Microstructure and mechanical properties of the as-cast Mg-Zn-Mn-Ca alloys

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Abstract. As-cast Mg-Zn-Mn-Ca alloys are the candidates for medical implants. The microstructure and mechanical properties of the as-cast Mg-Zn-Mn-Ca alloys were investigated by using optical microscope (OM), X-ray diffraction (XRD) and scanning electron microscope (SEM). The results suggested that the addition of Zn significantly refined the grain size of the as-cast magnesium alloys, and hence improved the mechanical properties of the alloys. Meanwhile, the secondary phase mainly distributed in the grain boundaries and the solution treatment made parts of secondary phases dissolved into the matrix, resulting in enhancement of the plasticity of the as-cast Mg-Zn-Mn-Ca alloy.

Keywords: Mg-Zn-Mn-Ca alloys, microstructure, mechanical properties

1. Introduction
Medical metal materials, such as traditional metallic biomaterials of stainless steels, titanium and cobalt-chromium-based alloys, are widely used in medicine fields because of their high strength, good toughness, fatigue resistance, corrosion resistance and excellent processing molding ability. However, the disadvantages of the traditional materials are the possible release of toxic metallic ions and particles through corrosion. First, they will lead to inflammatory cascades which result in biocompatibility reduction and tissue loss [1]. Second, the traditional material implants, remaining as permanent fixtures in the case of plates and stents, must be removed by a second surgical procedure after the sufficient heal of tissue, which increases costs and further morbidity to patients. At last, the elastic modulus of current metallic biomaterials did not match with that of natural bone tissue, which causes stress shielding effects [2]. Therefore, a new material that is non-cytotoxic, degrade and biocompatible need to be developed.

Magnesium and its alloys have shown the potential to serve as biodegradable medical metal implant to cure bone fracture and vascular tissue due to their degradability, biocompatibility and appropriate elastic modulus (40-45GPa). The value of the elastic modulus is very close to that of human bone (10-20GPa) [3]. However, the fast degradation rate of magnesium in vivo-environment limited their clinical application. Although the traditional industrial magnesium alloy, such as AZ31 and WE43 containing Al and RE elements showed a relatively high strength and good corrosion resistance, Al and RE are neurotoxin elements. The elements of Al and RE can cause nerve toxicity and restraining growth to human body [4]. It is great important to find a new kind of magnesium alloys for the production of medical metal implants.
Actually, there are only few kinds of elements that can be used as enhanced elements of biological magnesium alloy, including Zn, Ca and some very small amount of RE elements. The Ca is an essential element of the human body, and is also an important component for human bone. It was reported that Ca can improve the mechanical properties and corrosion resistance. The optimum performance in mechanical properties, corrosion resistance and biocompatibility was obtained when the Ca content less than 1% in magnesium alloys [5]. In addition, Zn is also an essential element for human body. It can promote the body growth, enhance the immune function and accelerate the repair of damaged tissue. It was reported that adding Zn element into magnesium alloys improved both the tensile strength and the corrosion resistance successfully [6,7].

In the present investigation, the elements of Zn, Ca and Mn were added into the magnesium, and new kinds of Mg-Zn-Mn-Ca alloys were produced. The microstructure and mechanical properties of the Mg-Zn-Mn-Ca alloys were investigated by using optical microscope (OM), X-ray diffraction (XRD), scanning electron microscope (SEM) in order to find the effect of alloying elements on the mechanical properties.

2. Experiment procedure

2.1. Materials preparation
Magnesium alloys were prepared from pure magnesium ingots, pure zinc chips, Mg-5%Mn and Mg-9.4%Ca master alloy. The materials were melted by electrical resistance furnace under the protection of SF$_6$ and N$_2$ mixed gas in the graphite crucible at 720°C, and the ratio of SF$_6$ and N$_2$ is 1:10. The addition order of alloying elements was Zn, Ca, Mn. The melting was stirred for 5 min, and then preserved for 20 min at the melting condition for stabilization. At last, the melting was poured into mild steel mold which had been preheated at 200°C. The as-cast alloys with nominal compositions of Mg-2Zn-0.2Mn-0.2Ca (defined as Alloy1) and Mg-4Zn-0.2Mn-0.2Ca (defined as Alloy2) were produced. The chemical compositions of as-cast alloys A and B were examined by XRF, as shown in table 1.

| Alloys    | Zn  | Mn  | Ca  | Mg   |
|-----------|-----|-----|-----|------|
| Alloy1    | 1.96| 0.25| 0.15| Bal. |
| Alloy2    | 4.03| 0.23| 0.23| Bal. |

2.2. Microstructure and mechanical properties
Specimens with the shape of bulk were cut from the achieved alloy ingots then the samples were mechanically wet ground with 250 to 7000 silicon carbide grit papers. Microstructure observation was conducted by using an optical microscope (OM, AXIO2IMAGER A2m) and a scanning electron microscope (SEM, HITACH S3400N) equipped with EDS analysis. Tensile tests were performed by using an universal testing machine at a displacement rate of 1.0 mm/min at ambient temperature. Specimens with a diameter of 5mm and a gauge length of 25 mm were machined for tensile test. For each testing material, three specimens were examined. Vickers micro-hardness test was conducted by using an automatic digital HDX-1000 TMC/LCD micro-hardness tester with a load of 0.1Kg and a dwelling time of 10s.

3. Results and discussion

3.1. Microstructure of the Mg-Zn-Mn-Ca alloys
The optical micrographs of Mg-Zn-Mn-Ca alloys with different Zn contents were shown in figure 1. It showed that the grain size of as-cast Mg-Zn-Mn-Ca alloys decreased as the Zn content increased. The grain size was about 215μm when the content of Zn was 2wt%. When the Zn content increased to 4wt%, the grain size reduced to 140μm. It indicated that the Zn has a great effect on grain refinement.

The distribution and the morphology of the secondary phases were also shown in figure 1. The
secondary phase was mainly strip-like distributing at the grain boundary while some granular phases were also found inner grain. It was observed that the amount of the secondary phases increased with the increase of Zn content. The EDS analysis (figure 2) showed that the secondary phases at the grain boundary and inner grain were both composed of Mg, Zn and Ca elements. The tiny peaks of MgZnCa phase were found at the XRD graph (figure 3) but the EDS analysis showed that the atomic ratio of Zn/Ca was not precise 1.25.

Figure 1. Optical microstructure of the as-cast Mg-Zn-Mn-Ca alloys:
(a)(c) Mg-2Zn-0.2Mn-0.2Ca, (b)(d) Mg-4Zn-0.2Mn-0.2Ca.

Figure 2. SEM morphology of as-cast Mg-xZn-0.2Mn-0.2Ca alloy:
(a)(b)2wt.%Zn, (c)(d)4wt.%Zn, (e) EDS analysis of the eutectic (MgZnCa+α-Mg) phase of as-cast Mg-2Zn-0.2Mn-0.2Ca alloy, (f) EDS analysis of the eutectic (MgZnCa+α-Mg) phase of as-cast Mg-4Zn-0.2Mn-0.2Ca alloy.
3.2. Mechanical properties of the Mg-Zn-Mn-Ca alloys

Figure 4 was the typical strain-stress curve of the Mg-Zn-Mn-Ca alloys, and the mechanical properties of the Mg-Zn-Mn-Ca alloys with different content of Zn were summarized in table 2. The yield strength (YS) increased slightly with the increment of the Zn content. The ultimate tensile strength (UTS) and elongation also increased with the increment of the Zn content. The value of the ultimate tensile strength increased significantly than that of the yield strength. The yield strength increased by 18.2%, and the ultimate tensile strength increased by 15.4%.

The vickers hardness value of the as-cast Mg-2Zn-0.2Mn-0.2Ca alloys was 49.3Hv. The hardness value of the as-cast Mg-4Zn-0.2Mn-0.2Ca alloys was 53.4Hv. The result showed that Zn can improve the strength of the alloy slightly because of the presence of the secondary phase.

![Figure 3. XRD patterns of the as-cast Mg-Zn-Mn-Ca alloys.](image)

Table 2 showed mechanical properties of as-cast Mg-Zn-Mn-Ca alloys. Compared the as-cast magnesium alloys, the enhancement of the UTS was mainly due to the grain refinement, solution strengthening and secondary phase strengthening. As reported, the segregation of alloying element at the front of grain growth formed an intensive constitutional undercooling in a diffusion layer ahead of the advancing solid/liquid interface, which then restricted the grain growth and promoted the nucleation of the primary magnesium grain [8]. Some secondary phases were dispersed in the matrix and reacted with the dislocation during deformation, resulting in improvement of mechanical properties.

![Figure 4. Typical stress-strain curve of as-cast Mg-Zn-Mn-Ca alloys.](image)
Table 2. Mechanical properties of the as-cast Mg-Zn-Mn-Ca alloys with different content of Zn.

| Specimen             | Yield strength (Mpa) | Tensile strength (Mpa) | Elongation (%) | Hardness (Hv) |
|-----------------------|----------------------|------------------------|----------------|---------------|
| as-cast Mg-2Zn-0.2Mn-0.2Ca | 58.4                 | 177.6                  | 13.1           | 49.3          |
| as-cast Mg-4Zn-0.2Mn-0.2Ca | 69.0                 | 205.0                  | 14.7           | 53.4          |

4. Conclusion
The main secondary phase in Mg-2Zn-0.2Mn-0.2Ca and Mg-4Zn-0.2Mn-0.2Ca alloys is MgZnCa phase. The volume fraction of the secondary phase increased as the Zn increased.

The addition of Zn had a great effect on refining grain, which could improve the mechanical properties of the as-cast alloys.

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