Influence of Ca addition on microstructure, mechanical properties and corrosion behavior of Mg-2Zn alloy

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Abstract: The microstructure, mechanical properties and corrosion behaviors of as-cast ternary Mg-2Zn- x Ca ($x=0, 0.2, 0.4, 0.8$) alloys have been investigated in this study. Results indicate that the microstructure of Mg-Zn-Ca alloys can be significantly refined with increasing Ca concentration. Moreover, the alloys with different contents of Ca exhibit the different phases formation behaviors, i.e. α -Mg + $\text{Ca}_2\text{Mg}_6\text{Zn}_3$ phases for Mg-2Zn-0.2Ca and Mg-2Zn-0.4Ca alloys, and α -Mg + $\text{Ca}_2\text{Mg}_6\text{Zn}_3$ + Mg_2Ca phases for Mg-2Zn-0.8Ca alloy, respectively. Among all the alloys, the maximum ultimate tensile strength and elongation (161 MPa and 9.1%) can be attained for the Mg-2Zn-0.2Ca alloy. Corrosion tests in Hanks' balanced salt solution indicated that Ca addition is detrimental to corrosion resistance of Mg-2Zn alloy. The relationship between as-cast microstructure and properties for different Ca-containing alloys is also discussed in detail.

Key words: magnesium alloys; Mg-Zn-Ca; microstructure; mechanical properties; corrosion behaviors

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Due to low Young's modulus ($\sim 45\text{GPa}$), low density ($1.7\text{--}2.0\text{ g}\cdot\text{cm}^{-3}$), and good biodegradable properties, magnesium and magnesium alloys are in a region of interest as potential orthopedic, craniofacial, and cardiovascular materials [1]. Many researchers are currently developing new biodegradable magnesium alloys and investigating all kinds of properties [2]. Among all the alloys, Mg-Zn-Ca especially attracts the scientists' attention because of their high strength (yield strength $>200\text{ MPa}$, ultimate tensile strength $>250\text{ MPa}$), high ductility (elongation $>20\%$), moderate bio-corrosion properties, and good biocompatibility [3, 4]. Summarizing the development status of Mg-Zn-Ca alloys, it is found that Zn content generally surpasses or equals to 4wt.% if Ca addition is less than 1wt.% [1, 5-13] or Zn concentration $<10\text{wt.}\%$ if Ca addition is $\geq 1\text{wt.}\%$ [14-20]. The purpose of high Zn addition is to ensure high mechanical properties by solid-solution strengthening, grain boundary strengthening and precipitation strengthening, while the role of Ca is to refine the grain size and enhance the ignition point [21]. However, it is also noted that high Zn or high Ca concentration is generally detrimental to corrosion resistance [15, 22-25]. Therefore, the growing trend in

recent years is developing low-alloyed Mg-Zn-Ca alloys, which can coordinate mechanical and corrosion properties simultaneously. For example, Hofstetter et al. developed a Mg-1Zn-0.3Ca alloy and obtained a good combination of mechanical and corrosion properties by optimizing hot deformation process [4]. Zhang et al. also developed a Mg-1.0Zn-0.5Ca alloy by extrusion deformation, which exhibited the strength of 215 MPa and elongation of 44% [26]. From previous studies, it can be found that most of them mainly concentrated on developing the low-alloyed wrought Mg-Zn-Ca alloys. However, learning about the knowledge of the microstructure of as-cast alloys is also very useful in evaluating the properties of wrought alloys, especially understanding phase formation behaviors during age-hardening treatment. To date, few papers to date have been devoted to studying the microstructure of low-alloyed as-cast Mg-Zn-Ca alloys and understanding the relationship between as-cast microstructure and properties.

Recently, new Mg- x Zn-0.2Ca alloys were developed by the authors and the changes of as-cast microstructure and properties with increasing Zn content were also investigated [27]. However, the effects of Ca content on the as-cast microstructure, mechanical and corrosion properties in this alloy system were not studied in detail. Based on the above situation, the corresponding work has been performed and the relationship between the as-cast microstructure and properties of different Ca-containing alloys are also discussed in detail.

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1 Experimental procedures

1.1 Materials and preparation of samples

Alloys of nominal composition Mg-2Zn- x Ca ($x=0, 0.2, 0.4, 0.8$, by weight percent, hereafter denoted as 0Ca, 0.2Ca, 0.4Ca and 0.8Ca alloys) were prepared from pure Mg ingot (99.99wt.%), pure Zn piece (99.99wt.%) and Mg-33wt.%Ca master alloy. Pure magnesium ingot was first melted in an electric resistance furnace with a low-alloy steel crucible under the protection of 99%CO₂ + 1%SF₆. When the magnesium melt temperature reached 660 °C, pure zinc and Mg-Ca master alloy were added, and then the melt was stirred for 2 minutes. Afterwards, the temperature of the melt was raised to 730 °C and kept for 15 minutes. After that, the melt was decreased to 700 °C and poured into the water-cooling copper mold to obtain the as-cast ingots. No homogenization treatment was performed.

1.2 Microstructure examination and properties tests

All the specimens for microstructure observation were prepared with standard metallographic procedures. An OLYMPUS-BX51M optical microscopy (OM) and a field-emission scanning electron microscope (FE-SEM) Supra 55 with energy-dispersive X-ray spectroscopy (EDS) were used to observe the microstructure of different Ca-containing specimens. Average grain size was estimated using the line intercept method on the SEM micrographs. Preliminary examination of phases in as-cast alloys was carried out using a Rigaku DMAX-RB X-ray diffractometer with Cu K α radiation. The distribution and

types of phases were observed by a 200 kV Tecnai G2 F20 transmission electron microscopy (TEM). TEM specimens were prepared by twin-jet electro-polishing (Tenupol-5).

Dog-bone specimens for tensile tests were machined with 35 mm gauge length, 2 mm thickness and 10 mm width. Tensile tests were performed on an Instron5569 materials testing machine at a displacement rate of 1 mm·min⁻¹. Three parallel specimens were taken for each group experiment in the tensile test.

1.3 Corrosion tests

Immersion tests were conducted in a Hanks' balanced salt solution without glucose using the specimens with a dimension of 10 mm × 10 mm × 2 mm. The Hanks' solution was prepared using bi-distilled water and high-purity chemicals according to reference [17]. pH value of the solution was adjusted to 7.4 at 37±0.5 °C through the manual addition of H₃PO₄. The immersion solution was refreshed every 24 h. After an immersion for 7 days, samples were removed from the solution and cleaned with chromic acid to remove surface corrosion products without removing any amount of metallic Mg. Then the specimens were rinsed with distilled water, cleaned ultrasonically in acetone, and dried in air. Finally, surface morphologies of corroded samples were observed by SEM.

2 Results

2.1 As-cast microstructure

Figures 1 and 2 show the as-cast microstructure of Mg-2Zn- x Ca ($x=0, 0.2, 0.4, 0.8$) alloys observed by OM and EBSD,

Fig. 1: As-cast microstructure of Mg-2Zn- x Ca ($x=0, 0.2, 0.4, 0.8$) alloys observed by OM: (a) 0Ca; (b) 0.2Ca; (c) 0.4Ca; (d) 0.8Ca

respectively. From Figs. 1 and 2, it can be seen that with an increase in Ca content, the dendritic structure is becoming very refined, and the addition of 0.8wt.% Ca to Mg-2Zn alloy can induce grain refinement from 388 μm to 175 μm . The positive role of Ca element in refining the grains has also been reported by other researchers^[15-16, 21].

Figure 3 shows the SEM photographs of as-cast Ca-containing alloys. Similar with that as shown in Figs. 1 and 2, it clearly shows the tendency of grain refinement with increasing Ca concentration. Secondary phase tends to be precipitated along the grain boundary with further Ca addition. For the 0.8Ca alloy, the net-like structure can be formed and few granular phases can

Fig. 2: As-cast microstructure of Mg-2Zn-xCa ($x=0, 0.2, 0.4, 0.8$) alloys observed by EBSD: (a) 0Ca; (b) 0.2Ca; (c) 0.4Ca; (d) 0.8Ca

Fig. 3: As-cast microstructure of Mg-2Zn-xCa ($x=0, 0.2, 0.4, 0.8$) alloys observed by SEM: (a) 0Ca; (b) 0.2Ca; (c) 0.4Ca; (d) 0.8Ca

be observed at the inner grains. That is, Ca addition can change the morphology and distribution of the precipitated secondary phase.

To identify the phase constitutes, XRD tests of as-cast samples with different Ca contents were performed and the patterns are shown in Fig. 4. According to the phase diagrams of binary Mg-Ca, Mg-Zn and ternary Mg-Zn-Ca^[28,29], the maximum solubility of Ca and Zn in magnesium is 0.2wt.% and <2.0wt.%, respectively, at room temperature in the equilibrium state. Thus with the additions of Ca and Zn above its solubility limit, excess Ca and Zn can appear in the forms of intermetallics as a secondary phase. As seen in Fig. 4, the peaks corresponding to α -Mg matrix and MgZn can be observed for 0Ca alloy, which is confirmed in binary Mg-Zn phase diagram. A small amount of granular phase particles precipitated along the grain boundary (Fig. 4a). With increasing Ca content to 0.2wt.% and 0.4wt.%, α -Mg solid solution + $\text{Ca}_2\text{Mg}_6\text{Zn}_3$ phase can be identified in the XRD pattern. By continuing to increase Ca content such as 0.8Ca alloy, it clearly shows that α -Mg solid solution + $\text{Ca}_2\text{Mg}_6\text{Zn}_3$ phase + Mg_2Ca phase can be formed. That is to say, different Ca-containing alloys exhibit different phases formation behaviors.

TEM analyses of different Ca-containing alloys were also performed in this study to confirm the characteristics of phases formation. Figure 5 presents TEM bright-field images of as-cast 0.2Ca alloy and the corresponding selected area diffraction patterns (SADP). It can be seen that the alloy matrix is α -Mg solid solution as indicated by SADP images, taken along $[1\bar{2}10]$ zone axis shown in Fig. 5(a, d). From the SADP analysis, $\text{Ca}_2\text{Mg}_6\text{Zn}_3$ phase with strip-like or globular morphologies (zone axis $[1\bar{2}10]$ and zone axis $[0001]$), shown in Fig. 5(a, e, and b, f), was observed

Fig. 4: XRD patterns of as-cast samples for Mg-2Zn-xCa ($x= 0, 0.2, 0.4, 0.8$) alloys

in the 0.2Ca alloy. Meanwhile, it was also found that the ternary $\text{Ca}_2\text{Mg}_6\text{Zn}_3$ phase can coexist with α -Mg in the forms of eutectic phases, as shown in Fig. 5(c, g).

Figure 6 shows TEM bright-field images and the corresponding SADPs for as-cast 0.8Ca alloy. From Fig. 6, it is clear that the precipitated phases basically distribute along the grain boundary and there is the continuous net-like structure, which is in accordance with SEM results shown in Fig. 2. Moreover, few precipitated phases can be observed in the inner grain besides the α -Mg matrix. The second phase distributing along the grain boundary was identified to be $\text{Ca}_2\text{Mg}_6\text{Zn}_3$ phase (hexagonal structure), as shown in Fig. 6(a, c and d) (a2 and a3, zone axis $[2\bar{4}23]$). Some parallel strip-like phases, marked as a1 in Fig. 6(a), were found to coexist with $\text{Ca}_2\text{Mg}_6\text{Zn}_3$ phase. Further analysis confirmed that

Fig. 5: TEM bright-field images of as-cast 0.2Ca alloys and corresponding selected area diffraction patterns (SADP): (a) (b)(c) TEM Bright-field images; (d) SADP for α -Mg phase shown in (a); (e) SADP for $\text{Ca}_2\text{Mg}_6\text{Zn}_3$ phase shown in (a); (f) SADP for $\text{Ca}_2\text{Mg}_6\text{Zn}_3$ phase shown in (b); (g) SADP for α -Mg phase shown in irregular line in (c)

Fig. 6: TEM bright-field images of as-cast 0.8Ca alloys and corresponding selected area diffraction patterns (SADP): (a) TEM Bright-field images; (b) SADP for a1 phase (Mg_2Ca) shown in (a); (c) SADP for a2 phase ($\text{Ca}_2\text{Mg}_6\text{Zn}_3$) shown in (a); (d) SADP for a3 phase ($\text{Ca}_2\text{Mg}_6\text{Zn}_3$) shown in (a)

these strip-like phases are Mg_2Ca (monoclinic structure), which can be identified from SADP images, taken along $[011]$ zone axis shown in Fig. 6(b). Compared with Figs. 5 and 6, it clearly shows that with Ca addition, the microstructure can change from α -Mg+ $\text{Ca}_2\text{Mg}_6\text{Zn}_3$ for 0.2Ca alloy to α -Mg+ $\text{Ca}_2\text{Mg}_6\text{Zn}_3$ + Mg_2Ca for 0.8Ca alloy, which coincides with XRD analysis shown in Fig. 4.

2.2 Mechanical and corrosion properties

Tensile strength, yield strength and elongation from different Ca-containing alloys are listed in Table 1. From the table, it is

found that tensile strength and elongation firstly increase and then decrease with increasing Ca content, and 0.2Ca alloy has the maximum tensile strength and elongation values (161 MPa and 9.1%).

Corrosion properties of different Ca-containing alloys after immersion for 168 h in a Hanks' solution at 37 °C were also evaluated, and the corresponding results are shown in Fig. 7. It can be seen that with the increase of Ca content, the corrosion rate continuously increases from 0.14 $\text{mg}\cdot\text{cm}^{-2}$ per day for 0Ca alloy to 0.82 $\text{mg}\cdot\text{cm}^{-2}$ per day for 0.8Ca alloy. For 0.2Ca and 0.4Ca alloys,

Table 1: Alloy composition investigated in this study and their tensile properties

Materials	Tensile strength (MPa)	Yield strength (MPa)	Elongation (%)
Mg-2.0Zn	123	55	6.3
Mg-2.0Zn-0.2Ca	161	72	9.1
Mg-2.0Zn-0.4Ca	143	64	7.3
Mg-2.0Zn-0.8Ca	132	73	3.0

the middle value of corrosion rate can be attained, i.e. $0.17 \text{ mg}\cdot\text{cm}^{-2}$ per day and $0.28 \text{ mg}\cdot\text{cm}^{-2}$ per day, respectively.

Figure 8 shows SEM micrographs of the corroded products after immersion for 168 h in a Hanks' solution at 37°C . From Fig. 8, it can be seen that the insoluble corrosion layer with a number of cracks was formed on the surface of different Ca-containing alloy samples. The formation of cracks resulted from the dehydration of the surface layer in air. With the increase of Ca content, the thickness of the corrosion layer increased, and the width and depth of the cracks produced in the corrosion layer also enlarged. The crack width and depth in the corrosion layer of the 0.8Ca alloy were the largest (Fig. 8d).

After removing the corrosion products, SEM surface micrographs were taken and are shown in Fig. 9. It can be seen

Fig. 7: Corrosion rate of Mg-2Zn-xCa ($x=0, 0.2, 0.4, 0.8$) alloys after immersion for 168 h in a Hanks' solution at 37°C

from Fig. 9(a), (b), and (c) that different Ca-containing alloys have different corrosion surface morphologies. A large amount of dense pitting corrosion holes can be seen for 0Ca alloy and the corrosion is relatively uniform. Compared with 0Ca alloy, the corrosion of 0.2Ca alloy is more serious and the corrosion holes are obviously dense, and the size of these holes is large. For 0.8Ca alloy, these pitting corrosion holes are interconnected and the corrosion cavities

Fig. 8: SEM micrographs of corroded products of Mg-2Zn-xCa ($x=0, 0.2, 0.4, 0.8$) alloys after immersion for 168 h in Hanks' solution at 37°C : (a) 0Ca; (b) 0.2Ca; (c) 0.4Ca, (d) 0.8Ca

Fig. 9: SEM micrographs of corroded surface of Mg-2Zn-xCa ($x=0, 0.2, 0.8$) alloys after removing the corrosion products: (a) 0Ca; (b) 0.2Ca; (c) and (d) 0.8Ca; (e) magnified micrographs shown in rectangular shape in (c); (f) further magnified micrographs shown in rectangular shape in (e)

with different sizes are produced. These corrosion cavities could propagate from the surface to the inner layer and even go through sole grains to form.

3 Discussion

In this study, the grain refinement of Mg-2Zn alloy with more Ca addition is very obvious. This can be attributed to the formation of constitutional undercooling in a diffusion layer ahead of the solid/liquid interface. Due to the accumulation of alloying elements (Ca and Zn) at the front of grain growth which limits the growth stage, the grain size is decreased^[30].

From the microstructure analysis shown in Figs. 3–6, it can be found that when Ca content is 0.2wt.% and 0.4 wt.%, only two phases are formed: α -Mg+Ca₂Mg₆Zn₃. With more Ca addition, three phases, i.e. α -Mg+Mg₂Ca+Ca₂Mg₆Zn₃, can be formed in the as-cast samples. Moreover, the binary phase Mg₂Ca can be embraced by the ternary phase Ca₂Mg₆Zn₃, and thus may serve as a nucleus for the ternary phase^[16], as shown in Fig. 6(a). From the OM and SEM images shown in Figs. 1 and 3, it is clear that the volume fractions of the secondary phases increase with the increase of Ca content, leading to more interlinked phases on the grain boundaries. Thus for 0.8Ca alloys as seen in Fig. 2, the precipitated phases can be assembled along the

grain boundary so that the net-like structure can be formed. It is known that the mixing enthalpy between Zn and Ca is $-22 \text{ kJ}\cdot\text{mol}^{-1}$, which is much greater than that of Mg-Zn ($-4 \text{ kJ}\cdot\text{mol}^{-1}$) and Mg-Ca ($-6 \text{ kJ}\cdot\text{mol}^{-1}$)^[31]. When Ca is added, it tends to bond with Zn atoms rather than Mg atoms and, as a result, $\text{Ca}_2\text{Mg}_6\text{Zn}_3$ phase can be formed. However, with more Ca addition and the depletion of Zn atoms for the formation of ternary phases, Ca can possibly bond with Mg atoms, leading to the formation of Mg_2Ca phase. Moreover, with increasing Ca content, the amount of Mg_2Ca phase formation increases while $\text{Ca}_2\text{Mg}_6\text{Zn}_3$ phase tends to be stable (Fig. 2).

In Table 1, the UTS and elongation of Mg-Zn-Ca alloy increase firstly with the increase of Ca content and then decrease after the further addition of Ca element. The increase of UTS for Mg-Zn-Ca alloy with Ca content up to 0.2wt.% can be firstly speculated from the grain refinement (Figs. 1 and 2) according to Hall-Petch law^[32]. On the other hand, it was reported that ternary $\text{Ca}_2\text{Mg}_6\text{Zn}_3$ phase is an effective strengthening phase, while the binary Mg_2Ca phase, a brittle phase dispersed along grain boundaries, easily produces crack sources, which can propagate and induce the brittle fracture^[6, 15, 33]. For the 0.2Ca alloy, only $\alpha\text{-Mg} + \text{Ca}_2\text{Mg}_6\text{Zn}_3$ phases can be formed. With the strengthening role of $\text{Ca}_2\text{Mg}_6\text{Zn}_3$ phase and the grain refinement, it is easy to understand why this alloy can obtain the highest mechanical properties. But for the 0.8Ca alloy, $\alpha\text{-Mg} + \text{Mg}_2\text{Ca} + \text{Ca}_2\text{Mg}_6\text{Zn}_3$ phases can be formed. With the coexistence of Mg_2Ca and $\text{Ca}_2\text{Mg}_6\text{Zn}_3$ phases, especially the increase of brittle Mg_2Ca phase, the strength tends to be decreased. In addition, the net-like grain boundary structure weakens the bonding force of the grains and easily becomes the cracking initiation sites, especially in the coarser precipitates located at the triangle junction of three grains. Therefore, though attaining the better grain refinement for the 0.8Ca alloy, its strength and elongation all decrease.

Figure 7 clearly shows that the corrosion resistance decreases with the increase of Ca content. As is well known, the standard electrode potentials of the formed phases in Mg-Zn-Ca alloy are in the following order: $\text{Ca}_2\text{Mg}_6\text{Zn}_3 > \alpha\text{-Mg} > \text{Mg}_2\text{Ca}$ ^[6, 33].

For the 0.8Ca alloy, Mg_2Ca phase acts as an anode and Mg matrix as a cathode. With a large amount of corrosion of Mg_2Ca phase, they are detached and corrosion holes would be formed. More seriously, with the corrosion continuing, these corrosion holes can even connect with each other and form corrosion cavities. In turn, the cavities can accelerate the corrosion process due to contacting more corrosive liquid. Thus it is easy to understand why the 0.8Ca alloy can obtain the worst corrosion resistance.

For the 0.2Ca alloy only two phases, i.e. $\alpha\text{-Mg} + \text{Ca}_2\text{Mg}_6\text{Zn}_3$, are formed. $\text{Ca}_2\text{Mg}_6\text{Zn}_3$ phase can serve as a cathode while Mg matrix acts as an anode at the interface between $\text{Ca}_2\text{Mg}_6\text{Zn}_3$ and Mg matrix. Due to the relatively lower amount of $\text{Ca}_2\text{Mg}_6\text{Zn}_3$ (Fig. 2), the galvanic reaction between $\text{Ca}_2\text{Mg}_6\text{Zn}_3$ and $\alpha\text{-Mg}$ cannot be very serious compared with 0.8Ca alloy. Therefore, 0.2Ca alloy can obtain a higher corrosion resistance than 0.8Ca alloy. The difference of corrosion resistance between 0.2Ca and

0.8Ca alloys can also be confirmed from their corroded surface morphologies as shown in Figs. 8 and 9.

For the 0Ca alloy, it can be seen that the amount of Mg_2Ca phase precipitated is very much lower and thus the galvanic reaction is smaller. Therefore, the 0Ca alloy can obtain the highest corrosion resistance among all the alloys in this study.

4 Conclusions

In this study the effects of Ca content on the microstructure, mechanical behaviors and corrosion properties in the as-cast low-alloyed Mg-Zn-Ca alloys were investigated. Summarizing the results, the conclusions can be drawn as follows:

- (1) With Ca addition, the grain is refined, and the amount of precipitated secondary phases increases with more Ca addition.
- (2) Different precipitation behaviors of phases are observed for different Ca-containing alloys. As-cast microstructures of 0.2Ca alloy and 0.4Ca alloy are composed of $\alpha\text{-Mg}$ and $\text{Ca}_2\text{Mg}_6\text{Zn}_3$ phases while that of 0.8Ca alloys contain $\alpha\text{-Mg}$, Mg_2Ca and $\text{Ca}_2\text{Mg}_6\text{Zn}_3$ phases as revealed by XRD and TEM analyses.
- (3) With the increase of Ca content, ultimate tensile strength (UTS) and elongation to fracture all firstly increase and then decrease. Among three alloys, 0.2Ca alloy exhibits the best combination of UTS (161 MPa) and elongation to fracture (9.1%), which can be explained from grain refinement and secondary phase strengthening.
- (4) With the increase of Ca content, the corrosion rate increases correspondingly, which can be explained from characteristics of their different phases precipitated.

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