

# Influence of aggressive ions on the degradation behavior of biomedical magnesium alloy in physiological environment

Yunchang Xin<sup>a,b</sup>, Kaifu Huo<sup>a,c</sup>, Hu Tao<sup>a</sup>, Guoyi Tang<sup>b</sup>, Paul K. Chu<sup>a,\*</sup>

<sup>a</sup> Department of Physics and Materials Science, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong, China

<sup>b</sup> Advanced Materials Institute, Tsinghua University, Shenzhen Graduate School, Shenzhen 518055, China

<sup>c</sup> Hubei Province Key Laboratory of Refractories and Ceramics, College of Materials and Metallurgy, Wuhan University of Science and Technology, Wuhan 430081, China

Received 10 December 2007; received in revised form 10 May 2008; accepted 14 May 2008

Available online 11 June 2008

## Abstract

Various electrochemical approaches, including potentiodynamic polarization, open circuit potential evolution and electrochemical impedance spectroscopy (EIS), are employed to investigate the degradation behavior of biomedical magnesium alloy under the influence of aggressive ions, such as chloride, phosphate, carbonate and sulfate, in a physiological environment. The synergetic effects and mutual influence of these ions on the degradation behavior of Mg are revealed. Our results demonstrate that chloride ions can induce porous pitting corrosion. In the presence of phosphates, the corrosion rate decreases and the formation of pitting corrosion is significantly delayed due to precipitation of magnesium phosphate. Hydrogen carbonate ions are observed to stimulate the corrosion of magnesium alloy during the early immersion stage but they can also induce rapid passivation on the surface. This surface passivation behavior mainly results from the fast precipitation of magnesium carbonate in the corrosion product layer that can subsequently inhibit pitting corrosion completely. Sulfate ions are also found to stimulate magnesium dissolution. These results improve our understanding on the degradation mechanism of surgical magnesium in the physiological environment.

© 2008 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.

**Keywords:** Magnesium alloys; Biomaterial; Degradation; Aggressive ions

## 1. Introduction

Stainless steels, cobalt-based alloys and titanium alloys are widely studied and applied clinically in hard tissue implants, especially in load-bearing applications, due to their high strength, ductility and good corrosion resistance. However, they cannot degrade spontaneously and a second surgical procedure is usually needed to remove the metal implants from the body after the tissues have completely healed. Repeated surgery increases the cost as well as patient morbidity. In this respect, biodegradable magnesium-based alloys can be a potential solution. Many clinical cases as well as in vivo and in vitro assessments have

demonstrated that magnesium alloys possess good biocompatibility [1–3]. Some studies have also shown that the dissolved magnesium ions may promote bone cell attachment and tissue growth on the implants [4–6]. Unfortunately, pure magnesium and its alloys corrode too quickly at physiological pH (7.4–7.2), as well as in physiological media containing high concentrations of aggressive ions, thereby losing mechanical integrity before tissues have sufficient time to heal [1,3,7,8]. This has become the main limitations in clinical applications. The fast degradation rates of Mg alloy are generally considered to result from aggressive ions in the physiological environment, such as chlorides, phosphates, carbonates and sulfates. The aggressive behavior of chloride ions to Mg alloys has been widely investigated and it is generally accepted that chloride ions can transform the protective MgO/Mg(OH)<sub>2</sub> into soluble MgCl<sub>2</sub>

\* Corresponding author. Tel.: +852 27887724; fax: +852 27889549.

E-mail address: [paul.chu@cityu.edu.hk](mailto:paul.chu@cityu.edu.hk) (P.K. Chu).

[9], thus accelerating magnesium dissolution. Phosphates, carbonates and sulfates in the physiological environment may also attack magnesium. However, their influences have rarely been systematically investigated. In addition, the synergetic effect and mutual influence of these ions on the degradation behavior of Mg are not well understood. Electrochemical approaches, such as the potentiodynamic polarization test, open circuit potential evolution and the electrochemical impedance spectrum (EIS), have been widely employed to investigate the corrosion process of alloys, and they are powerful tools to deduce the corrosion mechanism involved [10–12]. However, there have been few reports to date investigating the corrosion mechanism of magnesium alloys in a physiological environment by systematic electrochemical approaches.

In this work, phosphate, carbonate and sulfate ions with the same concentrations as in human body fluid were introduced separately into a sodium chloride solution. Electrochemical approaches including potentiodynamic polarization, open circuit potential evolution and EIS were employed to investigate the degradation behavior of Mg alloys in the solutions containing these ions. In conjunction with scanning electron microscopy (SEM) and Fourier transform infrared (FTIR) characterization, the synergetic effects and mutual influence of the different ions on the degradation behavior of magnesium were systematically investigated and analyzed. The results show that phosphate ions can slow down the corrosion rates significantly, and that carbonate ions can induce surface passivation and totally inhibit pitting corrosion induced by chloride ions. Also, sulfate ions stimulate the corrosion of magnesium. Our results aid our understanding of the degradation mechanism of surgical magnesium in a physiological environment.

## 2. Experimental

### 2.1. Sample preparation

Commercial die-cast AZ91 Mg alloys purchased from YiHo Corporation, Shenzhen, China were used. The dimensions of the samples used in the experiments were 15 mm × 15 mm × 3 mm. They were ground with No. 4000 waterproof diamond paper, polished and ultrasonically cleaned in alcohol. Four types of solutions were prepared using NaCl, NaHCO<sub>3</sub>, K<sub>2</sub>HPO<sub>4</sub> and Na<sub>2</sub>SO<sub>4</sub>. The concentrations of the chloride, phosphate, carbonate and sulfate ions in the four solutions mimic those in human body fluids [13] and are listed in Table 1.

### 2.2. SEM and FTIR

The samples after immersion for 7 days were taken out of the solutions and ultrasonically cleaned in distilled water. The surface morphology of the samples was observed by SEM. FTIR from 4000 to 400 cm<sup>-1</sup> was also conducted to identify the functional groups in the corrosion products.

### 2.3. Degradation rate measurement

The volume of emitted hydrogen during immersion is related to the dissolution of magnesium:



The corrosion products do not influence the relationship between hydrogen evolution and magnesium dissolution. The degradation rate of magnesium can thus be monitored by the evolved hydrogen volume, and this method is reliable, easy to implement and not prone to errors inherent in the weight loss method [9]. In addition, this technique has the advantage that variations in the degradation rates can be monitored by the hydrogen evolution rates, allowing the study of the degradation rate variation vs. exposure time. The samples were soaked in 200 ml solutions for 7 days at an ambient temperature of 37 ± 0.5 °C. It has been verified that the dissolved oxygen does not influence the result of the measurements [9] and thus our experiments were carried without deaeration. The emitted hydrogen volumes were measured as a function of immersion time.

### 2.4. Electrochemical tests

The electrochemical corrosion behavior of the AZ91 magnesium alloy was investigated in the four solutions by potentiodynamic polarization tests, the open circuit potential evolution ( $E_{\text{corr}}-t$ ) and EIS using Gamry Reference 600. A three-electrode cell with the sample as the working electrode, calomel electrode as the reference electrode and platinum electrode as the counter electrode were used. As magnesium reacted in the solution quickly, the potentiodynamic polarization test commenced as soon as the samples were soaked in the solution. A scanning rate of 1 mV s<sup>-1</sup> was used in the potentiodynamic polarization test. In the  $E_{\text{corr}}-t$  test, changes in the open circuit potential were monitored as a function of immersion time for about 240 ks. The data were recorded every 120 s. The impedance data were recorded from 100 kHz to 10 mHz with a 10 mV sinu-

Table 1  
Ion concentrations in the four solutions

Concentration (mmol l <sup>-1</sup> )	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Cl	HPO <sub>4</sub> <sup>-2</sup>	HCO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>-2</sup>
Blood plasma	142.0	5.0	2.5	1.5	103.0	1.0	27.0	0.5
Solution #1	103	–	–	–	103.0	–	–	–
Solution #2	103	2.0	–	–	103.0	1.0	–	–
Solution #3	130	2.0	–	–	103.0	1.0	27.0	–
Solution #4	130.5	2.0	–	–	103.0	1.0	27.0	0.5

ID	Title	Pages
1774	Influence of aggressive ions on the degradation behavior of biomedical magnesium alloy in physiological environment	8

**Download Full-Text Now**



<http://fulltext.study/article/1774>



Categorized Journals

Thousands of scientific journals broken down into different categories to simplify your search



Full-Text Access

The full-text version of all the articles are available for you to purchase at the lowest price



Free Downloadable Articles

In each journal some of the articles are available to download for free



Free PDF Preview

A preview of the first 2 pages of each article is available for you to download for free

<http://FullText.Study>