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Bio-corrosion behavior of magnesium-fluorapatite nanocomposite for biomedical applications

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ABSTRACT

Recent studies indicate that there is a high demand for designing magnesium alloys with adjustable corrosion rates and precipitation ability of bone-like apatite layer on the surface of magnesium alloys in body. An approach to this challenge might be the application of nanocomposites based on magnesium alloys. The aim of this work was fabrication and bio-corrosion evaluation of a nanocomposite that was made of magnesium alloy AZ91 as matrix and fluorapatite (FA) nano particles as reinforcement. Magnesium-fluorapatite nanocomposite (AZ91-20FA) was made via the blending–pressing–sintering method. In vitro corrosion measurements were performed for characterization of initial materials and produced composite. The results showed that the addition of FA nano particles to magnesium alloy as reinforcement can reduce the corrosion rate and accelerate the formation of bone-like apatite layer and in turn provide better protection for matrix alloy. It is suggested that the formation of bone-like apatite layer on the surface of magnesium alloy might contribute to the good osteoconductivity of magnesium alloys.

1. Introduction

The purpose of biodegradable implants is to help tissue regeneration by materials degradation and concurrent implant replacement through the surrounding tissue [1]. Magnesium has been recently recognized as a biodegradable material for bone substitute materials due to its excellent properties, relatively low Young's modulus, proper strength and biocompatibility [2]. While fast corrosion kinetics is generally beneficial in biodegradable implants, the problem for magnesium alloys is that their corrosion rate is too high [3]. Recent studies indicate that there is a high demand for designing magnesium alloys with adjustable corrosion rates [4] and precipitation ability of bone-like apatite layer on their surface in the body [5,6]. An approach to this challenge might be the application of nanocomposites based on magnesium alloys. The advantage of using nanocomposites as biomaterials is the adjustable corrosion properties by choosing the appropriate composites [7].

Calcium compositions were known to reduce the susceptibility of magnesium to corrode when added in amounts of a few tenths of weight percents [8]. As a natural bone composition, hydroxyapatite (HA:$Ca_{10}(PO_4)_6(OH)_2$) is known to possess a low solubility in body environment [7]. In vitro results have shown that fluorapatite (FA: $Ca_{10}(PO_4)_6F_2$) nano particles could provide lower dissolution, better protein adsorption, comparable or better cell attachment than HA and significantly improve alkaline phosphates activity [9]. Also FA nano particles could provide sufficiently low levels of fluoride to act upon surrounding cells for improving bone-like apatite formation [10]. F^- ion promotes the mineralization and crystallization of calcium phosphate in the bone forming process [11]. Recently, FA has attracted much attention and has been increasingly investigated as a clinical restoration material due to the extensive findings of FA in bone and teeth and the favorable effect of fluoride ion on bone growth [12]. Consequently, based on the advantages of FA compared to HA, FA is believed to be a promising choice as the second phase for the fabrication of the AZ91-FA nanocomposites. The aim of the present research was the fabrication and bio-corrosion evaluation of magnesium-fluorapatite nanocomposite.

2. Materials and methods

The magnesium-fluorapatite nanocomposite was produced by mixing AZ91 magnesium alloy powder and 20 wt.% FA nano particles as reinforcement. In order to produce AZ91 magnesium alloy powder, AZ91 billet (nominal composition: 9 wt.% Al and 1 wt.% Zn) was chipped via machining process. These chips were crushed to powder by mechanical ball milling under argon atmosphere. The ball milling parameters were selected as the follows: ball/powder ratio: 15:1, rotational speed: 250 rpm, and time: 12 h. FA nano particles were produced by mixing of calcium hydroxide ($Ca(OH)_2$), phosphorous pentoxide (P_2O_5) and calcium fluoride (CaF_2) by planetary high energy ball milling using zirconia vial and zirconia balls with ball/powder ratio: 35:1, rotational speed: 300 rpm and time: 6 h [9]. Composite fabrication was performed

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through blending–pressing–sintering method. AZ91 magnesium alloy powder with 20 wt.% FA nano particles were mixed by ball milling (ball/powder ratio: 5:1, rotational speed: 150 rpm, and time: 15 min), uniaxial pressing was applied at 880 MPa pressure and the pressed materials were sintered at 400 °C for 1.5 h under argon atmosphere.

Scanning electron microscopy (Philips XL 30: Eindhoven, The Netherlands) and transmission electron microscopy (Philips CM 200 FEG: Eindhoven, The Netherlands) operating at an accelerating voltage of 200 kV, were utilized for microstructure study.

The electrochemical corrosion test was carried out in a Ringer solution at 37 °C. The experimental setup consisted of a conventional three-electrode cell containing the working electrode, a saturated calomel electrode (SCE) and a platinum mesh as the counter. The test was carried out using an Ametek potentiostat (model PARSTAT 2273) and the potentiodynamic polarization was run at a scan rate of 0.5 mV/s initiated at −250 mV below the open circuit potential. The corrosion current was estimated by linear fit and Tafel extrapolation to the cathodic and anodic parts of the polarization curves.

Immersion test of obtained samples was performed by immersing them in simulated body fluid (SBF), because this procedure has been widely used to prove the similarity between in vitro and in vivo behavior of biomaterials [13–15]. The standard SBF solution was prepared according to Kokubo's protocol [16]. The immersion test was performed in temperature control shaking water bath for various times (5, 24, 48, and 72 h) under physiological condition of pH 7.41 at 36.5 ± 0.5 °C. After the pre-selected immersion times, the samples were filtered, rinsed with distilled water and dried in air. The sample's weight was measured before and after the immersion by a balance with an accuracy of 0.001 g. The immersed samples were cleaned using 180 g/l chromic acid to remove the surface corrosion product and then rinsed with ethanol, dried in air and finally weighted to calculate the weight loss (weight before immersion − weight after clean). The corrosion rate was calculated using Eq. (1) [17].

$$CR = W / At \tag{1}$$

Where CR is the corrosion rate, W is the weight loss, A is the original surface area exposed to the corrosive media and t is the exposure time.

Phase structure analysis was carried out by X-Ray Diffractometer (XRD, Philips Xpert) using Ni filtered Cu kα (λ cu kα = 0.154186 nm, radiation at 40 kv) over the 2θ range of 10–90°.

3. Results and discussion

Fig. 1 shows (a) SEM photomicrographs of AZ91-20FA sample and (b) TEM photomicrographs of AZ91-20FA sample. The SEM photomicrograph reveals a relatively uniform distribution of the FA nano particles in the AZ91 matrix. Although, some FA agglomerates can be seen in the matrix from the TEM photomicrograph. One of these agglomerates has been shown by an arrow.

Fig. 2a shows the electrochemical polarization curves of the AZ91 and AZ91-20FA samples in Ringer solution at 37 °C. As it is observed, a significant change of the corrosion current could be observed by adding FA nano particles as reinforcement. The corrosion current (i_{corr}) for AZ91 and AZ91-20FA was 2.5×10^{-4} and 4.3×10^{-6} respectively. Thus, AZ91-20FA shows the lower corrosion current, than AZ91, indicating that AZ91-20FA has better corrosion resistance

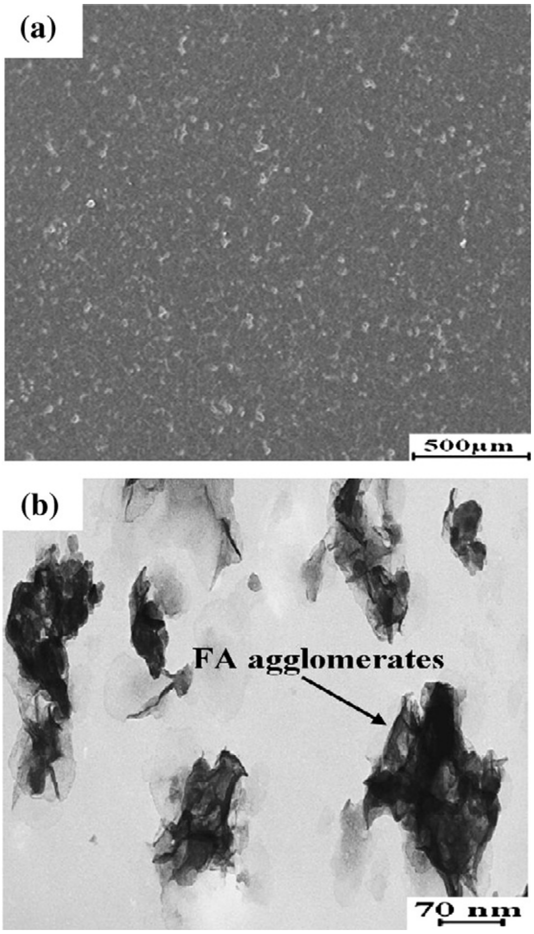

Fig. 1. (a) SEM photomicrograph of AZ91-20FA sample and (b) TEM photomicrograph of AZ91-20FA sample.

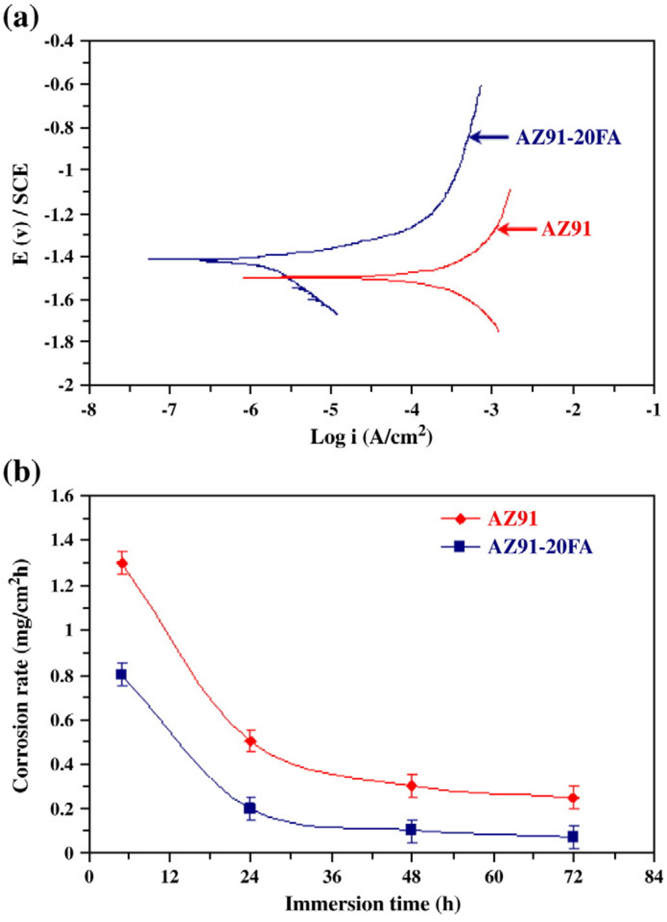

Fig. 2. (a) Electrochemical polarization curves of the AZ91 and AZ91-20FA samples in Ringer solution at 37 °C and (b) variation of the corrosion rate of immersed AZ91 and AZ91-20FA samples in SBF solution as a function of the immersion time.