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Research paper

Strengthening of Mg based alloy through grain refinement for orthopaedic application

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A B S T R A C T

Magnesium is presently attracting a lot of interest as a replacement to clinically used orthopaedic implant materials, due to its ability to solve the stress shielding problems, biodegradability and osteocompatibility. However, the strength of Mg is still lower than the requirement and it becomes worse after it starts degrading fast, while being exposed in living body environment. This research explores the effectiveness of 'grain refinement through deformation', as a tool to modify the strength (while keeping elastic modulus unaffected) of Mg based alloys in orthopaedic application. Hot rolled Mg-3 wt% Zn alloy (MZ3) has been investigated for its potential in orthopaedic implant. Microstructure, mechanical properties, bio-corrosion properties and biocompatibility of the rolled samples are probed into. Grain size gets refined significantly with increasing amount of deformation. The alloy experiences a marked improvement in hardness, yield strength, ultimate tensile strength, strain and toughness with finer grain size. An increment in accelerated corrosion rate is noted with decreasing grain size, which is correlated to the increased grain boundary area and mechano-chemical dissolution. However, immersion test in simulated body fluid (SBF) reveals reduction in corrosion rate after third day of immersion. This was possible owing to precipitation of protective hydroxyapatite (HA) layer, formed out of the interaction of SBF and the alloy. More nucleation sites at the grain boundary for fine grained samples help in forming more HA and thus reduce the corrosion rate. Human osteosarcoma cells show less viability and adhesion on grain refined alloy.

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1. Introduction

Biodegradable implants have attracted a great deal of attention in recent time (Lu et al. 2014; Song et al. 2009; Zhang et al., 2010; Guan et al., 2013). Characteristics of an ideal implant include good mechanical strength, biocompatibility and corrosion rate, which must match with the healing rate of tissues. Magnesium (Mg) and its alloys are currently receiving much attention due to their potential as orthopaedic implants and devices. This is because of their low density of 1.78–2.0 g/cm^3 (Guan et al., 2013) comparable to that of human bone (1.8–2.1 g/cm^3) (Xue-Nan and Zheng, 2010). The Young's modulus of Mg alloys ranges between 35–45 GPa, which is also in similar range to that of natural bone (3–20 GPa) (Xuefei et al., 2013). As a result, when used as implant, Mg alloys can reduce the stress shielding effect on the surrounding bone. In addition, Mg alloys are found to have good machinability, castability, weldability and formability at elevated temperature (King 2007), all of which make it easier to synthesize orthopaedic implants of complicated shapes. Furthermore, Mg plays an important role in bone fracture healing and implant stabilization (Zhen et al., 2013; Kanazawa et al. 2007; Littlefield et al., 1991). The Young's modulus of other clinically used orthopaedic implant materials are as follows: 200 GPa for 316L stainless steel, 105–125 GPa for Ti alloys and 240 GPa for CoCrMo alloys (Long, 1998). A vast mismatch of mechanical properties and elastic modulus causes severe stress shielding effect, leading to reduction in density and thinning of bone (Chen and Thous, 2015). Mg and its alloys, with similar density and mechanical properties of bone, can be a great solution to this problem. Further, biodegradability of Mg can be an added advantage, as the implant would be totally replaced by growing bone tissue. This would ensure no requirement of second surgery to retrieve temporary implants/prosthesis.

However, as cast pure magnesium offers low tensile strength of $\sim$50 MPa and poor ductility of $\sim$6% (Li et al., 2013). The strength of human cortical bone lies in the range of 90–190 MPa (Bandyopadhyay and Bose, 2013). Further, Mg possesses low formability at room temperature due to its HCP structure, with limited number operative slip planes. Hence, pure Mg is not suitable as bone implant as it does not take much load before failing. Another major problem with Mg, in any commercial application, is its high corrosion rate in aqueous environment, which persists as a problem for orthopaedic application also. Magnesium is very reactive with a standard electrode potential of -2.37 V, with respect to standard hydrogen electrode (SHE). It has the Pilling–Bedworth ratio less than 1 ($\sim$.79) (Aallison and Cole, 1993), which indicates its oxide film cannot effectively protect the alloy. Thus, it degrades fast in Chlorine ion containing medium. Alloying elements, like Al, Zn, rare earth elements, are often found effective in reducing the corrosion rate of Mg and are used widely in commercially available Mg alloys.

Researchers have studied various commercially available Mg alloys for orthopaedic application. Mg alloys, like, AE21, AZ31, AZ91(having Al, Mn and Zn as alloying addition), Mg–Zn–Y etc. (Zhang et al., 2010; Zhen et al., 2013) are studied to find out their suitability as biocompatible and biodegradable orthopaedic implant. Their corrosion products have been found to be physiologically useful (Lowe and Valiev, 2014). AZ31 and AZ91 (Zhen et al., 2013) are found to effectively enhance the osteogenesis response and help in new bone formation, which is demonstrated by higher mineral deposition rate. Higher osteoblastic activity is been predicted with better tensile strength in AZ91, as compared to pure magnesium, owing to the alloying elements present in the former (Chung et al., 2009; Muller et al., 2007).

However, presence of Al or/and rare earth elements above a certain level makes the Mg-alloys inappropriate for biomedical application in long term exposure. For example, presence of $>$2.8 mol% of Al^{3+} ion in human brain causes Alzheimer's disease and dementia (Gupta et al., 2005; El-Rahman, 2003). Rare Earth elements (Pr, Ce, Y, etc.) can cause hepatotoxicity (Nakamura et al., 1997). Song et al. (2007) has pointed out Ca, Mn and Zn as biocompatible alloying elements to Mg for bio-medical application. Human body usually contains approximately 24 g of Mg per 70 kg body weight (Touyz, 2003) and daily demand for Mg in human body is around 350 mg/day. Normal Mg content in the human blood is in the range of 1.7–2.22 mg/dL (Lowe and Valiev, 2014). Zinc is also essential for human body (Tapiero and Tew, 2003). It is associated with the activities of more than 300 enzymes. Further, Zn stimulates bone formation and inhibits bone resorption (Yamaguchi et al., 1987; Yamaguchi, 1998). Moreover, both Mg and Zn, if in excess, get excreted out through urinal route (Barker et al., 1959; McCance and Widdowson,1942). Hence, an alloy of Mg and Zn is not supposed to create any serious issue, if used as biodegradable implant material. Calcium could be another choice as alloying element, considering its biocompatibility and osteo-conductivity. However, Ca-rich oxides, produced as corrosion products, are insoluble and 'chalk-like'. This could cause problems *in-vivo,* if piled up rapidly. In addition, presence of calcium makes the Mg-alloy brittle by significantly reducing the failure strain (Chen and Thous, 2015).

Both Zn and Mg have HCP crystal structure. Zinc is generally added to strengthen the alloy by solid solution strengthening mechanism (Mordike and Lukac, 2006) and ageing. Addition of Zinc up to 3 wt% provides an increment in strength. However, beyond this amount, the intermetallic precipitates act as crack initiation sites and reduce the ductility (Gao et al., 2008). Zinc also enhances the corrosion resistance of Mg alloy (Gao et al., 2008). MgZn intermetallic phase is reported to be formed as precipitate up to 3 wt% of Zn addition in Mg. Beyond that, a new intermetallic phase, $Mg_{51}Zn_{20}$, is formed. This one is more prone to corrosion and increases the corrosion rate of the alloy, acting as anodic site (Lotfabadi et al., 2013). Hence, considering both mechanical and corrosion behaviour, Mg–3Zn is the found to be the best composition for orthopaedic application.

However, the strength of these alloys is often not enough for orthopaedic application. The aim is to keep the elastic modulus close to that of bone for reducing stress shielding effect, while increasing the strength and ductility to achieve higher toughness. Simultaneous improvement in ductility, formability and strength can only be achieved by grain refinement (Mohri, 1998). Severe plastic deformation (SPD) is a method for improving the strength of polycrystalline