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### SIGNIFICANCE OF HYBRID HEAT TREATMENT AND ECAPPASSES ON THE DEGRADATION BEHAVIOR OF Zn-3Mg ALLOY FOR POTENTIAL IMPLANT DEVICES

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#### ARTICLE INFO

#### ABSTRACT

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Zn-based alloys were reported as alternative to Mg-based biodegradable materials. Earlier research results on Zn-Mg alloys revealed non-uniform corroded surface, low strength and ductility still remain major limitations for its utilization as implant material. Fabrication methods such as alloying system and heat treatment have been used to enhance the above mentioned properties but little success was noticed. In this study, cast Zn-3Mg alloy was subjected to heat treatment then followed by single equal channel angular pressing (1-ECAP) pass after which its corrosion performance was analyzed. Heat treated Zn-3Mg alloy was successfully processed further using ECAP die at about 200°C. It was noticed that initial heat treatment was able to partially dissolve as-cast dendrite structure. A remarkable improvement on microstructure homogeneity leading to almost ultra-fine grain size was noticed after 1-ECAP pass. In addition, slight enhancement on degradation resistance was noticed on ECAP treated sample compared to as-cast and homogenized samples. This reveals that heat treatment followed by 1-ECAP pass produced an enhanced microstructure of Zn-3Mg alloy which subsequently improved its degradation performance. This encouraging result could enhance the potential of Zn-3Mg alloy to be used for biodegradable implant applications.

#### INTRODUCTION

Up recent, Zn-based alloys have seen an increase in researches aimed towards becoming an alternative biodegradable metal to highly investigated Mg-based and Fe-based alloys for bone fracture fixation and dental implant applications (Kubasek and Vojtech, 2012). These elements are prone to be dissolved in aqueous solution containing chloride ion electrolytes because of their low corrosion potential (Bowen *et al.*, 2013). This new research attention towards zinc-based alloys arose largely because of the success

reported by Zberg *et al.* (2009) on Mg-Zn-Ca bulk metallic glasses (with about 50 wt.% of Zn content). Even though some of the limitations of Mg-based alloys reported within the past few decades still remain unresolved completely, yet, at the moment it remains the most investigated potential biodegradable metal (Zheng *et al.*, 2014). Observed setback on magnesium included fast degradation rate, which causes loss in mechanical properties before implant healing period (Zhou and Gong, 2012) and accumulation of a large amount of hydrogen gas around implant

region due to quick degradation of magnesium implant (Witte *et al.*, 2005). These limitations widen the research areas to other prospective metals with low corrosion potential and suitable to be used in physiological environment such as Zn-based alloys (Cheng *et al.*, 2013). Recently, several studies have been conducted on the potentiality of Zn and Zn-Mg alloys for biodegradable implant applications focusing on their mechanical and degradation properties. The studies recommend an improvement is required on these properties, especially on their strength and ductility (Vojtech *et al.*, 2011). Several approaches such as alloying methods, and heat treatment have been investigated (Wang *et al.*, 2007; Dambatta *et al.*, 2013). Past reports revealed that these two techniques were only able to increase the ductility at the expense of strength and vice versa (Yan *et al.*, 2013).

Recently, there are several attempts to utilize equal channel angular pressing (ECAP) technique (Aydin, 2012) for improving the mechanical and degradation properties of Zn-based alloys by transforming their microstructure into ultra-fine grains (UFG). This technique is capable of producing large and fully dense samples, which resulted in better mechanical and degradation properties (Wang and Zuberova, 2008; Orlov *et al.*, 2011). However, there is limited information on the literature that reports about the application of ECAP technique to improve the degradation properties of as-cast Zn-Mg alloys, especially for biomedical implants. Among the various possible compositions of Zn-Mg alloys, the present study focuses on 3wt% of Mg content (Zn-3Mg). This eutectoid composition has the lowest melting temperature of 364°C and hence, inspires the researchers to use less processing energy (Okamoto, 1994). Furthermore, it was reported that, the degradation resistance of Zn-Mg alloys reduces gradually when Mg contents exceed more than 4wt% (Prosek *et al.*, 2008). This present study aims to investigate the significance of hybrid heat treatment and ECAP pass on the degradation behavior of Zn-3Mg alloy for potential implant devices.

#### **MATERIALS PREPARATION**

High-purity Zn and Mg ingots were used to prepare Zn-3Mg alloy (97wt% of Zn and 3wt% of

Mg) using conventional casting method. The raw materials were melted at 550°C using an induction furnace under argon gas atmosphere. Molten metals were mechanically stirred for 2 minutes to enhance their microstructure homogeneity and then poured into preheated (approx. to 150°C) rectangular shaped cast iron mould. Square samples with size of 8 x 8 x 120 mm were obtained from the casting process. Selected samples were subjected to homogenization treatment using a high-temperature vacuum tube furnace at 360°C for 15 hours dwelling time followed by water quenching. Heat treated samples were further processed through a single ECAP pass at processing temperature of 200 ± 5°C. This temperature allows the processing of the billet without any cracks observed on its surface. The ECAPed samples were extruded at a constant speed of 1 mm/s using Instron-5569 universal testing machine. To reduce the friction between the die and processed samples, molybdenum disulfide (MoS<sub>2</sub>) was used as a solid lubricant. The microstructure of samples was observed using an optical microscope (Nikon Microphot-FXL, Japan) after being ground, polished and etched with an acid solution (50g CrO<sub>3</sub>, 15g Na<sub>2</sub>SO<sub>4</sub> and 1000ml water). Potentiodynamic polarization (PDP) test was conducted using Potentiostat (VersaStat-3, USA) with graphite rod and saturated calomel electrode (SCE) served as the counter and reference electrodes respectively. A Kokubo's simulated body fluid (SBF) was prepared as specified in other works (Santos *et al.*, 2007) and it was used as the electrolyte solution. The temperature and pH of the solution were maintained at 36±1°C and 7.4 respectively. The PDP tests were performed at -0.2 to +0.7 V potential range against the open-circuit potential (OCP) at 2 mV/s scan rate.

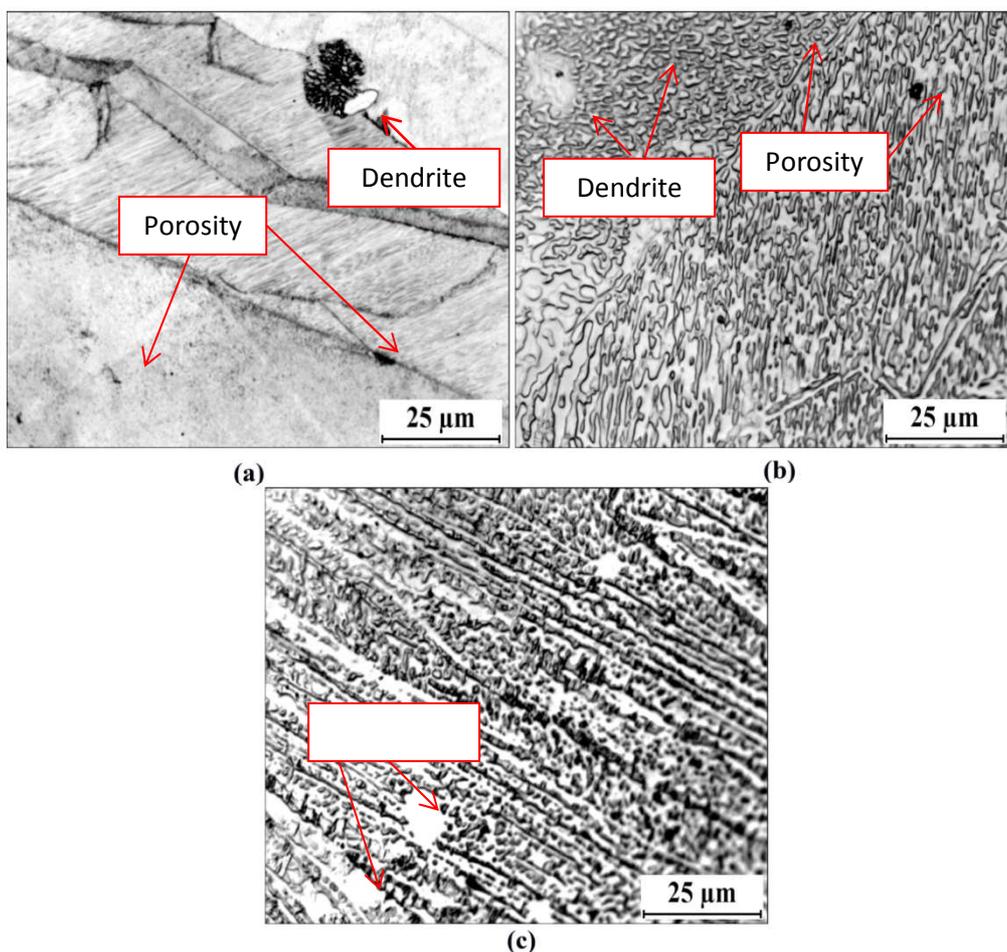
#### **RESULTS AND DISCUSSION**

##### **Microstructure characterization**

Figure 1(a - c) shows the microstructure of as-cast (designated as AC), homogenized (designated as HT), and single ECAP pass (designated as SEP) Zn-3Mg samples. The microstructure, elemental compositions and compound analysis of as-cast and heat treated Zn-3Mg samples were reported in details elsewhere (Farahany *et al.*, 2013).

Cast Zn-3Mg alloy (Fig. 1a) consists of typical casting structure of irregular large lamellar colonies of  $Mg_2Zn_{11}$ , and dendritic shape Zn-rich phases dispersed within the matrix. Heat treatment for a long duration (15hrs) apparently broken dendrite's structures, and transformed them into a fraction of precipitates within the alloy's matrix (Fig. 1b). However, the existence of casting defects (porosity) was observed on both figures 1(a and b). Fig. 1c shows the microstructure of homogenized followed by single ECAP pass

Zn-3Mg sample. Sample processed through a single ECAP pass altered the microstructure significantly and led to refined grains sizes compared to as-cast and only heat treated samples. Single ECAP pass seems able to dissolve and transform the dendrites into connected precipitate within the alloy's matrix with existence of few coarsened dendrites being observed. Heat treatment followed by single ECAP pass led to improve microstructure refinement compared to as-cast sample.



**Figure 1:** Microstructure of Zn-3Mg alloy (a) as-cast, (b) homogenized (c) homogenized followed by single ECAP pass.

**Degradation analysis**

Figure 2 shows the potentiodynamic polarization curves of investigated Zn-3Mg samples. Table 1 indicates the corrosion results obtained from the polarization analysis. Observed from the Tafel extrapolation results on table 1, the corrosion current density ( $I_{corr}$ ) of the tested samples decreases in the

following sequences: SEP < HT < AC. Generally, studies have shown that, the lower the corrosion current density of a sample, the lower its corrosion rate. The above results imply that, heat treatment followed by single ECAP pass slightly retards the degradation rate compared to as-cast and heat treated samples.

This could be attributed to improved microstructure homogeneity, reduced casting defects (porosity) and uniform distribution of Mg<sub>2</sub>Zn<sub>11</sub> phases on heat treated followed by single ECAP pass sample. These findings seem to be in agreement with previous study, which reports that good corrosion resistance of Zn-Mg alloys is connected to the presence of

Mg<sub>2</sub>Zn<sub>11</sub> and MgZn<sub>2</sub> phases, with former given best corrosion resistance (Prosek et al., 2008). Furthermore, since Tafel extrapolation is mainly related to samples initial surface corrosion, this result seems to be in good agreement with previous Tafel result (Zhao et al., 2008).

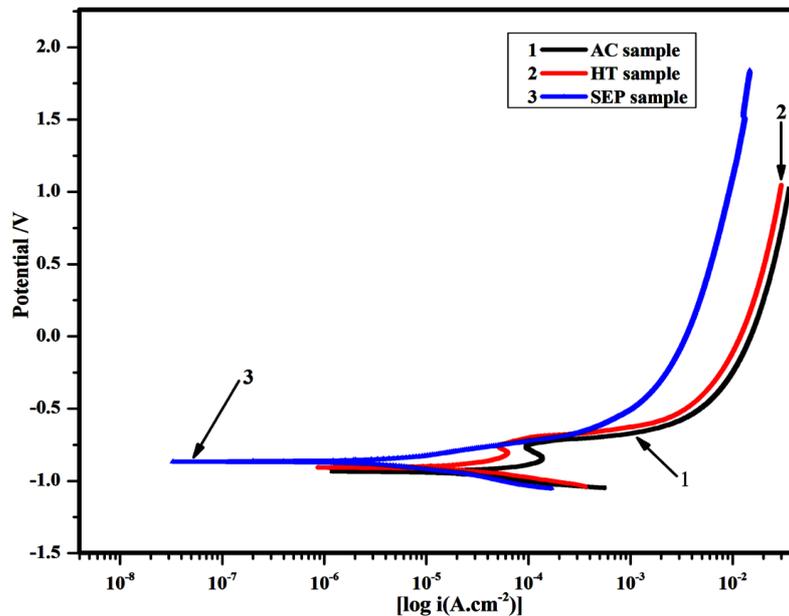


Figure 2: shows the potentiodynamic polarization curves of investigated Zn-3Mg samples.

Table 1: Zn-3Mg samples polarization corrosion and microhardnes results

Sample	E <sub>corr</sub> (V)	I <sub>corr</sub> (μA.cm <sup>-2</sup> )	Corrosion rate (mmpy)
AS	-1.007	4.095	0.316
HT	-1.149	3.396	0.298
SEP	-1.108	2.680	0.235

**CONCLUSION**

ECAP technique was successfully employed on Zn-3Mg alloy at an appropriate processing temperature of 200 ± 5 °C which given surface fracture free samples. Sample subjected to only heat treatment process was able to dissolve some of the as-cast sample dendrite structure. Heat treated samples shows slight improvement on degradation resistance compare to as-cast sample. Significant grain size refinement was observed on heat treated followed by single ECAP pass processed sample. This led to homogeneous microstructure consisting of nearly equiaxed

grain sizes. Hence, conducting heat treatment followed by justa single ECAP pass seems able to improve the degradation resistance of Zn-3Mg alloy. This observed improvement could enhance its potential for biodegradable implant applications.

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