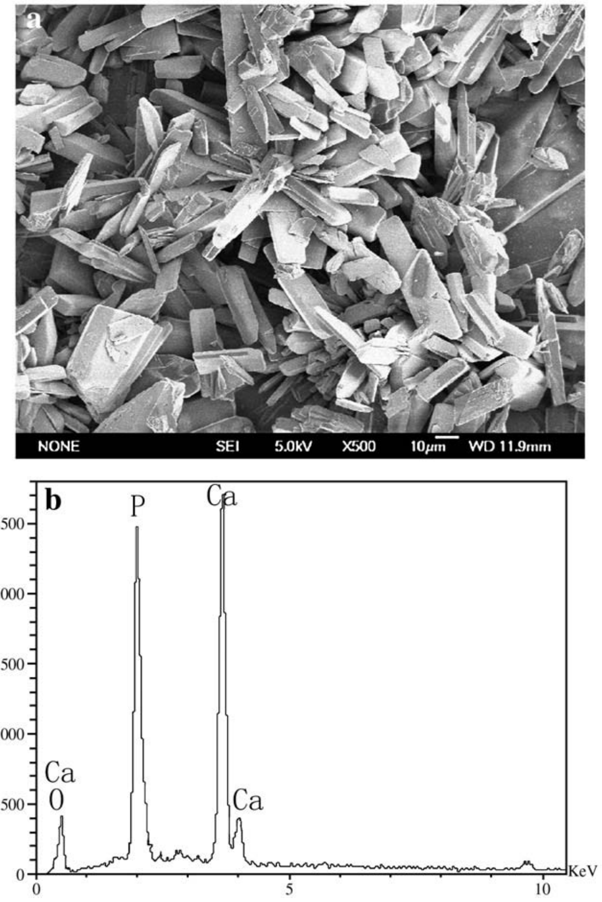

Fig. 2. Topology (a) and composition (b) of DCPD coating.

2.2. Corrosion test

Corrosion test was conducted in the simulated body fluid (SBF). The SBF was prepared according to the procedures described by Kokubo and Takadama [18]. Suitable amounts of reagent grade chemicals were dissolved in de-ionized water with the following sequence: sodium chloride, sodium bicarbonate, potassium chloride, dipotassium hydrogen phosphate, magnesium chloride hexahydrate, hydrochloride acid, calcium chloride, sodium sulfate and tris-hydroxymethyl aminomethane. The pH of this solution was buffered to 7.4 at 36.5 ± 0.5 °C.

The chemically treated specimens were subjected to corrosion test in SBF. Specimens without any surface treatment (labeled as untreated) were used as controls. Each specimen was soaked in 500 mL SBF at 37 °C for 3, 5, 7, 14, and 21 days, respectively. The changes of solution pH and specimen weight were recorded and the Ca and P concentrations in SBF were measured at each time point. Three specimens were used in each of these measurements. A Perkin Elmer 3100 atomic absorption spectrometry (AAS) was used to measure the calcium concentration in the solution. Molybdenum blue method was applied to determine the concentration of phosphate, in which the results were quantified with a Biotek MQX200 microplate reader.

2.3. Characterization methods

The topology of the specimens before and after soaking in SBF was observed using JEOL JSM 6335F field emission scanning electron microscope (FESEM). The crystal structure was identified with Bruker D5005 X-ray diffractometer (XRD). The surface composition was analyzed using Amary 1000A energy dispersive X-ray spectroscopy (EDX).