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Initial formation of corrosion products on pure zinc in simulated body fluid

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ABSTRACT

Zinc was recently suggested to be a potential candidate material for degradable coronary artery stent. The corrosion behavior of pure zinc exposed to r-SBF up to 336 h was investigated by electrochemical measurements and immersion tests. The morphology and chemical composites of the corrosion products were investigated by scanning electron microscope, grazing-incidence X-ray diffraction, X-ray photoelectron spectroscopy and Fourier transform infrared spectrometer. The results demonstrate that the initial corrosion products on the pure zinc mainly consist of zinc oxide/hydroxide and zinc/calcium phosphate compounds. The pure Zn encounters uniform corrosion with an estimated corrosion rate of 0.02–0.07 mm y^{-1} during the immersion, which suggests the suitability of pure Zn for biomedical applications.

1. Introduction

Zinc (Zn) was recently suggested as a potential material for degradable coronary artery stents because of its biological merits and ideal degradation rate [1–3]. In human physiology, Zn is considered to be an essential trace element and takes part in many important biological reactions [4]. A major biological role of Zn is that it is closely regulated passage via channels within the cells wall. Once Zn has entered the cytoplasm, it plays many different roles, such as the regulation of DNA replication [5], apoptosis coordination [6], and metal-based enzymes [7]. The recommended dietary allowance (RDA) for Zn is 2 mg d^{-1} for infants, 11 mg d^{-1} for men and 8 mg d^{-1} for women [8]. Some *in vivo* tests reveal that Zn exhibited a strong antiatherogenic character [9], good hemocompatibility [10] along with non-cytotoxicity to endothelial cell [11].

Although Zn is one of the few physiologically relevant metallic elements, it had not received much research attention for application in biodegradable stents prior to 2011. It was shown that Zn degradation proceeds in rat's arteries at a rate of 0.01–0.02 mm y^{-1} [8], nearly identical to the 0.02 mm y^{-1} benchmark value for ideal bioabsorbable materials. However, due to its low tensile strength of <120 MPa [12], which is unacceptable for stent applications, Zn-based alloys with improved ductility, strength and corrosion uniformity have been introduced by several research groups [12–15]. In addition, it was suggested that by using Zn and its alloys, many of the core engineering problems associated with Mg and Fe could be avoided.

Corrosion behavior, including the corrosion rate measurement and formation of corrosion products, is crucial for understanding the basic corrosion processes underpinning absorption of biodegradable metals. However, to date, only a limited number of studies have been reported on the corrosion behavior of Zn in physiological conditions. Cheng et al. [11] compared the corrosion behavior of five pure metals including Zn by electrochemical measurement and static immersion test in Hank's solution. It is found that the corrosion rate of Zn was between Fe and Mn. Chen et al. [16] compared the corrosion behavior of pure Zn with Fe and Mg in phosphate buffered saline (PBS). They found that for transient assays, the corrosion rate placed Zn between Fe and Mg. However, in a long-term course the corrosion rate of Zn developed faster than Fe and Mg because of the unique localized corrosion.

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Liu et al. [17] studied the corrosion of ultra-pure Zn and its mini-tube in Hank's solution, which showed appropriate corrosion rate of 0.027–0.036 mm y^{-1}. Due to lack of suitable standard for corrosion evaluation of Zn-based biodegradable metals *in vitro*, some researches focused on the corrosion profiles of Zn in different corrosive medium. Törne et al. [18] researched the degradation of zinc in saline solutions, plasma, and whole blood. It was not possible to tell which solution was more appropriate to predict the degradation profile of Zn during clinical application. The corrosion mechanism of Zn *in vitro* is still unclear. Thus, in order to better understand the corrosion control of Zn, it is necessary to study its continuous corrosion process during the course of degradation.

Different artificial solutions mimicking the physiological environment, such as PBS, Hank's solution, Ringer's solution, revised simulated body fluid (r-SBF), and human plasma [18–25] have been used for *in vitro* tests. The concentrations of major components of the commonly used test media are listed in Table 1. Compared to whole blood, r-SBF has similar inorganic constituents other than cells and many organic molecules, such as amino acids and proteins. Thus, the r-SBF was selected in this *in vitro* study to simulate the blood plasma.

In order to elucidate the corrosion mechanism, pure Zn was chosen for the tests, with the aim to reduce the effects of other elements that might interfere with the interpretation of the degradation behavior of the matrix. The corrosion behavior of pure Zn immersed in r-SBF was investigated in the present work to provide more details regarding the corrosion processes and mechanisms of pure Zn. This fundamental understanding of *in vitro* study will pave the way for potential biomedical applications.

2. Experimental

2.1. Sample preparation

Zn with 99.99% purity was purchased from China New Metal Materials Technology Co.Ltd. The Zn samples were cut into 2 mm thick discs with a 10 mm diameter. Samples were mechanically ground with silicon carbide sandpapers, polished with diamond abrasive paste, followed by ultrasonic rinsing in milli-Q water, acetone and ethanol successively to remove surface contaminants. The samples were then dried and stored in a vacuum.

2.2. Electrochemical measurements

Electrochemical measurements, including potentiodynamic polarization (PDP) test and electrochemical impedance spectroscopy (EIS), were performed by an electrochemical analyzer (ModuLab XM). A three electrode cell set-up was used wherein the pure Zn samples, saturated calomel electrode (SCE) and a platinum sheet (1 cm × 1 cm) were used as the working, reference and counter electrodes, respectively. For the working electrode, the backside of the samples was connected with a copper wire and then sealed with epoxy to expose the research surface area of 1 cm^2. A stable open circuit potential was established prior to all tests. The potentiodynamic polarization tests were carried out at a constant scan rate of 1 mV s^{-1}, initiating from −1.4 V_{SCE} to −0.5 V_{SCE}. The corrosion potential E_{corr}, corrosion current density I_{corr}, and cathodic Tafel slopes β_c were determined by the Tafel linear extrapolation of the cathodic branches with an over potential of ca. 50 mV. An average of three samples was taken for each group and new samples with corrosion products were prepared for every time point. EIS studies were carried out at open circuit potential of 10 mV sinusoidal amplitude over 100 kHz to 10 m Hz frequency range. Four samples were immersed in the r-SBF and taken out at specific time intervals for the EIS test. The impedance data were analyzed with the ZSimpWin software package and fitted to the equivalent curves. All experiments were conducted at 37 ± 0.1 °C in r-SBF (NaCl 8.035 g L^{-1}, KCl 0.225 g L^{-1}, $NaHCO_3$ 0.355 g L^{-1}, $K_2HPO_4{\cdot}3H_2O$ 0.231 g L^{-1}, $MgCl_2{\cdot}6H_2O$ 0.311 g L^{-1}, $CaCl_2$ 0.292 g L^{-1} and Na_2SO_4 0.072 g L^{-1}).

2.3. Immersion tests

The corrosion behavior tests of Zn samples were carried out by *in vitro* immersion in r-SBF. The pH was adjusted to 7.4 by adding appropriate amount of tris(hydroxymethyl) aminomethane buffer (Tris-HCl). The samples were soaked in the solution with a volume-to-sample area ratio of 20 mL cm^{-2}. Then the samples were immersed in 40 mL r-SBF at 37 °C. During the immersion, the pH values of r-SBF were determined by the FE 20 pH meter (Mettler Toledo). The amount of released zinc ions into the r-SBF was evaluated using an atomic absorption spectrophotometer (AAS, Thermo Scientific M Series). In order to assess the corrosion behavior and the corrosion product formation during the initial degradation stage, the samples soaking up to 336 h were taken out at different temporal intervals and investigated. For different time intervals, the corrosion products on the sample surfaces were removed in the chemical cleaning solution according to ISO 8407 [26]: 100 g/L NH_4Cl for 2–5 min at 70 °C. Afterwards, the samples were rinsed by ethanol and dried before being weighed. The weight loss (mg cm^{-2}) was calculated using the following equation [27]:

$$\text{weightloss} = (m_i - m_f)/A \quad (1)$$

where m_i is the initial weight of the sample before immersion (mg), m_f is the final weight of each sample after immersion (mg), and A is the sample surface area exposed to r-SBF (cm^2). In addition, the corrosion rate derived from weight loss (CR_w, mm y^{-1}) of pure Zn can be calculated by the following equation according to ASTM G31-72 [28]:

$$CR_w = 87.4 \times (m_i - m_f)/(ADt) \quad (2)$$

where m_i is the initial weight of the sample before immersion (mg), m_f is the final weight of each sample after immersion (mg), A is the exposed area (cm^2); D is the alloy density (g cm^{-3}); and t is the immersion time (h).

2.4. Characterization of corrosion products

Surface morphology of Zn samples after immersion was investigated using a scanning electron microscope (SEM, FEI Quanta 200) coupled with an Oxford Instrument INCA X-max^N-sight EDX analyzer. X-ray photoelectron spectroscopy (PHI 5600 XPS spectrometer) was used to characterize the surface chemical states of samples after immersion. The XPS spectra were recorded using AlK_α radiation (1486.6 eV) as excitation source. The chemical groups of the corrosion products were characterized by Fourier transform infrared spectrometer (FTIR, Nicolet 5700) in the 4000–600 cm^{-1} wave number range. Grazing-incidence X-ray diffraction (GIXRD) measurements were conducted on the Smart Lab X-ray diffractometer (Rigaku) with CuK_α radiation at an incident angle of 0.1° to determine the structure of the coatings. The XRD spectra were collected at angles between 10° and 90° at a rate of 0.02° s^{-1}. Reference standards from the Joint Committee on Powder Diffraction Standards (ICDD-JCPDS) database were used to identify the various compounds of the corrosion layer.

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