Effect of Ca Content on Properties of Extruded Mg-3Zn-0.5Sr-xCa Alloys for Medical Applications

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Mg-3Zn-0.5Sr-xCa(wt.%) (x=0, 0.2, 0.5) alloys were fabricated by casting and hot extrusion. X-ray diffraction (XRD) and optical microscopy observation showed that the microstructure of Mg-3Zn-0.5Sr-xCa alloys was composed of α-Mg matrix and Mg17Sr2 phase precipitated along grain boundaries. The tensile strength of the alloy increased from 255MPa to 305MPa with increasing Ca content from 0 to 0.5wt%, but the elongation to fracture of the alloys was 19.45%, 28.7% and 15.2% respectively, indicating that coarse precipitation increased the risk of crack initiation and propagation along the grain boundaries leading to reduced ductility of Mg alloys. The polarization curves revealed that Mg-3Zn-0.5Sr-0.2Ca has the highest corrosion potential and the lowest corrosion current density indicating the optimum corrosion resistance. In cytotoxicity test, Mg-3Zn-0.5Sr-xCa alloys were harmless to mouse osteoblastic and Mg-3Zn-0.5Sr-0.2Ca alloy exhibited optimal biocompatibility.

Keywords: Mg-Zn alloys, corrosion resistance, cytotoxicity, biocompatibility.

1. Introduction

Magnesium alloys have attracted extensive attention for medical applications because of their good biocompatibility, biodegradability and elastic modulus similar to natural bone as orthopaedic and cardiovascular implant1-3. Nevertheless, traditional Mg alloys are degraded before the tissue is healed after implantation, leading to failure of the surgery, which limits the applications of the magnesium alloys to a great extent4-5. Alloymg and deformation treatment are two methods to reduce the degradation rate of Mg alloys6-9. Zn, Sr and Ca are essential trace elements and non-toxic to human10-12. The proper amount of Zn precipitated along the grain boundaries of Mg matrix could restrict grain growth and play the dual roles of aging strengthening and solution strengthening13, 14. Brar et al.15 reported that when the addition of zinc is 2wt% or 4wt%, the Mg alloy has optimal mechanical and degradation properties. Sr could improve bone strength and density and indicated beneficial effects on corrosion resistance and deformability16-19. When Sr content is over 0.3wt%, the finer grains and more homogeneous precipitation of Mg alloys occurs. However, when the content of Sr is more than 1.2wt%, the eutectic structure with continuous network distribution appears along grain boundaries attributed to coarse grains and inferior properties. Hence, the addition of Sr in this paper is 0.5wt%. The front of solid-liquid interface generates constituent supercooling after adding Ca element, which could enhance nucleation rate and inhibit grain growth. Thereby, Ca might enhance the strength and ductility of Mg alloys. Moreover, Ca largely improves the corrosion resistance of alloys20-22. Comparing to as-cast Mg alloys, finer grains and preferable properties were possessed by as-extruded Mg alloys2,10,23. Therefore, Mg-3Zn-0.5Sr-xCa (x=0, 0.2, 0.5) alloys were fabricated through casting and hot extrusion, while the properties of the alloys were evaluated by tissue analysis, corrosion resistance and cytotoxicity tests.

2. Experimental process

The experimental raw materials were commercial pure Mg (99.99%), pure Zn (99.99%), pure Ca (99.97%) and Mg-20wt%Sr master alloy. After casting, aging treatment and extrusion, bars with a diameter as 12 mm were obtained and then were cut into 4 mm thick specimens. Specimens were polished, etched with an etchant containing 10g picric acid, 10mL acetic acid, 50mL anhydrous ethanol and 10mL distilled water. Microstructure was observed using metallographic microscope (OLTMPS GX51) and crystallographic phase was investigated using X-ray diffraction (XRD, RIGAKU-3014). Tensile tests were carried out with a CMT5105 universal testing machine at room temperature. The tensile test specimens had a dog-bone shape with a diameter of 5mm and a gauge length of 30mm. A four-electrode cell with a sensing electrode, the specimen as a working electrode, a graphite electrode as a counter electrode and a saturated calomel electrode as a reference electrode was used for electrochemical tests. Polarization curve was measured by potentiostatic scanning at a scan rate of 5×10-4 V·s-1 and electrochemical impedance has an adopted amplitude of 5mV AC signal with test frequency at a range of 105 ~10-2 Hz. The electrochemical corrosion test was conducted in simulated body fluid (SBF) at 37°C. Cytotoxicity assessment samples of different compositions were processed into Φ10×4mm discs and polished with metallographic sandpaper to remove scale.
Then samples were cleaned with deionized water and alcohol for 5 minutes respectively, then dried in cold air and sterilized at 121°C for 20 minutes. Well-grown mouse osteoblasts were incubated in 96-well cell culture plate at 1×10³ cells/100µL in each well and cultured for 24h at 37°C in a humidified atmosphere with 5% of CO₂, 100µl of extract or 100µl of a negative control (α-minimum Eagle’s medium) could then substitute for the medium. Extracts were prepared as an extraction medium with the surface area to an extraction medium ratio 1.25cm²/ml and diluted by 100% for back-up. In this test, the cell viability was obtained by Cell Counting Kit-8(CCK8) method and the relative growth rate (RGR) was calculated. Cytotoxicity was evaluated according to the cytotoxicity evaluation criteria of ISO 10993.5: 1999.

3. Results and Discussion

XRD pattern (Fig. 1) show the phases of as-extruded Mg-3Zn-0.5Sr-xCa alloys consisted of α-Mg matrix and Mg₁₇Sr₂ intermetallic compound phase. The optical microscopy images of the microstructure of Mg-3Zn-0.5Sr-xCa alloys revealed that the addition of Ca caused grain refinement, as shown in Figures 2((a)-(c)). The Mg-3Zn-0.5Sr-0.5Ca alloy had the finest grain size and coarse precipitation. Table 1 lists the mechanical properties of the Mg-3Zn-0.5Sr-xCa alloys and Table 1 shows that with addition of 0.2wt%Ca, the yield strength (YS) of the alloy decreased from 164MPa to 126MPa, but its ultimate tensile strength (UTS) remained almost unchanged and its elongation to fracture increased from 19% to 29%. With the addition of the Ca content to 0.5wt%, the YS of the Mg alloy slightly increased from 164MPa to 185MPa, and the UTS increased significantly to 305MPa, while the elongation to fracture decreased from 19% to 15%. The Mg-3Zn-0.5Sr-0.5Ca alloy had maximum UTS and YS due to its finest grain size which causes the maximum grain boundary strengthening effect as quantified by the Hall-Petch relationship. Meanwhile, the presence of a large amount of Mg₁₇Sr₂ intermediate phase along grain boundaries could also enhance the strength of alloys because of precipitation strengthening. However, its elongation to fracture is only 15%, which indicates that the coarse Mg₁₇Sr₂ particles could become the sites for crack initiation, resulting in inferior ductility of the alloys. Although the UTS of Mg-3Zn-0.5Sr-0.2Ca alloy is 257MPa, it could satisfy the mechanical performance requirements of natural bone (UTS in the range of 140-190MPa) on the other hand, the elongation to fracture of Mg-3Zn-0.5Sr-0.2Ca alloy improved remarkably and reported 29%, which can decrease “Stress shielding” effects. Therefore, the comprehensive mechanical properties of the Mg-3Zn-0.5Sr-0.2Ca alloy are optimal for medical applications.

![Figure 1](image)

**Table 1.** The mechanical properties of Mg-3Zn-0.5Sr-xCa alloys

<table>
<thead>
<tr>
<th></th>
<th>Ultimate Tensile Strength /MPa</th>
<th>Yield Strength /MPa</th>
<th>Elongation %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural Bone</td>
<td>140-190</td>
<td>100-190</td>
<td>&lt;3</td>
</tr>
<tr>
<td>Mg-3Zn-0.5Sr</td>
<td>255</td>
<td>164</td>
<td>19</td>
</tr>
<tr>
<td>Mg-3Zn-0.5Sr-0.2Ca</td>
<td>257</td>
<td>126</td>
<td>29</td>
</tr>
<tr>
<td>Mg-3Zn-0.5Sr-0.5Ca</td>
<td>305</td>
<td>185</td>
<td>15</td>
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Figure 2. The optical micrographs of Mg-3Zn-0.5Sr-xCa alloys perpendicular to extruded direction, (a) Mg-3Zn-0.5Sr; (b) Mg-3Zn-0.5Sr-0.2Ca; (c) Mg-3Zn-0.5Sr-0.5Ca

Figure 3. The polarization curves of Mg-3Zn-0.5Sr-xCa alloy samples in the SBF solution

Figure 4. The electrochemical impedance spectroscopy (EIS) plot of Mg-3Zn-0.5Sr-xCa alloy samples in the SBF solution
In vitro cytotoxicity of Mg-3Zn-0.5Sr-xCa alloys were estimated by measuring the RGR of mouse osteoblasts with different concentration of extracts and negative control, as shown in Fig. 5. It could be seen that the RGR values in all extracts surpassed 100%, which indicated that the cytotoxicity of extracts was Grade 0 and satisfied the cytotoxicity requirements. Moreover, the RGR values of cells incubated in 100% extraction medium for 3 days were 136%±10%, 178%±7% and 104%±2% respectively, which revealed that Mg-3Zn-0.5Sr-0.2Ca alloy has the optimum biocompatibility. The morphologies of mouse osteoblasts cultured in extracts for 1 and 3 days were well growth and similar to that of negative control group, as shown in Fig. 6((a)-(h)). It was further demonstrated that Mg-3Zn-0.5Sr-xCa (x=0, 0.2, 0.5 wt%) alloy have good biocompatibility and could be employed as medical implants.

4. Conclusion

Mg-3Zn-0.5Sr-xCa (x=0, 0.2, 0.5) alloys were fabricated by casting and hot extrusion. The microstructure of the alloys consisted of the α-Mg matrix and Mg$_{17}$Sr$_2$ particles, which were distributed along grain boundaries. The mechanical properties of alloys satisfy the requirements of Mg alloys as biomedical materials. By conducting electrochemical experiments, it has been confirmed that the Mg-3Zn-0.5Sr-0.2Ca alloy has the highest corrosion resistance. The RGR values of the alloys were all greater than 100% in extracts with diverse concentration, which revealed that Mg-Zn-Sr-xCa alloys were nontoxic for medical applications. Overall, in the present study, all three Mg alloys were promising for clinical applications and the comprehensive performance of the Mg-3Zn-0.5Sr-0.2Ca alloy was optimum.

5. References


