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Microstructures, mechanical properties, and degradation behaviors of heat-treated Mg-Sr alloys as potential biodegradable implant materials

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ABSTRACT

In previous studies, Mg-Sr alloys exhibited great biocompatibility with regard to test animals, and enhanced peri-implant bone formation. The objective of the present study was to investigate the effects of heat treatments on the mechanical and corrosion properties of Mg-Sr alloys. Various heat-treated Mg-*x*Sr (x = 0.5, 1, and 2 wt%, nominal composition) alloys were prepared using homogenization and aging treatments. Mechanical tests were performed at room temperature on the as-cast, homogenized, and peak-aged alloys. As the Sr content increased, the volume fraction of $Mg_{17}Sr_2$ phases within the as-cast alloys increased; in addition, the mechanical strength of the alloys initially increased and subsequently decreased, while the ductility decreased. Following the homogenization treatment, the mechanical strength of the alloys decreased, and the ductility increased. Nano-sized $Mg_{17}Sr_2$ phases were re-precipitated during the aging treatment. The age-hardening response at 160 °C was enhanced as the Sr content increased. Following the aging treatment, there was an increase in the mechanical strength of the alloys; however, there was a slight reduction in the ductility. Immersion tests were conducted at 37 °C for 360 h, using Hank's buffered salt solution (HBSS), to study the degradation behavior of the alloys. As the Sr content of the Mg-Sr alloys increased, the corrosion rate (CR) increased owing to the galvanic effect. The homogenization treatment consequently reduced the CR dramatically, and the aging treatment had a slight effect on the CR. The peak-aged Mg-1Sr (wt%) alloy exhibited the best combination of properties. The tensile yield strength (TYS), ultimate tensile strength (UTS), elongation, compressive yield strength (CYS), ultimate compressive strength (UCS), compressibility, and CR of the as-cast Mg-1Sr (wt%) alloy were 56.0 MPa, 92.67 MPa, 1.27%, 171.4 MPa, 243.6 MPa, 22.3%, and 1.76 mm/year, respectively. The respective results obtained for the peak-aged Mg-1Sr (wt%) alloys were 69.7 MPa, 135.6 MPa, 3.22%, 183.1 MPa, 273.6 MPa, 27.6%, and 1.33 mm/year. Following immersion in HBSS, the primary corrosion products of the peak-aged Mg-1Sr (wt%) alloy were $Mg(OH)_2$, MgO, $MgCO_3$, $Mg_3(PO_4)_2$, $MgHPO_4$, and $Mg(H_2PO_4)_2$, which enhanced the corrosion resistance by forming a composite corrosion film.

1. Introduction

Mg alloys have great potential to serve as biodegradable implant materials for medical applications because of their significant functions, appropriate mechanical properties, and controllable degradation behaviors in biological systems (Li and Zheng, 2013; Staiger et al., 2006; Witte, 2010). Mg is an element that is essential for the nutrition of the human body; for adults, the recommended allowance of Mg is 420 mg/day (Erdman Jr. et al., 2012; Murphy, 2002). Moreover, 50–60% of the Mg in the human body exists in the bones, and it plays an important role with regard to bone formation (Aydın, 2013; Erdman Jr. et al., 2012; Schwartz and Reddi, 1979). In addition to its excellent biocompatibility, Mg also has a low density of 1.74 g/cm^3, and a low Young's modulus of 41–45 GPa compared with those of titanium alloys (110–117 GPa), stainless steels (189–205 GPa), and cobalt-chromium alloys (230 GPa) (Avedesian and Baker, 1999; Staiger et al., 2006). The density and Young's modulus of cortical bones are 1.8–2.1 g/cm^3 and 3–20 GPa, respectively (Staiger et al., 2006). Hence, the stress-shielding effect caused by Mg-alloy implants is lower than those of other metal implants (Staiger et al., 2006).

Though Mg alloys offer remarkable advantages as biodegradable implant materials, their low strength and high corrosion rate (CR) in biological systems limit their use in medical applications (Makar and Kruger, 1993; Song, 2007). Mg-alloy implants always lose functional integrity before the diseased tissues heal completely (Chen et al., 2014). The high degradation rate of such implants can also increase the local

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Mg-ion concentration and pH value (Witte et al., 2005). Moreover, it will accelerate the hydrogen evolution process, which can lead to the deterioration of the surrounding tissues (Virtanen, 2011). Since the microstructures of Mg alloys strongly influence their corrosion behaviors and mechanical properties, methods such as alloying and heat treatments are considered effective approaches to overcome the aforementioned issues (Aung and Zhou, 2010; Chen et al., 2015). A number of Mg alloys, such as AZ91, WE43, Mg-Dy-Gd-Zr, Mg-Ca, Mg-Zn, and Mg-Ag, have been studied with regard to clinical applications (Adams et al., 2016; Čížek et al., 2004; Gu et al., 2009; Mengucci et al., 2008; Tie et al., 2012; Zhang et al., 2014, 2010). The results of these studies have shown that alloying and heat treatments can obviously improve the mechanical properties and corrosion resistance of such alloys.

Sr is a trace element that exists in the human body; 99% of the Sr in the human body exists in the bones (Schroeder et al., 1972). Sr is a natural bone-seeking element that accumulates in skeletons, preferentially in new trabecular bones, and is used in the anti-osteoporosis drug Strontium Ranelate (Bornapour et al., 2013; Jørgensen and Schwarz, 2011; Tie et al., 2016). Moreover, when Sr is added in excess of the solid solubility limit of Mg, it will segregate to the grain boundaries or intermetallic particles on the grain boundaries, and these particles will induce grain refinement via the grain-growth restriction mechanism (Cheng et al., 2013; Lee et al., 2000; StJohn et al., 2013). The addition of Sr is proven to improve the strength and corrosion resistance of Mg alloys (Bornapour et al., 2015; Brar et al., 2012; Zhao et al., 2017). Gu et al. studied hot-rolled Mg-Sr binary alloys as biodegradable metals; they found that amongst the studied alloys, the as-rolled Mg-2Sr (wt%) alloy exhibited the highest strength and lowest CR (Gu et al., 2012). As-rolled Mg-2Sr (wt%) has also exhibited acceptable biocompatibility during in vitro and in vivo studies, and promotes bone mineralization and formation without significant adverse effects (Gu et al., 2012). During our previous research, as-rolled Mg-1Sr (wt%) alloys exhibited appropriate corrosion properties and biocompatibility in test animals, and the addition of Sr enhanced the peri-implant bone formation compared with the pure-Mg reference group (Tie et al., 2016). Their acceptable osteogenic properties, mechanical properties, and degradation properties indicate that Mg-Sr alloys can be applied as biodegradable implant materials (Tie et al., 2016).

However, the effects of homogenization and aging treatments on the mechanical and degradation properties of Mg-Sr alloys are seldom reported. In this study, Mg-0.5Sr, Mg-1Sr, and Mg-2Sr (wt%; respectively designated as J0, J1, and J2 alloys in accordance with ASTM B951-11 standard) alloys were designed to study the microstructures, mechanical properties, and degradation behaviors of the heat-treated Mg-Sr alloys (ASTM, 2011). The microstructures of the Mg-Sr alloys were analyzed, as well as the effects of the heat treatments. The mechanical properties were investigated at room temperature. The corrosion properties were evaluated using immersion tests. X-ray photoelectron spectroscopy (XPS) was used to identify the corrosion products. Based on the results, the effects of the heat treatments on the Mg-Sr alloys, as biodegradable materials, were determined.

2. Material and methods

2.1. Alloy preparation

The J0, J1, and J2 alloys consisted of a Mg matrix with nominal Sr contents of 0.5, 1.0, and 2.0 wt%, respectively. The alloys were prepared using high-purity Mg (99.99 wt%; Boyu, Shenyang, China) and a Mg-20 Sr (wt%) master alloy (Boyu, Shenyang, China). High-purity Mg was melted in a Ni-free duplex stainless steel (Fe-20Cr-10Mn-3Mo-N) crucible under a protective atmosphere (Ar + 2% SF6) at 750 °C. The Mg-20 wt% Sr master alloy was added to the melt at 720 °C. The melt was stirred for a period of 30 min at 200 rpm, purged at 710 °C for 10 min, and then held at 700 °C for 15 min under protective gas to achieve the homogenization of the alloying elements and the settlement of the impurities. The melt was cast into a H13 steel mold, which was preheated to 400 °C, and solidified in air. The ingots had dimensions of 60 × 120 × 200 mm^3. Following casting, specimens were cut from the central sections of the ingots for further investigation. The homogenization treatment was executed at 450 °C for 12 h, followed by water quenching. The aging treatment was performed at 160 °C over periods of 30–300 h; this was followed by water quenching.

2.2. Compositional analysis and microstructural characterization

The chemical compositions of the alloys were analyzed using an inductively coupled plasma-optical emission spectrometer (ICP-OES; VARIAN, Palo Alto, USA) (ASTM, 2015). The specimens intended for microstructural characterization were ground with emery papers up to 3000 grit, and mechanically polished with 0.5-μm diamond paste. Following polishing, an ultrasonic cleaner was used to clean the surfaces of the specimens. Then, the specimens were etched using a solution consisting of 2.1 g of picric acid, 5 ml of glacial acetic acid, 5 ml of distilled water, and 35 ml of ethanol. An optical microscope (DSX500; Olympus, Japan) with a polarization system was applied to characterize the optical microstructure. The average grain sizes were measured using the line-intercept method (ASTM, 2013). A scanning electron microscope (SEM, SSX-550; Shimadzu, Japan) equipped with an energy dispersive X-ray spectroscopy (EDS) instrument was utilized to observe the microstructure and analyze the surface elemental composition.

Transmission electron microscopy (TEM) specimens were prepared by punching 3-mm-diameter discs from ~200-μm-thick foils, which were cut from the products. The specimens were subsequently mechanically ground to ~120 μm. The 3-mm-diameter discs were then twin-jet-electropolished, using a solution of 2.5 vol% $HClO_4$ in ethanol, at −45 °C and 40 V. The TEM examinations were performed using a TEM instrument (Tecnai G220; FEI, USA), which was operated at 200 kV, for the phase identification.

X-ray diffraction (XRD) measurements were also employed for the phase analysis. An X-ray diffractometer (X' Pert Pro; Philips, Netherlands) was operated under an asymmetric 2θ scanning mode, with Cu $K\alpha_1$ radiation (wavelength λ = 0.15406 nm) and an X' Celerator detector. The initial angle was 20° and the final angle was 90°. The step length was 0.02°, and the duration of each step was 3 s. The diffraction peak of the β phase was simulated using X' Pert Highscore Plus software (version 2.1).

2.3. Mechanical tests

A Vickers hardness testing machine (450SVD; Wolpert, USA) was used for the hardness measurements, using a load of 500 g for 10 s. Five points were tested for each test condition. Tension and compression tests were executed at room temperature using a universal testing machine (CMT5305; MST, Shanghai, China), according to the standards of ASTM E8/E8M and ASTM E9 (ASTM, 2009, 2016). Tensile specimens with a gauge length of 30 mm, diameter of 6 mm, and threaded heads of 10 mm were used. Compression specimens with a diameter of 11 mm and length of 16.5 mm were used. Both the tension and compression tests were performed at a strain rate of 1×10^{-3}/s. For each test condition, five specimens were examined.

2.4. In vitro immersion tests

Weight loss tests were performed using Hank's buffered salt solution (HBSS) at 37 °C. The composition of the HBSS is listed in Table 1 (Tie et al., 2010). Specimens, with dimensions of 10 × 10 × 10 mm^3, were machined for the immersion tests. Each surface was ground with emery papers up to 3000 grit, and sterilized with 70% ethanol for 15 min prior to the immersion tests. All the subsequent procedures were performed under sterile conditions at 37 °C. The specimens were immersed in 50 ml of HBSS for 12 h to achieve pre-corrosion conditions, and