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Mechanical properties and corrosion resistance of hot extruded Mg–2.5Zn–1Ca alloy

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ABSTRACT

It is demonstrated that the mechanical properties and corrosion resistance of Mg–2.5 wt%Zn–1 wt%Ca alloy are enhanced by the microstructural changes imparted by hot extrusion. A processing procedure is developed to form hollow tubes with an outer diameter of ~2.0 mm and wall thickness of ~0.1 mm, which is well suited for subsequent stent manufacturing. The influence of thermal and mechanical processing on corrosion and plasticity was found to be associated with grain-size reduction and the redistribution of intermetallic particles within the microstructure, providing significant improvement of performance over the cast alloy. Observation of the fracture surfaces reveals a mode transition from brittle (cast) to ductile (processed). Enhanced mechanical properties and decreased resorption rate represent significantly improved performance of this alloy after the novel processing sequence. Based on the improved properties, the produced Mg alloy is more suitable for practical *in vivo* applications.

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1. Introduction

Biodegradable implants with satisfactory mechanical properties provide significant advantages in certain applications, as the requirement for a second surgical procedure for removal is eliminated. Early use of magnesium alloys as a resorbable biomaterial dates from the 1930s [1,2]. One problem commonly encountered is that the rapid corrosion experienced in the body, leading to the accumulation of subcutaneous gas bubbles [3]. The interest in magnesium alloys has been reactivated as new compositions with much lower dissolution rates have been developed.

Degradable magnesium alloys have significant advantages over biodegradable polymers and ceramics as potential biomaterials due to their appropriate mechanical properties and excellent biocompatibility, especially in cardiovascular disease treatment [4,5]. Conventional implant stents typically use corrosion resistant metals such as stainless steels, Ti, Co, and Cr based alloys. The stents remain in the body permanently even when they are no longer needed [6,7]. Biodegradable polymers and ceramic-based composites, although promising, but they may not provide sufficient strength, ductility, or biocompatibility for orthopedic applications [8,9]. It is therefore essential for an orthopedic biodegradable implant to have a degradation rate that matches the healing or regeneration process of blood vessels.

The advantages of Mg alloys over other biomaterials as a replacement of permanent vascular implants have attracted considerable attention [10]. However, both *in vitro* and *in vivo* evaluations of the current Mg alloys show that they degrade much faster than desired [11,12]. Therefore, there is of great interest to enhance the mechanical properties and reduce the corrosion rate to satisfy the requirements of cardiovascular disease treatment in biological stress environment [13]. Magnesium alloys are difficult to deform because of the poor ductility caused by their hexagonal structure and limited slip systems. Thus, it is necessary to develop processes that can simultaneously enhance the plasticity and control the rate of biodegradation.

Numerous studies have addressed separately the mechanical or corrosion properties, while none of them considered the influence of processes on both performance aspects of implant stents. It is desirable to maintain the required mechanical strength of Mg alloy implant stent when it degrades at a prescribed rate. From the corrosion perspective, different surface modification techniques have been used for improving corrosion resistance [14–16]. However, the rate of degradation increases sharply once the specially treated surface is dissolved [17–19]. For most metals, improvements

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in mechanical properties and corrosion resistance can also be effectively achieved through alloying and processing [20,21]. In addition, for medical Mg alloys, the biocompatibility of many alloying elements is limited [22–24]. Moreover, most of the research on biodegradable Mg alloys focused on original alloys, ignoring the dynamic response when it is processed from one state to another. Some processing steps are necessary for the manufacture of the implant stent when it is transformed from the original alloy to the desired geometrical shape. Thus, the properties of alloys are inevitably altered in this process [25]. Based on the complicated processing routines for a precise micro-tube, the difference between processed samples and original ones are explored in this work.

Ca and Zn elements are reported to have good biocompatibility [19,23,26]. The mechanical and corrosion properties of cast Mg–Zn–Ca with different compositions have been extensively investigated as the most promising biodegradable materials. It is also reported that yield strength of Mg alloys increased with RE additions, corrosion rates also systematically increased, however, this depended on the type of RE element added and the combination of elements added [27]. In this paper, based on design of alloy composition, we introduced a typical processing sequence required for forming Mg–Zn–Ca alloy tubes with ~2 mm outer diameter and ~0.1 mm wall thickness. There is a high demand of these micro-tubes for stent applications. The optimum design of alloy composition, vacuum melting, heat-treatment, integrated plastic deformation and micro-tube forward extrusion are included in the processing technique. Significant improvements in mechanical properties and better corrosion resistance were achieved through this processing sequence. This work aims to determine whether the grain size or plastic deformation during the forming processes of implant stent are the predominant factors controlling the degradation response, and to what extent the mechanical properties and corrosion resistance of Mg–2.5Zn–1Ca alloy can be altered simultaneously by the processes imparted, when taking into account that both of them would influence each other during the degradation process for a implant stent.

2. Experimental procedures

2.1. Preparation of materials and heat-treatment

The composition of the experimental alloy was Mg–2.5 wt %Zn–1 wt%Ca. Commercially pure Mg (99.99 wt%), Zn (99.99 wt%) and Mg–10 wt%Ca intermediate alloy powders were melted and cast in vacuum induction melting furnace (Institute of Vacuum Technology, Shenyang, China) in a high purity argon atmosphere. Differential scanning calorimetry (DSC) was performed (Netzsch – 400, Germany) at constant heating and cooling rates of 10 K/min between 20 and 600 °C to evaluate the thermal properties of the cast samples. The results of analysis were used for selecting the temperature for heat-treatment and subsequent plastic deformation. The cast ingots were subjected to solution heat-treatment and homogenizing annealing. The solution heat-treatment temperatures were 390 ± 5 °C, 410 ± 5 °C and 430 ± 5 °C; the holding time was 24 h. The annealing temperatures were 390 ± 5 °C, 400 ± 5 °C and 410 ± 5 °C; the holding time was also 24 h. All treated samples were ultrasonically cleaned in distilled water and dried in air before further characterization.

2.2. Hot extrusion

A cast ingot was machined into cylinders with a diameter of 72 mm after the oxide skin was removed. The extrusion equipment was a 3150 kN hydraulic pressure machine (Tianduan Press Co. Ltd. China). The extrusion die temperature was set at 300 ± 5 °C, and the sample was heated in a muffle furnace (SRJX-4-13, Shanghai Zhongheng Instrument Co. Ltd. China) prior to extrusion. The extrusion speed was set at 4 mm/s. The extruded rod diameter is 12 mm, representing an extrusion ratio of 36:1. The extruded rods were machined into tubular billets with outer diameter of 10 mm and inner diameter of 3 mm. These tubular billets were subjected to conventional tube extrusion at 360 ± 5 °C. The sample was put in the die and the two were heated together to ensure an accurate pressing temperature. Tubes with outer diameter of 3.0 mm and wall thickness less than 0.16 mm were obtained; this is close to the desired size of micro-tubes for stent implants. Further processing steps are needed to manufacture microtubes with precise size. These steps include slight drawing, straightening and polishing, which have negligible influence on the properties of material. Eventually, we got a micro-tube with outer diameter of ~2.0 mm that satisfied for an implant stent manufacture.

2.3. Microstructural characterization

First, the cast and extruded samples were polished and etched with a mixture of 2 ml of acetic acid (36%), 2 ml of nitric acid (68%), and 196 ml of water. Microstructures of all the samples were then observed in a MeF3 optical microscope (Reickert-Jung Co. Austria) after mechanical polishing and etching with Nital. Scanning electron microscope (JSM-5600LV, JEOL Ltd. Japan)-energy dispersive spectrometer (Kevex-7000, USA) (SEM-EDS) analysis was performed to investigate the elemental distribution. X-ray diffractometry (D/max-γB rotating anode XRD, Rigaku Co. Japan) using Cu K_α radiation was employed for the identification of the constituent phases in the cast, heat-treated, and extruded samples.

2.4. Mechanical testing

Standard surface-smooth tensile samples were machined according to American Society of Testing Materials (ASTM) international standards E8M-93. The length and cross-sectional diameter of the specimens were 17 mm and 4 mm respectively. The tensile tests were carried out in a universal material testing machine (AG-10TA, Shimadzu Co. Japan) with a strain rate of 0.05 mm/s, at 20 °C. To control the precision, 3 samples were tested as a group for each tensile test. Tensile strengths, yield strengths and elongations of Mg–2.5Zn–1Ca were established from the stress–strain curves.

2.5. Corrosion testing

The preparation, cleaning, and evaluation of corrosion testing were carried out according to ASTM G1-1999; the immersion test was conducted according to ASTM G31-72 (2004) in Hank's solution, one of the most commonly used balanced salt solutions in biomedical experiments. The cylindrical corrosion test sample size is 20 mm diameter and 3 mm height. In particular, because of the relative bulk of the micro-tube, immersion test was conducted with a surrogate sample processed according to the same methodology, maintaining the same extrusion ratio. Experimental samples were immersed in a 50 ml solution for 8 days at a temperature of 37 °C. Three samples were tested in parallel for each group. The samples were removed from Hank's Balanced Salt Solution, rinsed with distilled water, dried at room temperature, and subsequently ultrasonically cleaned in a solution of 200 g/L CrO_3 + 10 g/L $AgNO_3$ (Sinopharm Chemical Reagent Co. Ltd. China) at room temperature for 10 min. Corrosion resistance variation of samples was monitored by the pH value of the corrosion media. The corrosion weight loss rate was used for calculating the average corrosion

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