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Effect of biologically relevant ions on the corrosion products formed on alloy AZ31B: An improved understanding of magnesium corrosion ☆

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ABSTRACT

Simulated physiological solutions mimicking human plasma have been utilized to study the in vitro corrosion of biodegradable metals. However, corrosion and corrosion product formation are different for different solutions with varied responses and, hence, the prediction of in vivo degradation behavior is not feasible based on these studies alone. This paper reports the role of physiologically relevant salts and their concentrations on the corrosion behavior of a magnesium alloy (AZ31B) and subsequent corrosion production formation. Immersion tests were performed for three different concentrations of Ca^{2+}, HPO_4^{2-}, HCO_3^- to identify the effect of each ion on the corrosion of AZ31B assessed at 1, 3 and 10 days. Time-lapse morphological characterization of the samples was performed using X-ray computed tomography and scanning electron microscopy. The chemical composition of the surface corrosion products was determined by electron dispersive X-ray spectroscopy and X-ray diffraction. The results show that: (1) calcium is not present in the corrosion product layer when only Cl^- and OH^- anions are available; (2) the presence of phosphate induces formation of a densely packed amorphous magnesium phosphate corrosion product layer when HPO_4^{2-} and Cl^- are present in solution; (3) octacalcium phosphate and hydroxyapatite (HAp) are deposited on the surface of the magnesium alloy when HPO_4^{2-} and Ca^{2+} are present together in NaCl solution (this coating limits localized corrosion and increases general corrosion resistance); (4) addition of HCO_3^- accelerates the overall corrosion rate, which increases with increasing bicarbonate concentration; (5) the corrosion rate decreases due to the formation of insoluble HAp on the surface when HCO_3^-, Ca^{2+}, and HPO_4^{2-} are present together.

1. Introduction

Biodegradability and similar mechanical properties to human bone make magnesium a promising candidate for implantable materials used in medical devices. Recent efforts to develop more biocompatible metallic implants have focused not only on magnesium alloy design to match the engineering requirements demanded of medical devices [1–3], but also on understanding the degradation behavior in specific biomedical application environments [4–7]. The biodegradation of metallic magnesium is fundamentally linked to studies of its "corrosion", which is dependent on the interface dynamics between the material and its environment. Identifying and understanding the biological and material factors that govern the corrosion kinetics and mechanisms are of prime importance to the successful development of biodegradable implants.

Currently, applying in vitro test results generated using simulated body fluids (SBFs) to predict in vivo degradation behavior is unreliable because factors affecting the complex biomedical environment, such as the concentrations of salts, flow dynamics, protein absorption and active tissue formation, cannot be replicated solely by immersion in SBFs. Previous studies have used various solutions, such as NaCl solution [8,9], Hank's balanced salt solution [10,11], SBF [12–14] and Dulbecco's modified Eagle's medium (DMEM) [15,16] to study the corrosion behavior of magnesium alloys. Additionally, the effect of different inorganic ions, such as Cl^-[13,17,18], Ca^{2+}[13], HCO_3^-[17–20], and HPO_4^{2-}[13,18,21], have been investigated. However, the mechanism(s) of corrosion and corrosion product formation upon exposure to individual ions combined with salts and their concentrations is not well established.

This paper is an attempt to identify the effects of biologically relevant salts and their concentrations on the corrosion behavior and corrosion product formation using the standard immersion test. It is thought that this fundamental understanding of in vitro corrosion studies will ultimately provide a basis for comparison

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Table 1
The ionic composition and concentration of each test solution and blood plasma.

Concentration (mmol l^{-1})	Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	HCO_3^-	HPO_4^{2-}	SO_4^{2-}
Blood plasma [22]	142.0	5.0	2.5	1.5	103.0	27.0	1.0	0.5
Solution 1	103.0				103.0			
Solution 2	102.0		0.5		103.0			
Solution 3	98.0		2.5		103.0			
Solution 4	83.0		10.0		103.0			
Solution 5	103.4				103.0		0.2	
Solution 6	105.0				103.0		1.0	
Solution 7	113.0				103.0		5.0	
Solution 8	103.5				103.0	0.5		
Solution 9	130.0				103.0	27		
Solution 10	153.0				103.0	50		
Solution 11	100.0		2.5		103.0		1.0	
Solution 12	127.0		2.5		103.0	27	1.0	

with results from in vivo studies while isolating and characterizing the corrosion products associated with the biodegradation process.

2. Materials and methods

Cylindrical specimens 6.35 mm in diameter and 2 mm high were cut from a rod of as-drawn AZ31B magnesium alloy (Goodfellow Corp., USA), polished with up to 1200 grit silicon carbide sand, and cleaned with acetone and ethyl alcohol. The final height was adjusted to 1.3 mm after polishing.

Immersion tests were carried out in the various solutions shown in Table 1, in an Isotemp incubator (model No. 1602D Fisher Scientific, USA) at 37 °C for 1, 3 and 10 days to compare corrosion in each solution. The solutions were prepared with salt concentrations relevant to those found in blood plasma (Table 1) [22]. Solution 1 was a NaCl solution with a similar concentration of Cl^- to that of blood plasma. This concentration of Cl^- ions was common to all solutions. The Ca^{2+} concentration in solutions 2–4 was varied based on the concentration in blood plasma. In the same way, solutions 5–7 contained varying amounts of HPO_4^{2-}, and solutions 8–10 varying amounts of HCO_3^-. The types of salts present in solutions 11 and 12 were varied. These solutions were made with NaCl, $CaCl_2$, $Na_2HPO_4{\cdot}7H_2O$ and $NaHCO_3$. The ratio of volume of solution to sample was 330 ml cm^{-2} and the initial pH of the solutions was adjusted to 7.4 ± 0.05. The solutions were changed every day to minimize the influence of pH.

The pH of the solutions was measured with a pH meter (Oakton® pH2100, Eutech Instruments, Singapore) before changing the solution. The outward appearance and cross-sectional images of the samples after immersion for 10 days were observed using a digital camera and by micro-CT (Phoenix Nanotom-M™, GE Sensing & Inspection Technologies GmbH, Germany). X-ray emission parameters were 80 kV and 180 μA and the number of projections acquired (N_p) was 1800. The PCA file format (Phoenix CT Acquisition) obtained were converted to PCR file format (Phoenix CT Reconstruction) via a reconstruction step and three-dimensional and cross-sectional images of sample were investigated using VG Studio Max (v.2.1) software. Morphology and chemical composition of the corrosion products on the surface of samples were analyzed by scanning electron microscopy (SEM) (SU8000, Hitachi, Japan) after ion beam coating. Cross-section samples for SEM analyses were orthogonally cut using a sectioning machine (TechCut 5TM, Allied High Tech Products Inc., USA) after mounting the sample in epoxy resin (Epokwick® Epoxy resin, Buehler, USA). The thickness of the general corrosion product was measured using SEM images of cross-section samples and the depth of localized corrosion was measured using micro-CT data. Average values and standard deviations were determined after measuring 10 times for each sample. X-ray diffraction (XRD) patterns were obtained using a D8 Discover X-ray diffractometer (Bruker AXS GmbH, Germany) equipped with Cu$K_{\alpha 1}$ radiation source (wavelength λ = 1.5406 Å). The operating voltage and current were 40 kV and 40 mA, respectively, and the step size and speed were 0.01426° per step and 0.3 s per step in the 2θ range 10–80°.

3. Results

Immersion tests were carried out in the various solutions to monitor corrosion in the initial stage for 1 day at 37 °C and to

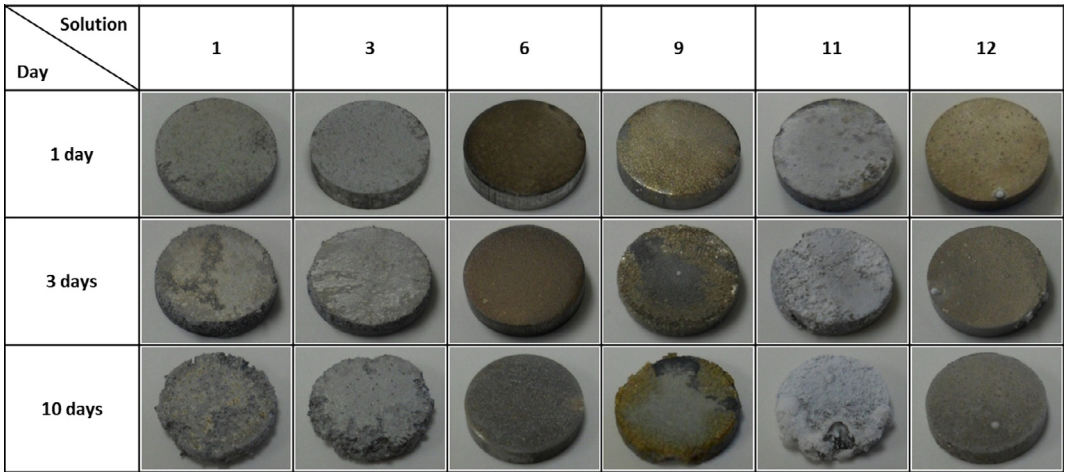

Fig. 1. Optical images of corroded AZ31B after immersion tests in solution.

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