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Influence of zinc on the microstructure, mechanical properties and in vitro corrosion behavior of magnesium–zinc binary alloys

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ABSTRACT

Magnesium–zinc alloy is a potential base material for biodegradable implant applications. In this study, the influence of zinc content (0.5–3 wt.%) in as-cast magnesium–zinc binary alloys towards the microstructure, mechanical properties and in vitro corrosion behaviour was studied. Increase in zinc content reduced the grain size of magnesium–zinc alloy. Mechanical properties such as yield strength, tensile strength and hardness improved with increase in zinc content. Potentiodynamic polarization results suggest that increase in zinc content enhanced the in vitro corrosion resistance of the alloy, which could be attributed to the combined effect of grain size refinement and even distribution of zinc on the alloy surface resulting in better passive film formation.

1. Introduction

Magnesium is considered as a candidate biomaterial for biodegradable implant applications. Magnesium corrodes in the physiological environment and the corrosion product is non-toxic and soluble in body fluid. It should be noted that magnesium is essential to human metabolism and also reported to improve bone strength. In addition, magnesium has similar mechanical properties to natural bone [1–5], especially the elastic modulus as compared to other metallic biomaterials such as stainless steel, titanium and cobalt–chromium alloys, which is a huge advantage over the traditional metallic biomaterials.

In terms of corrosion rate, magnesium exhibits an unacceptably high rate in the physiological conditions, which is indeed a major issue in the application of magnesium as biodegradable implants. Since the corrosion rate of magnesium is extremely high, magnesium implants will dissolve much before the tissues sufficiently heal. Further, large hydrogen gas pockets (due to cathodic reaction) will be created near the implant, which may potentially affect the healing process [6–8].

A wide range of magnesium alloys e.g, magnesium–aluminum–zinc (AZ series), magnesium–calcium, and rare-earth containing alloys, have been studied under in vitro and in vivo conditions for implant applications [6,7,9–13]. Zinc being a biocompatible element, magnesium–zinc alloy has been very attractive for such applications. The literature on in vitro and/or in vivo corrosion behavior of magnesium–zinc binary alloy is limited. Cai et al. [14] reported that the mechanical properties of magnesium–zinc alloys (1, 5 and 7 wt.% zinc) increased until the zinc content reached 5 wt.%, above which the mechanical properties of the alloy decreased. Similarly, they also observed that the in vitro corrosion resistance of 1 wt.% and 5 wt.% zinc-containing magnesium–zinc alloys was significantly higher as compared to pure magnesium, whereas the in vitro corrosion resistance of magnesium–zinc alloy with 7 wt.% zinc was slightly lower than that of the other magnesium–zinc alloys (1 wt.% and 5 wt.% zinc). However, it is important to note that high level of zinc will produce secondary phase particles. Although, the general in vitro corrosion resistance has been reported to improve by high zinc alloying, it may affect the localized corrosion behaviour due to galvanic effect, i.e., the electrochemical potential difference between the matrix

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Table 1
Chemical compositions of the as-cast magnesium–zinc binary alloys.

Alloy	Composition wt.%						
	Zn	Al	Mn	Cu	Fe	Ni	Mg
Mg–0.5Zn	0.52	0.002	0.004	0.0004	0.003	0.0005	Balance
Mg–1Zn	0.98	0.003	0.003	0.0003	0.004	0.0004	
Mg–2Zn	2.02	0.002	0.004	0.0005	0.002	0.0005	
Mg–3Zn	2.97	0.004	0.002	0.0004	0.004	0.0002	

Table 2
Chemical composition of simulated body fluid (SBF) [16].

Reagents	Amount
NaCl (g)	8.036
$NaHCO_3$ (g)	0.352
KCl (g)	0.225
$K_2HPO_4 \cdot 3H_2O$ (g)	0.230
$MgCl_2 \cdot 6H_2O$ (g)	0.311
1 M HCl (mL)	40
$CaCl_2$ (g)	0.293
Na_2SO_4 (g)	0.072
TRIS[a] (g)	6.063
1 M HCl (mL)	0.2

[a] TRIS = tris (hydroxylmethyl) aminomethane.

and secondary phase particles could cause corrosion. Recently, Kubàsek et al. [15] studied the biocorrosion behavior of Mg–Zn (1 and 3 wt.% Zn) in a chloride-containing solution (9 g/l NaCl solution) at an initial pH 6.5. They also reported that addition of zinc (1 wt.%) to magnesium improved the corrosion resistance of the alloy, but interestingly they observed that 3 wt.% zinc-containing alloy showed lower corrosion resistance than that of the 1 wt.% zinc-containing alloy, which is in contradiction to Cai et al. [14] work. Hence, there is a need for further study on the binary magnesium–zinc alloys, especially low level of zinc-containing magnesium–zinc alloys where the size and volume fraction of the detrimental secondary phase particles are expected to be low. In this study, the influence of low level of zinc-containing (0.5–3 wt.%) magnesium–zinc alloys on the mechanical properties and in vitro corrosion in simulated body fluid was studied.

2. Experimental methods

High purity magnesium (99.99 wt.%) and zinc (99.999 wt.%), which were purchased from Bilginoglu Industry in Turkey, were used to prepare magnesium–zinc binary alloys by melting magnesium in a graphite crucible under argon gas atmosphere at 750 °C. Zinc additions were made 1 min before casting for avoiding losses of zinc due to vapourisation. The molten alloy was then cast into a cast-iron mould (preheated to 250 °C) having 20 mm diameter and 200 mm length under protective CO_2+%0.8 SF_6 mixed gas. The chemical compositions of the alloys were analysed using a chemical analysis method (Spectrolab M8 Optical Emission Spectrometry (OES)), and they are presented in Table 1.

For microstructure analysis and in vitro corrosion experiments, samples (diameter = 17 mm and thickness = 8 mm) were cut from the ingot and ground with SiC paper up to 2500 grit and polished with 1 μm alumina solution followed by ultrasonic cleaning in acetone. The samples were also etched with 3.5 g picric acid, 6.5 ml acetic acid, 20 ml distilled water and 100 ml ethanol and then observed under optical microscope (Leica DM ILM) for microstructure analysis. Microstructures were also investigated using a Zeiss Supra 40 V scanning electron microscope (SEM) including energy-dispersive X-ray analysis (EDX) to determine the distribution of secondary phase particles. X-ray Diffraction (XRD) experiments were carried out on a PANalytical Empyrean X-ray diffractometer with monochromated CuKα radiation.

In order to measure the density of the Mg–Zn binary alloys,

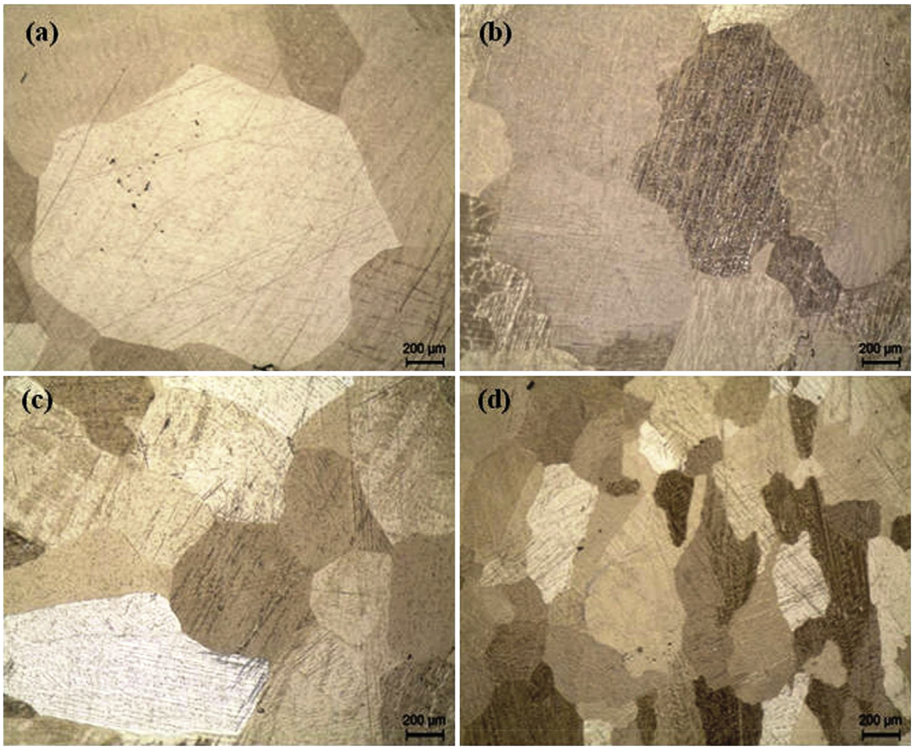

Fig. 1. Optical microstructures of as-cast magnesium–zinc alloys: (a) Mg-0.5Zn, (b) Mg–1Zn, (c) Mg–2Zn and (d) Mg–3Zn.