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Short communication

Fabrication of biodegradable Zn-Al-Mg alloy: Mechanical properties, corrosion behavior, cytotoxicity and antibacterial activities

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ABSTRACT

In this work, binary Zn-0.5Al and ternary Zn-0.5Al-*x*Mg alloys with various Mg contents were investigated as biodegradable materials for implant applications. Compared with Zn-0.5Al (single phase), Zn-0.5Al-*x*Mg alloys consisted of the α-Zn and $Mg_2(Zn, Al)_{11}$ with a fine lamellar structure. The results also revealed that ternary Zn-Al-Mg alloys presented higher micro-hardness value, tensile strength and corrosion resistance compared to the binary Zn-Al alloy. In addition, the tensile strength and corrosion resistance increased with increasing the Mg content in ternary alloys. The immersion tests also indicated that the corrosion rates in the following order Zn-0.5Al-0.5Mg < Zn-0.5Al-0.3Mg < Zn-0.5Al-0.1Mg < Zn-0.5Al. The cytotoxicity tests exhibited that the Zn-0.5Al-0.5Mg alloy presents higher viability of MC3T3-E1 cell compared to the Zn-0.5Al alloy, which suggested good biocompatibility. The antibacterial activity result of both Zn-0.5Al and Zn-0.5Al-Mg alloys against *Escherichia coli* presented some antibacterial activity, while the Zn-0.5Al-0.5Mg significantly prohibited the growth of *Escherichia coli*. Thus, Zn-0.5Al-0.5Mg alloy with appropriate mechanical properties, low corrosion rate, good biocompatibility and antibacterial activities was believed to be a good candidate as a biodegradable implant material.

1. Introduction

Zinc with the standard corrosion potential (−0.8 V vs. Standard Hydrogen Electrode (SHE)) between that of magnesium (−2.37 V vs. SHE) and iron (−0.4 V vs. SHE) is a promising candidate as a biodegradable metal [1]. The concentration of Zn in normal blood serum level is between 12.4 and 17.4 μmol/L which is vital for the immune system [2]. The daily recommendation of Zn for adult and infant is 10 and 2 mg per day, respectively, and it is a co-factor for alkaline phosphatase enzymes in bone and cartilage [3]. Zn and its alloys also present slower degradation rate compared to Mg and its alloys. Besides, it shows good biocompatibility, stimulates bone mineralization, and helps in pathological calcification [2,4]. However, similar to pure magnesium, the clinical use of pure zinc is limited because of its weak mechanical strength with a tensile strength of around 20 MPa and an elongation of about 0.2% [5]. Improvements in mechanical properties can be achieved by adding alloying elements such as Al, Mg, Mn and Sr. Additions of Al to zinc alloys enhance the tensile strength, hardness and corrosion resistance of pure zinc [6,7]. A number of research teams examined histological performance of AZ31 and their obtained results indicated that Mg containing 3 wt.% aluminum does not diffuse into the surrounding tissue during the degradation of the alloy [6–8]. Also, they reported that the small amounts of aluminum released continuously throughout the degradation process can be tolerable [6–8]. As another essential alloying element, Mg and its alloys were utilized for biomedical application in cardiovascular and musculoskeletal fields [3,6,9]. This is attributed to their good biocompatibility, low density, and close elastic modulus to human bone and non-toxicity [3,9]. Furthermore, addition of magnesium to pure Zn could enhance the tensile strength and hardness of pure Zn [1]. However, a study on the mechanical properties, corrosion behavior and antibacterial properties of Zn-Al-Mg alloys with various Mg contents could not be found in the literature. Hence, in the current study, microstructure, corrosion behavior and antibacterial properties of the binary and ternary Zn-based alloys were investigated.

2. Experimental procedure

Zn-based alloys were prepared by melting pure Zn chips (99.9 wt.%), pure Mg ingots (99.9 wt.%), and pure Al (99.9 wt.%) in an electrical

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resistance furnace under protective gas atmosphere (60% Ar/40% CO_2). The elements were placed in a mild steel crucible coated with boron nitride. The crucible was held at the temperature of 580 °C for 20 min to melt the materials and further 10 min to allow for homogenization of the melt. The nominal alloy composition was 0.5 wt.% Al, and 0.1, 0.3 and 0.5 wt.% Mg, with the balance being Zn. X-ray diffractometry (Siemens-D500) was used for phase identification using Cu-Kα radiation generated at 40 kV and 35 mA. Microstructural observation was performed using a scanning electron microscope (SEM; JEOL JSM-6380LA). Tensile tests were performed by using an Instron-5569 universal testing machine at a displacement rate of 2.0 mm/min at ambient temperature according to the ASTM-E8/E8M-08 standard [10]. Tensile test was repeated five times to examine the reproducibility of the results. The average microhardness ($n = 5$, where n indicates the number of replicates) of the alloys was measured with a Vickers hardness tester (Shimadzu) using a 5 kg load. A three-electrode cell was used for potentiodynamic polarization tests (PARSTAT 2263) in simulated body fluid (SBF) solution according to reference [9]. The electrochemical impedance spectra (EIS) were recorded over a frequency range of 0.01 Hz to 100 kHz using a VersaSTAT 3 machine. The samples were stabilized for 30 min according to reference [9]. The immersion test procedure was carried out based on the ASTM standard G31-72. The Kokubo SBF solution was prepared according to the previously reported method [11]. The average pH ($n = 5$) value of the SBF solution from three measurements was recorded during the experiment after an interval of 24 h. The Methylthiazolyldiphenyl-tetrazolium bromide (MTT) method was used to evaluate the MC3T3-E1 cell toxicity of the Zn-based alloys. The details of the MTT test can be preformed according to reference [12]. The antibacterial activity of the binary and ternary Zn-based alloys against *Escherichia coli* PTCC 1330 (Gram-negative bacteria) was investigated according to the disc diffusion antibiotic sensitivity testing. These bacteria were provided from Persian Type Culture Collection, Iran. The glassware was sterilized for 15 min in an autoclave at 121 °C prior to the experiment. The bacteria stock solution was prepared by mixing 5–10 Colony Bacteria Population with a sterile loop in Muller Hinton broth (Merck) and incubated for 24 h and was then compared with turbidity of suspension to 0.5 McFarland standard. For disc diffusion antibiotic sensitivity testing, a Muller-Hinton agar media (Merck) was swabbed with the respective organisms, and each sample was placed on the agar plate and incubated at 37 °C for 24 h in an incubator. The experiment was repeated three times and only the best image was photographed using a digital camera.

3. Results and discussion

Fig. 1 shows the SEM micrographs of the binary Zn-0.5Al which consists of α-Zn solid solution due to the high solubility of Al in Zn which is around 1.1 wt.% at 382 °C. In this regard, it was reported [2] that Zn–Al alloys are composed of a single phase microstructure and coarser grains. However, the ternary Zn-0.5Al-*x*Mg alloys with different Mg contents are composed of α-Zn and $Mg_2(Zn, Al)_{11}$ with a fine lamellar structure (Fig. 1b–d). The energy dispersive X-ray spectroscopy (EDS) analysis of different spot of the area A also revealed this area was composed of Zn (85 ± 2 wt.%), Al (13 ± 1 wt.%) and Mg (2 ± 1 wt.%), which further confirmed the formation of $Mg_2(Zn, Al)_{11}$. Similar elements were observed in area B. On the basis of the analysis, the grain boundaries were enriched with Zn, Al and Mg, indicating that the eutectic phase is composed of the intermetallic α-Zn and $Mg_2(Zn, Al)_{11}$ phases.

The XRD result of binary Zn-Al alloy shows the peaks of α–Zn; however, the ternary Zn-Al-Mg alloy shows the peaks of $Mg_2(Zn, Al)_{11}$ phases in addition to α-Zn (Fig. 2a). The mechanical properties of the binary Zn-0.5Al alloy in comparison with ternary Zn-0.5Al-Mg alloys showed that the ultimate tensile strength (79 ± 2 MPa) and elongation (1.5 ± 0.1%) of the binary alloy increased to 93 ± 3 MPa and 1.7 ± 0.1%, respectively after addition of 0.3 Mg to the binary alloy (Fig. 2b). Furthermore, the UTS and elongation further increase to 102 ± 4 MPa and 2 ± 0.1%, respectively when 0.5 wt.% Mg was introduced to the binary alloy [1]. This can be due to the presence of $Mg_2(Zn, Al)_{11}$ phase which impedes the grain boundary motion and grain growth of ternary Zn-Al-Mg alloy. Kubásek [3] also mentioned that the rows of secondary phases are separated from each other and this factor significantly affects the mechanical properties of the binary Zn-0.8Mg alloy. The hardness value of Zn-0.5Al was 71 ± 2 kg/mm^2, which increases to 79 ± 3 and 87 ± 3 kg/mm^2 with increasing the Mg content in the Zn-0.5Al-0.1Mg and Zn-0.5Al-0.3Mg alloys, respectively. The lower hardness value of binary Zn–0.5Al compared with ternary Zn-0.5Al-Mg alloy is attributed to the higher solubility of Al in Zn and the absence of the secondary phase. It was reported [2] that the presence of Al even at a higher content (1 wt.%) in the binary Zn–Al alloy is less effective in improving the hardness of Zn-based alloys. However, addition of 0.5 wt.% Mg causes the further increase of hardness value to 94 ± 4 kg/mm^2 due to the presence of a higher amount of the secondary phase at the grain boundary which could act as obstructions to grain boundary sliding. Similarly, Mostaed et al. [2] exhibited that the hardness value of binary Zn–Mg alloy is monotonically improved with increasing the Mg content. The

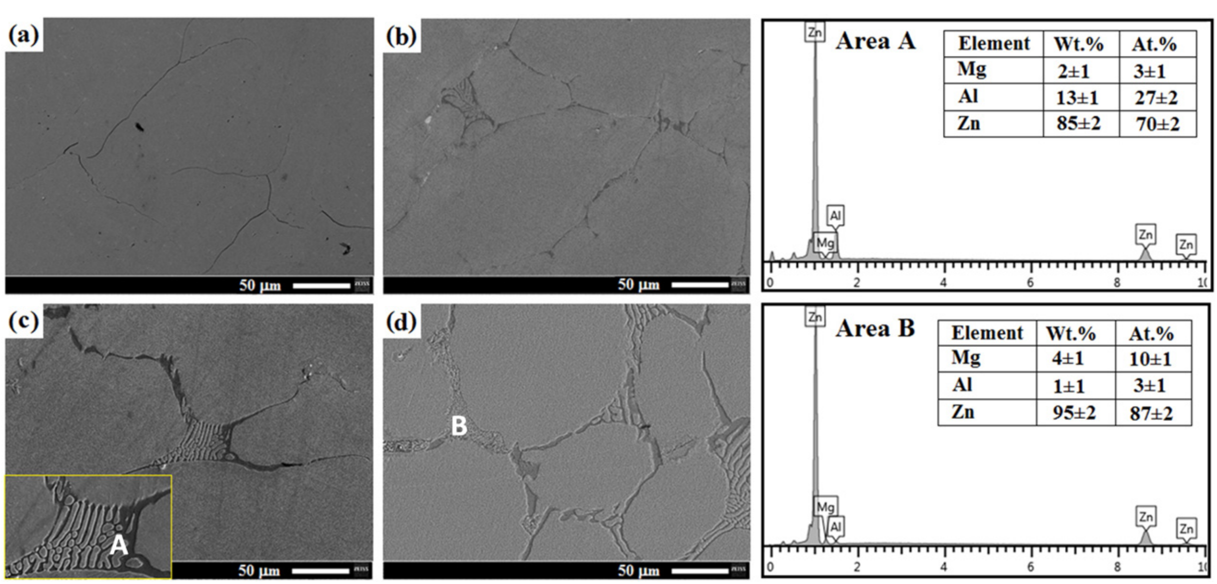

Fig. 1. Surface morphology of (a) Zn-0.5Al, (b) Zn-0.5Al-0.1Mg (c) Zn-0.5Al-0.3Mg and (d) Zn-0.5Al-0.5Mg and corresponding EDS analysis.