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Processing of Zn-3Mg alloy by equal channel angular pressing for biodegradable metal implants

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ABSTRACT

Zn-based alloys have been studied as new biodegradable metals owing to its slower corrosion rate compared to Mg-based alloys and its high potential for mechanical properties improvement. The present work attempts to improve mainly the mechanical properties of a eutectic Zn-3Mg alloy via equal channels angular pressing (ECAP). Cast Zn-3Mg alloy was homogenized at 370 °C for 15 h and quenched in water before subjected to 2 steps ECAP process. Results showed that the process decreases the alloy's grain size from 48 μm in the as cast to 1.8 μm after 2-passes of ECAP. A remarkably increase of yield strength, tensile strength and elongation was achieved from 65 MPa, 84 MPa and 1.3% (as cast) to 205 MPa, 220 MPa and 6.3% (2-ECAP), respectively. Corrosion rate of the alloy was fairly altered from 0.30 mm/year (as cast) to 0.24 mm/year (2-ECAP). The combination of homogenization and ECAP is therefore viewed as a potential process to improve mechanical properties of Zn-Mg alloys.

1. Introduction

Biodegradable metals have been studied as ideal materials for new generation of temporary load bearing medical implants owing to its combination of strength and biodegradability, which is superior to biodegradable polymers and ceramics (Zheng et al., 2014; Nasution and Hermawan, 2016). Magnesium (Mg)- and iron (Fe)-based alloys are the two classes of biodegradable metals mostly studied for those purposes and have been used to for making endovascular stents and bone pins and screws (Wu et al., 2012; Haude et al., 2016; Lee et al., 2016). Their mechanical properties, corrosion behavior and biocompatibility have been extensively investigated and improved to suit closely to the clinical requirements. However, in the in vivo setting, Fe-based alloys exhibit slow corrosion rate whilst most Mg-based alloys degrade too rapidly (Drynda et al., 2015; Hofstetter et al., 2015). Apart of the works to improve the corrosion behavior of these two classes of alloys, alternatively, zinc (Zn)-based alloys have recently been proposed as new potential biodegradable metals (Vojtěch et al., 2011; Bowen et al., 2013; Mostaed et al., 2016). Zinc is an essential element for humans as it supports the function of many enzymes, regulates inflammatory reactions and enhances bioactivity of bone cells (Fosmire, 1990). The cytocompatibility of Zn-based alloys have been studied against various cells such as fibroblast, osteoblast and osteosarcoma giving the evidence of the alloys potentiality for bone implant applications (Murni et al., 2015; Shearier et al., 2016; Shen et al., 2016).

However, the low strength of Zn (~20 MPa) and its brittleness are considered far from ideal for fabricating load bearing implants. But once alloyed Zn, such as Zn-1Mg, the alloy can reach a tensile strength of 150 MPa that is superior strength to some Mg-based alloys (Vojtěch et al., 2011; Gong et al., 2015). Alloying Zn with less than 4 wt% Mg was also reported to enhance the corrosion resistance (Prosek et al., 2008). Alloying of Zn via casting usually results into the occurrence of micro-segregation and thereby additional processes such as heat treatment and extrusion have been used to eliminate this defect (Gong et al., 2015; Dambatta et al., 2015). After being subjected to extrusion, Zn-1Mg alloy exhibited an improvement on both tensile strength and elongation from

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about 150 MPa and 1% to 200 MPa and 10%, respectively (Gong et al., 2015). Further improvement to the mechanical properties should be made possible via severe plastic deformation processes, such as high pressure torsion and equal channel angular pressing (ECAP). These processes have been used to transform micro to ultra-fine or nano-size grains of various Zn-Al alloys for industrial applications (Pürçek, 2005; Al-Maharbi et al., 2010; Aydın, 2012). During ECAP, a metal is subjected to an intense plastic straining through simple shear without corresponding change in its cross-sectional dimension. It was found to be capable of providing an increase in both strength and ductility as observed for cast Zn-Al alloys due to microstructural refinement and elimination or reduction of cast dendritic structure as well as casting defects (Al-Maharbi et al., 2010; Aydın, 2012). This process should be an ideal technique to improve the mechanical properties of cast Zn-Mg alloys specifically targeted for biomedical applications. Therefore, the present study employs an ECAP process to a homogenized cast Zn-3Mg alloy and is aimed mainly to show an improvement in the mechanical properties of the alloy. The Zn-3Mg alloy was selected based on the expectation for facilitating the ECAP at lower processing temperature as 3 wt% Mg is a eutectic composition having the lowest melting temperature (364 °C) in the Zn-Mg system (Vojtěch et al., 2011) and for maintaining corrosion resistance that was found to decrease in Zn-Mg alloys with lower Mg content after subjected to additional thermomechanical processing (Prosek et al., 2008).

2. Materials and methods

2.1. Materials preparation and ECAP process

A Zn-3Mg alloy (3 wt% Mg) was prepared from pure Zn (99.99% purity) and pure Mg (99.95% purity) ingots (Goodfellow Inc., UK) using a conventional casting method. The ingots were melted at 550 °C using an induction furnace protected by a flow of argon. The molten metal was mechanically stirred for 2 min before cast into a preheated (~150 °C) rectangular shaped cast iron mould and then cooled to room temperature. Billets having dimension of 8 × 8 × 120 mm were cut out from the cast and subsequently homogenized under vacuum at 370 °C for 15 h followed by water quenching. The billets were then subjected to ECAP at one pass (1-ECAP) and two passes (2-ECAP) using a hardened steel dies having 8 × 8 mm of square channel section and intersection angle of 120°. A progressive pressing force was applied at a constant speed of 1 mm/s using an Instron-5569 universal testing machine. Molybdenum disulfide was used as the solid lubricant to reduce friction between the die and the billets. The ECAP dies was heated at 200 °C to allow a smooth passage of the billets through the channel without cracking. Cracks were observed on billets processed at 100–190 °C while increasing the temperature above 210 °C led to partial melting of the billets.

2.2. Characterization and mechanical testing

All samples for microstructure observation were longitudinally cut (parallel to the ECAP direction). Their microstructure was observed under an optical microscope (Nikon Microphot-FXL, Japan) after being ground, polished with diamond suspension (from 3 μm to 1 μm) and colloidal silica suspension (0.04 μm), and finally etched with acid solution containing 50 g CrO_3, 15 g Na_2SO_4 in 1 L distilled water at 80 °C. The optical micrographs were used to measure the average grain size and percentage of porosity by using image analysis software (Microvisual Advance, IMT iSolution, Canada) with three replications. The average grain size was measured using ferret diameter which is the average caliper lengths of the grains. Microstructural observation and elemental analysis at higher magnification were done by using a Field Emission Scanning Electron Microscope (FESEM, Zeiss Supra VP35, Germany) equipped with Energy Dispersive X-ray Spectroscopy (EDS, Oxford Instrument, UK). Phase identification was conducted using an X-ray diffraction machine (XRD, Siemens-D500, Germany) with Cu Kα line generated at 40 kV and 35 mA. Further analysis of the XRD pattern was performed to determine the crystallite size of detected phases on both homogenized and ECAP samples using Debye–Scherrer equation: $T = \frac{C\lambda}{B\cos\theta}$, where T is the crystallite size (nm), λ is the wavelength of the X-rays (i.e. 1.541 Å for Cu Kα radiation), C is the shape factor equal to 0.9, θ is the Braggs angle, and B is the full-width at half-maximum (FWHM) of the selected peak (radians). Microhardness measurement was carried out using a Vickers hardness tester (DVK-2 Matsuzawa, Japan) by applying 5 kg load at room temperature for 15 s at five different locations on each polished specimen with three replications. Tensile test was conducted by using a universal testing machine (Instron-5569, Japan) at a constant strain rate of 0.5 mm/min on flat specimens having 9 mm gage length, 40 mm length and 3 mm thickness with at least three replications. The test and the determination of tensile strength, yield strength, maximum elongation and Young's modulus were done in accordance with the ASTM E8M standard (Standard Test Methods for Tension Testing of Metallic Materials).

2.3. Corrosion testing

Corrosion behavior of the metal samples was assessed using both simple immersion and electrochemical polarization methods. Test solution was prepared based on Kokubo's simulated body fluid (SBF) containing the following ions in mmol/L: 142 Na^+, 5 K^+, 2.5 Ca^+ 1.5 Mg^+, 4.2 HCO_3^-, 103 Cl^-, 1 HPO_4^{2-} and 0.5 SO_4^{2-} at adjusted pH of 7.4 (Kokubo and Takadama, 2006). For immersion test, metal samples of 7.9 × 7.8 × 3 mm were prepared, weighed and immersed (in triplicate) in stagnant SBF solution at 37 ± 1 °C. The samples were removed after 21 days and rinsed with distilled water then allowed to dry at room temperature. Prior to corrosion product cleaning, surface morphology, elemental compositions and formed corrosion products were analysed and evaluated. Corrosion products were then removed from the samples by a chemical cleaning as specified in the ASTM G1 standard (Standard Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens). Cleaned samples were then weighed to determine the weight loss. A flame atomic absorption spectrometry (Perkin Elmer, HGA 9000 model) technique was used to determine the concentration of Zn and Mg ions released by the samples into the SBF solution during the immersion test period. Corrosion rate of the samples was calculated by using equation: Corrosion rate = (KW)/(ATD), where the coefficient K = 8.76 × 10^4, W is the weight loss (g), A is the sample area exposed to the SBF solution (cm^2), T is the exposure time (h) and D is the density of the exposed material (g/cm^3). Electrochemical corrosion test was conducted using potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) methods by means of a potentiostat (VersaStat-3, Princeton Applied Research, US). The three-electrode system was used with the metal sample; graphite rod and saturated calomel electrode (SCE) served as the working, counter and reference electrodes, respectively. The test was carried out at 37 °C after 15 min stabilization time at the open-circuit potential (OCP) at a potential range from −200 to +700 mV against the OCP and a scan rate of 2 mV/s. Tafel fitting as suggested by Atrens et al. (2011) was used to approximate the corrosion potential and corrosion current which then used to calculate the corrosion rate of the alloy (CR) using the equation: $CR = 3.27 * 10^{-3} \frac{i_{corr} EW}{\rho}$, where EW is equivalent weight and ρ is density of the alloy.