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Influence of hybrid extrusion and solution treatment on the microstructure and degradation behavior of Mg-0.1Cu alloy

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ABSTRACT

Effects of hybrid extrusion and solution treatment on the microstructure and corrosion behavior of Mg-0.1Cu alloy in Hanks' solution are studied. The applied processing treatment is noted to alter the alloy microstructure. The amount of Mg_2Cu precipitation is significantly reduced by the solution treatment. The decrease of secondary phases relieves occurrence of galvanic corrosion and the lowest corrosion rate achieved for the as-solutionized alloy at 510 °C is approximately 1/53 of that of the as-cast alloy. Grain refinement after extrusion results in better corrosion resistance compared with the as-cast alloy. However, the as-extruded Mg-0.1Cu alloy after the solution treatment shows higher degradation rate than the as-solutionized alloy. It is due to the uniformity of recrystallized grain size may play prominent role on the corrosion compared with the dissolution of the Mg_2Cu phase by solution treatment.

1. Introduction

In recent years, magnesium (Mg) alloys as a new class of biodegradable materials for medicinal application have become one of the most attractive research topics [1–3]. Mg alloys provide both biocompatibility and suitable mechanical properties close to those of natural bone compared with currently used titanium alloys and stainless steels [4]. The absorption of Mg implants in the human body can avoid a second surgical procedure for removal which usually makes the patient suffer increasing risk of infection and surgical cost. However, the rapid degradation of Mg alloys in the physiological environment is still the main obstacle on the way to clinical application. Alloying has been widely designed to reduce the degradation rate of Mg alloys [5]. Most commonly used metal elements for alloying are those such as Al, Li, Zn, Zr and rare earth metals [6]. But Al and rare earth metals are suspected to cause adverse effects in organism [7–9]. In recent years, more trace nutrition elements in the body, such as Ca, Sr, Si, Zn, were considered for the alloying in magnesium to enhance the biocompatibility and biofunctions [10–14]. Besides, implant materials that possess antibacterial ability are desired due to the high risk of implant associated bacterial infection [15].

Copper (Cu) is one of the well-known antibacterial metals [16] and can offer a high antibacterial activity for other metals with proper Cu addition [17–19]. Cu is also one of the essential elements in the human body and plays an important role in the immune system [20,21]. A small amount of copper content in alloys or bioactive glass has been reported to improve the cytocompatibility and cell viability [22,23]. Therefore, Mg-Cu alloy is designed for the antibacterial and biodegradable strategies, as while the alloy degradation in the biological environment, release of Cu ions can provide a long-lasting antibacterial effect. Previous study showed that Mg-Cu alloy with proper release of Mg and Cu would provide favorable stimulation to osteogenesis and angiogenesis meanwhile perform an antibacterial characteristic [24]. But Cu is also a well-known detrimental impurity element which tends to accelerate the corrosion of magnesium [25], and the amount of Cu is normally limited to 1000 ppm [26]. When the concentration exceeds the tolerance limit, it could segregate and serve as an active catalyst for the electrochemical attack [27]. According to our previous studies [24,28] and considering the tolerance limit of copper in the Mg alloy, Mg-0.1wt%Cu alloy was chosen in this study to tailor its degradation for potential clinical applications.

Chemical heterogeneity caused by crystallization, precipitation, and segregation during the casting process may have a negative effect on the corrosion resistance of Mg alloys [29]. It is well known that the corrosion of Mg alloy is as a function of grain size and processing route, and the intermetallic phase distribution also consequently influences the corrosion behavior [30]. Extrusion is always applied to decrease the corrosion rate of magnesium alloy due to finer microstructure exhibits

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better corrosion resistance [31–33]. Heat treatment can cause microstructural change and redistribution of metal elements, thus improving the corrosion resistance of Mg alloys [5,34]. Bakhsheshi-Rad et al. [35] and Liu et al. [36] reported that the solution treatment could reduce the amount of secondary phase particles within grains and increased the corrosion resistance of Mg-Zn alloys. Therefore, it is possible to tailor the degradation by means of extrusion and solution treatment. However, effects of extrusion and solution treatment on the microstructure and degradation behavior of Mg-Cu alloy have rarely been investigated. And there is almost no report about how extrusion followed solution treatment affects corrosion behavior of Mg-Cu alloy. In this work, different temperatures of solution treatment with and without extrusion were investigated to figure out the relationship between microstructure and the corrosion behavior of Mg-Cu alloy. Better understanding of the processing and corrosion of Mg-Cu alloy is important for expediting its further clinical application for orthopedics.

2. Materials and methods

The as-cast Mg-0.1Cu alloy composed of 99.9 wt% Mg and 0.1 wt% Cu was fabricated by melting 99.99 wt% pure magnesium and 99.9 wt% pure copper chips. The raw materials were melted by electrical resistance furnace with a protecting gas mixture of SF_6 (1 vol.%) and CO_2 (balance) in a high purity graphite crucible at 750 °C. After stabilization for 30 min, molten metal was poured into a high purity graphite mold which had been preheated at 200 °C accompanied by a 30 s stirring process. An inductively-coupled plasma atomic emission spectrometry (ICP-AES, Optima 7300DV, USA) was applied to determine the chemical compositions of the ingot. Samples with dimensions of $\Phi 10 \times 3.5\,mm^3$ were prepared from part of the as-cast ingot by electric spark wire cutting. The rest was extruded into bar (Φ10 mm) and cut into samples with the same size. The Mg-0.1Cu samples were subjected to heat treatments described in Table 1. The solution treatment was carried out in air with the sample surface protected by carbon powders followed by water quenching. Then the samples were ground with SiC papers to 1500-grit, ultrasonically cleaned in the absolute ethanol, and finally dried in hot air flow. Some of the samples were mechanically ground and polished for microstructural observation.

The microstructure of the Mg-Cu alloy was characterized by optical microscopy (Leica MEF4A, Germany) and scanning electron microscopy (SEM, HITACHI S-3400N, Japan) equipped with energy-dispersive spectrometry (EDS, Oxford INCA energy 300, UK) to evaluate the composition of the microstructure. Grain size was determined by a linear intercept method: $D = 1.74 \times L$, where D is the grain size and L is the linear intercept size. The fraction of the secondary phase particles was evaluated by measuring the area fraction of the particles. The grain sizes and secondary phase fraction were averaged with values measured from 6 micrographs for every alloy. Differential scanning calorimetry (DSC) analysis was carried out with a NETZSCH DSC200F3 system under flowing argon at a controlled heating speed of 25 K/min.

Immersion tests were conducted by putting the samples in Hanks' balanced salt solution with a composition: $MgSO_4 \cdot 7H_2O$ 0.2 g/L, KCl 0.4 g/L, KH_2PO_4 0.06 g/L, NaCl 8.0 g/L, $Na_2HPO_4 \cdot 12H_2O$ 0.12 g/L, D-Glucose 1.0 g/L, $NaHCO_3$ 0.35 g/L and $CaCl_2$ 0.14 g/L at 37 ± 0.5 °C. The ratio of surface area/solution volume was set as $1.25\,cm^2/mL$ according to ISO10993. During immersion period, the pH value was recorded every day using a digital pH meter and the solution was daily refreshed to simulate the metabolism in vivo. Samples were removed after immersion of 7 and 14 days for surface morphology observation and then the corrosion product on the sample surface was removed by using 200 g/L of chromic acid and 10 g/L of $AgNO_3$ solution. The *in vitro* corrosion rate was calculated according to ASTM G31-12a using the following equations:

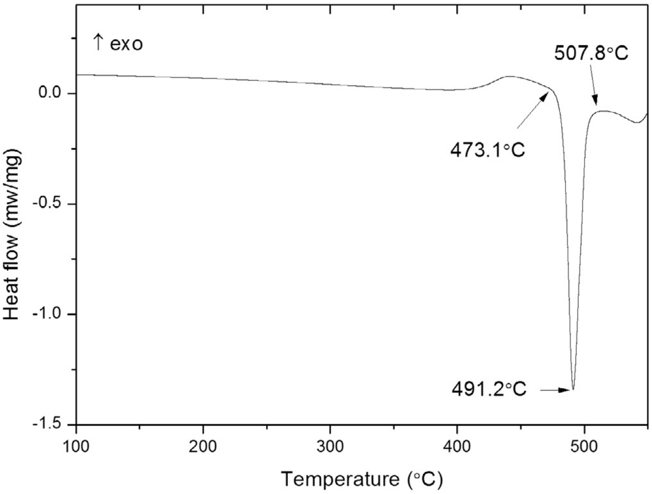

Fig. 1. DSC curve of the as-cast Mg-0.1Cu alloy.

$$CR = (K \times W)/(A \times T \times D) \tag{1}$$

where *CR* is the corrosion rate in mm/year, the constant *K* is 8.76×10^4, *W* is the mass loss in g after immersion test, *A* is the surface area of sample in cm^2, *T* is the time of immersion in h, and *D* is the density of the material in g/cm^3.

The surface morphologies of the samples after 7 days and 14 days immersion were examined by scanning electron microscopy (SEM, FEINova NanoSEM 450) with energy-dispersive spectrometry (EDS, Oxford X-MaxN). X-ray diffraction (XRD, RigakuD/MAX 2500 Diffractometer) with Cu K_α X-ray source was employed to analyze the composition of the corrosion products on the sample surface that were collected after immersion test.

Electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization were performed in a three-electrode cell on an electrochemical workstation (Reference 60, Gamry, USA), consisting of a sample as the working electrode, a platinum foil as counter electrode and saturated calomel electrode (SCE) as reference electrode. After immersion in HBSS, all the samples stayed at the open circuit potential (OCP) for 30 min to stabilize before the measurement. Potentiodynamic polarizations were measured at a scan rate of 0.5 mV/s. Fitting was performed with Gamry software and ZSimpwin 3.20 software (Echem Software, Michigan, USA). Three duplicates were taken for each group to control the experimental scatter for statistics.

3. Results

The DSC curve of the as-cast Mg-0.1Cu alloy is shown in Fig. 1. The curve reveals one peak that corresponds to the secondary phase

Table 1
Extrusion and heat treatment parameters.

	AC	AS45	AS48	AS51	AS53	AE	ES45	ES48	ES51	ES53
Extrusion	Untreated	Untreated	Untreated	Untreated	Untreated	390 °C, 1.2 m/min	390 °C, 1.2 m/min	390 °C, 1.2 m/min	390 °C, 1.2 m/min	390 °C 1.2 m/min
Solution treatment	Untreated	450 °C, 10 h	485 °C, 10 h	510 °C, 10 h	530 °C, 10 h	Untreated	450 °C, 10 h	485 °C, 10 h	510 °C, 10 h	530 °C, 10 h

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