Investigation on Microstructures and Mechanical Properties of Extruded Biodegradable Zn-1Mg-\(x\)Zr (\(x = 0-0.4\) %) Alloys

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Abstract. In this work, Zn-1Mg-\(x\)Zr alloys were cast, annealed and hot-extruded to investigate the microstructures and/or mechanical properties. The results show that, besides the primary Zn-rich dendrites and lamellar eutectic Zn + Mg\(_{2}\)Zn\(_{11}\) mixture, the addition of Zr produces extra block- or bar-like Zn\(_{22}\)Zr intermetallic compounds in the as-cast Zn-1Mg-\(x\)Zr alloys. The annealing process results in that the interdendritic eutectic mixture changes from lamellar morphology to discrete Mg\(_{2}\)Zn\(_{11}\) particles. The hot extruding process seriously deforms the primary Zn-rich crystals (with twinning inside), and breaks the Mg\(_{2}\)Zn\(_{11}\) and Zn\(_{22}\)Zr intermetallic compounds into small particles. Adding Mg and Zr to pure Zn significantly improves the micro-hardness, ultimate tensile strength (UTS), tensile yield strength (TYS) and compression yield strength (CYS). The addition of Zr to binary Zn-1Mg alloy slightly improves the micro-hardness, UTS, TYS and CYS, but contributes more to the elongations. The modification of the mechanical properties is related to the change of the microstructures due to the addition of alloying elements and hot-working deformation.

Introduction

As temporary implants in human body, biodegradable metallic materials have aroused great interest of researchers owning to their high mechanical properties and good biocompatibility. Among these materials, Mg [1-6] and Fe [7-11] alloys are two major systems that have been extensively investigated in the last decade. However, these two alloy systems possess obvious disadvantages that limit their clinical applications. Mg alloys corrode too fast in physiological environments so that the mechanical strength loses rapidly [6]. Moreover, the fast corrosion also results in production of excessive amounts of hydrogen that retard the healing process. In contrast, Fe alloys generally corrode slower than clinical needs. This means that large portions of the implant materials may stay in human body for a long time even after finishing their clinic roles [11].

Considering these drawbacks, attention is being distracted from Mg and Fe alloys to alternative Zn and its alloys. Zn is a biologically tolerable element. Its standard potential (-0.8 V) is between Fe (-0.4 V) and Mg (-2.4 V), indicating an intermediate corrosion rate [12]. Moreover, Zn has a low melting point, lower chemical reactivity and good machinability. These characters permit that they can be easily prepared by conventional processing technologies, such as gravity or die casting, hot rolling or hot extrusion [13]. Despite of these advantages, however, the mechanical properties of pure Zn are unsatisfactory. Therefore, Zn alloys with various elements were more extensively studied, e.g. Zn-Mg, Zn-Sr, Zn-Ca, Zn-Al, Zn-Cu, etc [13-16]. Moreover, some ternary Zn alloys were also developed, such as Zn-Mg-Mn [17] and Zn-Mg-Sr [18]. Till now, further improving the mechanical properties of biodegradable Zn alloys is still a hot topic.

In the research of biodegradable Mg alloys, Zn and Zr elements are commonly added to improve the mechanical and corrosion properties. The most important reason is that these elements are non-toxic. Mg exists in the human body as fourth most prevalent cation [19] and Zn is an essential...
element for the human body [20]. A small amount of Zr (<250 mg) in the human body also shows good biocompatibility and low toxicities [21]. Considering these aspects, it is of potential and fundamental interest to add Mg and Zr elements to Zn alloys. In the as-cast binary Zn-Mg alloys, it has been found that Mg alloying at 1 wt.% significantly improved the tensile strength of Zn [13,14]. In view of this background, it was decided to cast, anneal and hot-extrude Zn-1Mg-xZr (x = 0–0.4 %) alloys in this work. The microstructures and mechanical properties of the alloys were preliminarily investigated.

Experimental

Zn-based ternary alloys with nominal compositions Zn-1Mg-xZr (x = 0, 0.15, 0.25, 0.4 wt.%) were melted in an induction furnace under argon atmosphere (pure Zn (99.9 wt.%), pure Mg (99.99 wt.%) and Mg-30 wt.%Zr master alloy were used as the raw materials). After degassing and deslagging, the melt was poured into a cylindrical steel mold (Ф 60 × 150 mm) at 580°C. The actual compositions of the as-cast ingots were analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES), as listed in Table 1. In order to homogenize the structures, the as-cast ingots were annealed at 343°C for 36 h, followed by water quenching. The annealed ingots were then indirectly extruded at 250°C with an extrusion ratio of 16.7:1 to cylindrical rods.

Table 1. Actual compositions of the as-cast ingots detected by ICP-AES.

<table>
<thead>
<tr>
<th>Alloys</th>
<th>Mg (wt.%)</th>
<th>Zr (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn-Mg</td>
<td>1.030</td>
<td>0.000</td>
</tr>
<tr>
<td>Zn-1Mg-0.1Zr</td>
<td>1.090</td>
<td>0.005</td>
</tr>
<tr>
<td>Zn-1Mg-0.25Zr</td>
<td>1.010</td>
<td>0.232</td>
</tr>
<tr>
<td>Zn-1Mg-0.4Zr</td>
<td>0.947</td>
<td>0.541</td>
</tr>
</tbody>
</table>

Specimens were machined from the as-cast, as-annealed and as-extruded materials, respectively, following a standard mechanical polishing. The microstructures of the specimens were observed by a Leica DMR optical microscope after chemical etching in an acid solution (HF : H₂SO₄ : H₂O = 1 : 15 : 84, vol.%) for 1 s. The composition of the intermetallic compounds were analyzed on a Zeiss ULTRAPLUS FE-SEM, equipped with an energy-dispersive spectrometer (EDS). X-ray diffractometer (XPERT3 Powder) with Cu Kα radiation was employed to identify the microstructures in the extruded specimen.

Vickers hardness was determined using a micro-hardness tester (MH-5L, Shanghai Everone Precision Instruments Co., Ltd., China), with an applied 1000 g load and a loading time of 5 s. Tensile and compression tests were performed at room temperature on a SHIMADZU AG-Xplus 100 kN testing machine with deformation rate of 1.5 mm/min.

Results and Discussion

According to the binary Zn-Mg phase diagram [22], Zn-rich phase is crystallized primarily from the Zn-1Mg melt when the temperature falls below the liquidus line. With a further drop in the temperature, a eutectic reaction (364 °C: L → Zn + Mg₃Zn₁₁) then occurs. Fig. 1 show the microstructures of the as-cast Zn-1Mg-xZr alloys. As can be observed, the binary Zn-1Mg alloy consists of primary Zn-rich crystals and eutectic Zn + Mg₃Zn₁₁ mixture (see Fig. 1(a)). When Zr element is added, it seems that the primary Zn-rich crystals become more dendritic (see Figs. 1(b)-(d)). Furthermore, some intermetallic compounds begin to appear (as enclosed by the circles), and the amount is increased with increasing the Zr content. For more microstructural details, Figs. 2 show the magnified microstructures of the as-cast Zn-1Mg-xZr alloys (corresponding to Figs. 1). It is seen that the eutectic structure reveals typical lamellar morphology. The intermetallic compounds exhibit block- or bar-like shapes and are mainly distributed in the interdendritic regions.
Figure 1. Microstructures of the as-cast Zn-1Mg-xZr alloys: (a) Zn-1Mg, (b) Zn-1Mg-0.1Zr, (c) Zn-1Mg-0.25Zr, (d) Zn-1Mg-0.4Zr. The circles enclose the Zn\textsubscript{22}Zr intermetallic compounds.

Figure 2. Magnified microstructures of the as-cast Zn-1Mg-xZr alloys (corresponding to Fig. 1): (a) Zn-1Mg, (b) Zn-1Mg-0.1Zr, (c) Zn-1Mg-0.25Zr, (d) Zn-1Mg-0.4Zr.

To identify the intermetallic compounds, Fig. 3 shows the XRD pattern of the as-cast Zn-1Mg-0.25Zr alloy. Obviously, besides the above-mentioned Zn and Mg\textsubscript{2}Zn\textsubscript{11} phases, there exists a small amount of Zn\textsubscript{22}Zr phase. Considering that the intermetallic compounds show the same morphology in all the Zr-containing alloys, it can be determined that these compounds are Zn\textsubscript{22}Zr phase. This also indicates that Zr atoms prefer combining with Zn atoms to form an intermetallic compound in the ternary Zn-1Mg-xZr alloy.

Fig. 4 shows the as-annealed microstructures of the Zn-1Mg-xZr alloys, which were preserved by the rapid quenching. It can be observed that the lamellar morphology of the interdendritic eutectic mixture disappears. Instead, the interdendritic regions are occupied by discrete Mg\textsubscript{2}Zn\textsubscript{11} crystals [. However, the sizes and shapes of the Zn\textsubscript{22}Zr phase are less affected by the heat treatment, as can be more clearly observed in the magnified microstructures.
Fig. 5 shows the as-extruded microstructures of the Zn-1Mg-xZr alloys. Significantly different from the as-cast and as-annealed microstructures, the primary Zn-rich crystals are seriously deformed with twinning in the matrix (see the magnified images). The intermetallic compounds are broken into small particles and are homogenously distributed in the Zn matrix. However, it is not easy to distinguish the $\text{Zn}_2\text{Zr}$ from the $\text{Mg}_2\text{Zn}_{11}$ particles in the Zr-containing alloys. To observe their morphologies more clearly, Fig. 6 shows the BSE images of the Zn-1Mg and Zn-1Mg-0.4Zr alloys. Without the Zr addition, only broken black particles exist (Fig. 6(a)). When Zr is added, some white broken particles appear. An EDS analysis indicates that the black and white particles are $\text{Mg}_2\text{Zn}_{11}$ and $\text{Zn}_2\text{Zr}$ phases, respectively, as evidenced by the spectrums corresponding to positions A and B.
Figure 5. Microstructures of the as-extruded Zn-1Mg-xZr alloys: (a) Zn-1Mg, (b) Zn-1Mg-0.1Zr, (c) Zn-1Mg-0.25Zr, (d) Zn-1Mg-0.4Zr.

Figure 6. BSE images of the (a) Zn-1Mg and (b) Zn-1Mg-0.4Zr alloys. The EDS spectrums indicate the compositions of the black (position A) and white (position B) phases in the BSE images.

Fig. 7(a) shows the micro-hardness of the as-extruded pure Zn and Zn-1Mg-xZr alloys (note: pure Zn was also extruded as a reference material in this work). Clearly, pure Zn has the lowest micro-hardness (< 40 Hv). After alloying with Mg, the micro-hardness is increased significantly (> 90 Hv). When different amounts of Zr are further added, the micro-hardness is also slightly enhanced. Fig. 7(b) shows the tensile and compression properties of the extruded pure Zn and Zn-1Mg-xZr alloys. It is obvious that the ultimate tensile strength (UTS), tensile yield strength (TYS) and compression yield strength (CYS) of the pure Zn are very low. When Mg is added, the UTS, TYS and CYS are greatly improved. After further alloying with different amounts of Zr, these properties are also improved to some extent. However, the elongations of the alloys become smaller when compared to the pure Zn. Nevertheless, it should be noted that Zn-1Mg and Zn-1Mg-0.4Zr alloys possess the minimum and max elongations among all the investigated alloys, respectively. This indicates that the addition of Zr to the Zn-1Mg alloy contributes to the improvement of the elongations.
In order to improve the mechanical properties of pure metals, adding alloying elements and hot-working deformation are two commonly used methods in metallic materials processing [10]. Addition of solutes is an effective approach to refine the grains of cast metals due to the formation of the constitutional undercooling zone at the front of the solid/liquid interface. Moreover, adding alloying elements can also bring about solution strengthening or precipitation strengthening phases (e.g., Mg$_2$Zn$_{11}$ and Zn$_{22}$Zr phases in this work). In addition, hot-working deformation can also effectively refine the grain size. Compared to the pure Zn, the improvement of the UTS, TYS and CYS of the Zn-1Mg-xZr alloys is just attributed to these aspects. Compared to the binary Zn-1Mg alloy, the increase of the elongations by the addition of Zr element should be related to the formation of the Zn$_{22}$Zr phases.

Summary

The microstructures and/or mechanical properties of the as-cast, as-annealed and as-extruded Zn-1Mg-xZr alloys were studied, and it was found that:

(1) The as-cast binary Zn-1Mg alloy consists of primary Zn-rich dendrites and lamellar eutectic Zn + Mg$_2$Zn$_{11}$ mixture; when Zr element is added, some extra block- or bar-like Zn$_{22}$Zr intermetallic compounds are formed in the ternary Zn-1Mg-xZr alloys.

(2) After annealing followed by rapid quenching, the interdendritic eutectic mixture changes from lamellar morphology to discrete Mg$_2$Zn$_{11}$ crystals.

(3) After hot-extruding, the primary Zn-rich crystals are seriously deformed with twinning, and the Mg$_2$Zn$_{11}$ and Zn$_{22}$Zr intermetallic compounds are broken into small particles.

(4) Compared to the pure Zn, alloying with Mg and Zr significantly improves the micro-hardness, UTS, TYS and CYS; compared to the binary Zn-1Mg alloy, a further addition of different amounts of Zr slightly improve the micro-hardness, UTS, TYS and CYS, but contributes more to the elongations.

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References


