

Effect of Ca addition on microstructure, mechanical properties, solidification behavior, and fluidity of cast Mg-4Zn- x Ca-0.3Zr alloys

*Sheng-wei Bai^{1,2,3}, Ze-hua Li^{1,3}, Tong-shu Wang⁴, **Feng Wang⁵, Ke Chen^{1,2,3}, Yu-fei Li^{1,2}, Liang Zhan^{1,2}, Ming Ruan^{1,2}, Shi-wei Xin^{1,2}, Xiao Li^{1,2}, Jia-yi Liu^{1,2,3}, Bo-wen Chang^{1,2,3}, Zhi-zhong Liu^{1,2,3}, and Zhi-jun Feng^{1,2,3}

1. Shenyang Research of Casting Technology Co., Ltd., Shenyang 110167, China

2. Shenyang Research Institute of Foundry Co., Ltd. CAM, Shenyang 110022, China

3. State Key Laboratory of Advanced Casting Technologies, Shenyang 110022, China

4. Shenyang Aircraft Corporation, Shenyang 110136, China

5. School of Materials Science and Engineering, Shenyang University of Technology, Shenyang 110870, China

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Abstract: Mg-Zn-(Ca-Zr) alloys are regarded as promising biomedical magnesium alloys due to their low cost, superior strength-toughness matching, and excellent biocompatibility. However, the correlation among Ca content, solidification characteristics, mechanical properties, and casting fluidity remains unclear, limiting the targeted performance optimization of cast Mg-Zn-(Ca-Zr) alloys. To address this issue, this study focused on Mg-4Zn- x Ca-0.3Zr alloys ($x=0, 0.5, 1, 1.5, 2$, wt.%). In this study, XRD, SEM, EBSD, TEM, tensile testing, thermal analysis, and fluidity measurement were adopted to investigate the effects of Ca addition on the microstructure, mechanical properties, fluidity, and solidification path of the investigated alloys, while exploring the solidification behavior and the mechanism governing strength and ductility. Experimental results indicate that the addition of Ca promotes the formation of reticularly distributed lamellar coarse brittle secondary phases ($\text{Ca}_2\text{Mg}_6\text{Zn}_3$ and Mg_2Ca phases), which reduce grain boundary strength and deteriorate the mechanical properties of the alloys. Among them, the Mg-4Zn-0.3Zr alloy exhibits the optimal mechanical properties (UTS=261.7 MPa, YS=147.0 MPa, EL=8.8%). The addition of Ca significantly shortens the solidification temperature range of the investigated alloys and increases the content of secondary phases. Furthermore, under the combined effect of delayed dendrite coalescence, reduced overall and liquid-phase viscosity, and improved structure of the solid-liquid interface front, the fluidity of the alloys gradually increases with increasing Ca content. Specifically, the length of the fluidity sample for the Mg-4Zn-2Ca-0.3Zr alloy is 45.7% longer than that of the Mg-4Zn-0.3Zr alloy. Considering both formability and mechanical properties, the Mg-4Zn-0.5Ca-0.3Zr alloy exhibits the optimal comprehensive performance among all investigated alloys.

Keywords: Mg-Zn-(Ca-Zr) alloy; mechanical properties; solidification behavior; microstructure

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1 Introduction

As the lightest structural metallic materials, magnesium alloys have been widely applied in aerospace, 3C

electronics, automotive industry, and other fields^[1]. Among them, ZK-series (Mg-Zn-Zr) magnesium alloys are widely used high-strength wrought magnesium alloys at present^[2, 3]. Under the combined effects of solid solution strengthening, age hardening, and dispersion strengthening induced by Zn element, the mechanical properties and creep resistance of ZK-series alloys are enhanced compared to pure magnesium, with this enhancing effect becoming more pronounced as the Zn addition increases^[4]. Casting is one of the main preparation processes for ZK-series alloys, and the forming quality of castings

*Sheng-wei Bai

Ph. D., Engineer. His research interests mainly focus on high-performance magnesium alloy casting technologies and casting defect control.

E-mail: Baishengwei9706@126.com

**Feng Wang

E-mail: wf9709@126.com

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directly determines their subsequent processing and service reliability. However, the coarse microstructure of the alloy tends to induce defects such as pores, which deteriorate its workability^[5]. Therefore, introducing appropriate elements via alloying approaches to simultaneously optimize the casting properties, service stability, and mechanical properties of ZK-series alloys has become the key to further expanding their application scenarios.

Ca, as a low-cost, abundant, and reactive alkaline earth metal, is regarded as one of the most promising alloying elements for magnesium alloys. Studies have shown that adding Ca to pure magnesium can significantly improve the creep resistance of the alloy^[6, 7] and exert a certain inhibitory effect on oxidation^[8]. In recent years, biomedical magnesium alloys have emerged as a research hotspot in the field of degradable implant materials (such as bone nails, bone plates, and vascular stents) due to their excellent biocompatibility, degradability, and mechanical compatibility. The Mg-Zn-(Ca-Zr) series alloys have stood out among biomedical magnesium alloys owing to the biosafety of their composition^[9]. Compared with other biomedical magnesium alloys, Mg-Zn-(Ca-Zr) alloys possess multiple advantages including low cost, good strength and toughness, and outstanding biocompatibility, along with high alloying potential. They can achieve the matching of degradation rate and mechanical properties through composition regulation.

Since the initiation of research on Mg-Zn-(Ca-Zr) series alloys, researchers have investigated the relationship between alloy composition and types of secondary phases^[10-12]. It is generally acknowledged that the phase composition of Mg-Zn-(Ca-Zr) alloys depends on the Zn/Ca atomic ratio (at.%). Specifically, when the Zn/Ca ratio exceeds 1.2, the secondary phase in as-cast alloys consists of the $\text{Ca}_2\text{Mg}_6\text{Zn}_3$ phase; when the Zn/Ca ratio is less than 1.2, the secondary phase in the alloy is composed of both $\text{Ca}_2\text{Mg}_6\text{Zn}_3$ and Mg_2Ca phases^[11]. In Mg-Zn-Ca series alloys, the composition, content, and specific morphology of these secondary phases all exert varying effects on the mechanical properties of the alloys.

With the advancement of research on the composition and precipitated phases of Mg-Zn-(Ca-Zr) alloys, researchers have conducted investigations on their mechanical properties^[10-26]. Statistics on the mechanical properties of cast Mg-Zn-(Ca-Zr) magnesium alloys from existing reports are presented in Fig. 1^[10, 13-15, 17, 20, 22-26]. Currently, most research on cast Mg-Zn-(Ca-Zr) alloys has focused on three aspects: (1) adjusting the content of Zn and/or Ca elements^[13, 14] (cyan ellipse in Fig. 1); (2) single or composite alloying with other elements^[15, 16] (orange ellipse in Fig. 1); (3) modifying processing methods^[17] (e.g., ultrasonic treatment, mechanical vibration, and pink ellipse in Fig. 1).

In addition, only a few studies have focused on the cast formability of Mg-Zn-(Ca-Zr) alloys to date. Song^[27, 28] and Bai^[29] et al. conducted tests on the hot tearing susceptibility of Mg-Zn-(Ca-Zr) alloys and revealed the hot tearing

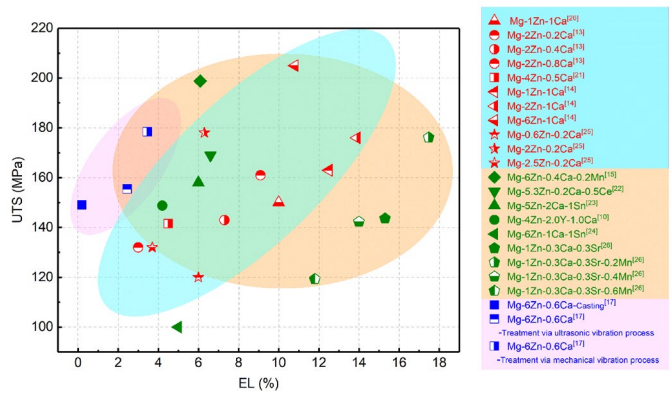


Fig. 1: Statistics on mechanical properties of some Mg-Zn-(Ca-Zr) series cast alloys in existing reports^[10, 13-15, 17, 20-26]

mechanism of the alloys. Experimental results indicated that due to the wide solidification temperature range of Mg-Zn-(Ca-Zr) alloys, they remained in the low-strength solid-liquid two-phase region for a long duration during solidification, thus exhibiting low hot tearing resistance. With the increase in Ca and Zn additions, the amount of residual liquid phase that participated in feeding increased, thereby enhancing the hot tearing arresting ability of the alloy. However, existing research on the comprehensive cast formability of Mg-Zn-(Ca-Zr) alloys remains insufficient. The effects of Ca addition on the formability and mechanical properties of the alloy remain unclear, and the coordinated optimization of formability and mechanical properties of Mg-Zn-(Ca) alloy castings cannot be achieved.

This study investigates the effects of compositional regulation on the mechanical and casting properties of Mg-Zn-(Ca-Zr) alloys. Using Mg-4Zn- x Ca-0.3Zr alloys ($x=0, 0.5, 1, 1.5, 2$, wt.%) as the research materials, it clarifies the correlations among alloy composition, phase constitution, microstructure, mechanical performance, solidification behavior, and fluidity, aiming to provide fundamental data and theoretical guidance for the optimized design and practical engineering application of Mg-Zn-(Ca-Zr) alloys.

2 Experiment process

The materials employed in the experiments comprised pure magnesium (99.99%) and pure zinc (99.9%) ingots, along with intermediate alloys of Mg-20Ca (wt.%) and Mg-30Zr (wt.%). The alloy preparation process was as follows. Firstly, metal ingots were cut in accordance with the nominal composition proportions. Subsequently, pure Mg and pure Zn (cut and with clean ground surfaces) were placed in a 30 kg crucible resistance furnace for melting. After pure Mg and Zn were completely melted, Mg-30Ca master alloy was added, followed by thorough stirring and slag skimming. When the furnace temperature rose to 780 °C, preheated Mg-30Zr master alloy was added in two batches, then thoroughly stirred again and slag skimmed. After standing for 50 min, the molten metal was poured into preheated sand molds (150 °C, hot air baking). The entire melting process of Mg-4Zn- x Ca-0.3Zr ($x=0, 0.5, 1, 1.5, 2$, wt.%) was conducted under the protection of a mixed gas of

$\text{CO}_2+0.2\text{vol.}\% \text{SF}_6$. The casting and its dimension are shown in Fig. 2. The actual chemical compositions of the investigated alloys were all determined by Inductively Coupled Plasma (ICP, ICP-OES), the nominal and actual chemical compositions of the alloys are listed in Table 1.

X-ray diffraction (XRD, SHIMADZU XRD-7000) with Cu $K\alpha$ radiation was used to identify the phases. The voltage was set at 40 kV, the scanning speed was $4^\circ\cdot\text{min}^{-1}$, and the angle scan range spanned from 20° – 90° . Additionally, a scanning electron microscope (SEM, Hitachi S-3400N) equipped with an energy dispersive spectrometer (EDS) was employed to observe the microstructure and fracture morphology of the investigated alloys. For sample preparation, the samples were sequentially ground with #1000 and #2000 SiC sandpapers, followed by mechanical polishing until the sample surfaces became mirror-like and free of scratches, and then etched with a 4vol.% nitric acid-ethanol solution for approximately 5 s. Electron backscatter diffraction (EBSD, Zeiss GeminiSEM 300) was used to characterize the microstructure of the investigated alloys. The sample preparation method for EBSD was as follows: The samples were mechanically polished, and then polished under an argon ion beam with parameters of 3° and 8 keV for 1 h, ensuring a bright surface. EBSD data were analyzed using Channel 5 software (HKL, Oxford, UK).

Room-temperature mechanical property tests of the investigated alloys were conducted on a CSS-44100 electronic universal testing machine at a speed of $2\text{ mm}\cdot\text{min}^{-1}$, the dimensional diagram of tensile testing is shown in Fig. 3. Each alloy was tested three times, and the average values of ultimate tensile strength (UTS), yield strength (YS), and elongation (EL) were calculated as the final mechanical properties of the alloy. A transmission electron microscope (TEM, JEOL JEM-2100) was used to further confirm and characterize the microstructure and composition of the secondary phases in the alloys. The preparation process of TEM samples was as follows. Firstly, a precision low-speed cutting machine was used to cut metal foils with a thickness of 500 μm , which were ground to 100 μm on #2000 SiC sandpapers and then punched into several small

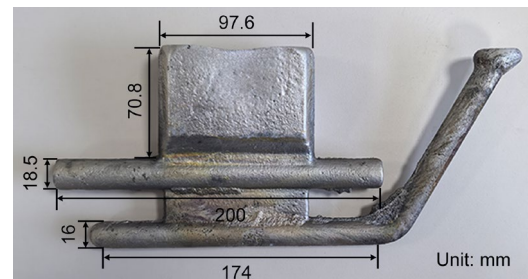


Fig. 2: Casting photographs and dimensions

Table 1: ICP test results of investigated alloys (wt.%)

Alloy	Mg	Zn	Ca	Zr	Zn/Ca (at.%)
Mg-4Zn-0.3Zr	Bal.	3.99±0.10	–	0.28±0.05	–
Mg-4Zn-0.5Ca-0.3Zr	Bal.	3.97±0.08	0.48±0.05	0.29±0.05	5.07
Mg-4Zn-1Ca-0.3Zr	Bal.	3.99±0.12	1.01±0.06	0.29±0.03	2.43
Mg-4Zn-1.5Ca-0.3Zr	Bal.	3.96±0.07	1.49±0.05	0.30±0.04	1.63
Mg-4Zn-2Ca-0.3Zr	Bal.	3.97±0.10	2.03±0.08	0.28±0.06	1.20

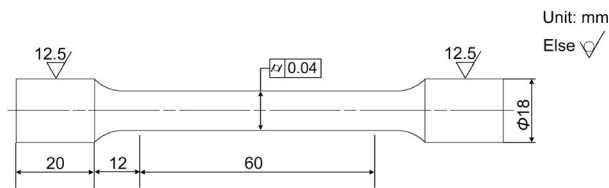


Fig. 3: Diagram of tensile test bar

discs with a diameter of 3 mm. Subsequently, the discs were further ground to 60 μm on #5000 SiC sandpapers, and then polished using an argon ion polisher (PIPS 691) under the parameters of $\pm 6^\circ$ and 5 keV until perforation. Finally, they were maintained under the parameters of $\pm 3^\circ$ and 3.5 keV for 20 min to slightly expand the thinned area.

A double thermocouple differential thermal analysis experimental device shown in Fig. 4 was used to collect and record temperature change information during the solidification of alloys, aiming to study the solidification behavior of investigated alloys. Two thermocouples were employed to measure the melt temperature at the center and edge of the crucible in real time, respectively. By plotting the

cooling curve of the melt at the crucible center, the critical reaction temperature could be determined. More importantly, the solid fraction curve of the alloy during solidification could be calculated via the Newtonian baseline method. This method is one of the simplest and most widely used approaches in computer-aided cooling curve analysis^[30-32]. The solid fraction at each moment was obtained by the following equation^[33]:

$$f_s = \frac{\int_{t_1}^t \left[\left(\frac{dT}{dt} \right)_{cc} - \left(\frac{dT}{dt} \right)_{b_1} \right] dt}{\int_{t_1}^{t_s} \left[\left(\frac{dT}{dt} \right)_{cc} - \left(\frac{dT}{dt} \right)_{b_1} \right] dt} \quad (1)$$

where cc denotes the cooling curve, b_1 represents the baseline, t_1 and t_s correspond to the start and end times of solidification, respectively.

The fluidity test was carried out using a single-spiral mold. The molten alloy was poured into a fluidity sand mold (the schematic diagram of the sand mold for fluidity sample is shown in Fig. 5) preheated to 150 $^\circ\text{C}$. After the casting cooled down, the spiral specimen was taken out, and its length was measured to evaluate fluidity.

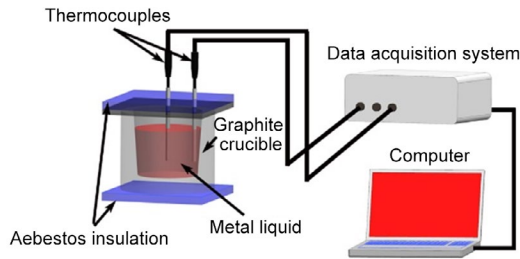


Fig. 4: Schematic of double thermocouple differential thermal analysis experimental device

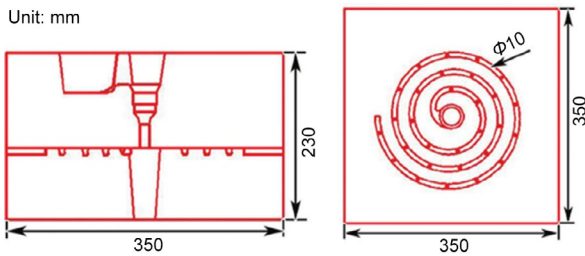


Fig. 5: Illustration of the fluidity mold

3 Experimental results

3.1 Phase and microstructure analysis

3.1.1 XRD results of investigated alloys

The XRD patterns of the investigated alloys are presented in Fig. 6. Diffraction peaks of α -Mg and MgZn phases are detected in Mg-4Zn-0.3Zr alloy, while diffraction peaks of α -Mg, $\text{Ca}_2\text{Mg}_6\text{Zn}_3$, and MgZn phases are observed in Mg-4Zn-0.5Ca-0.3Zr, Mg-4Zn-1Ca-0.3Zr, and Mg-4Zn-1.5Ca-0.3Zr alloys. In the Mg-4Zn-2Ca-0.3Zr alloy, additional diffraction peaks associated with the Mg_2Ca phase are detected, in addition to those of α -Mg and $\text{Ca}_2\text{Mg}_6\text{Zn}_3$ phases. With the

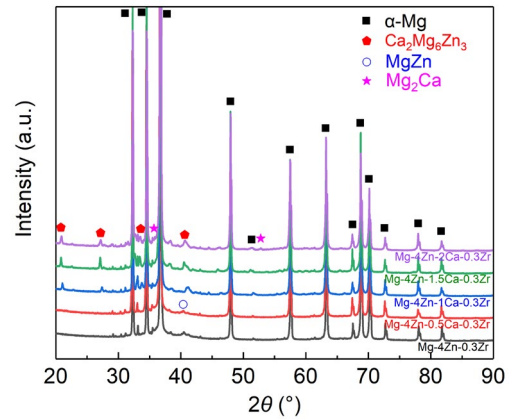


Fig. 6: XRD patterns of investigated alloys

increase in Ca content, the diffraction peak intensity of the MgZn phase gradually decreases, while that of the $\text{Ca}_2\text{Mg}_6\text{Zn}_3$ phase gradually increases.

3.1.2 Observation results of as-cast microstructures

Figure 7 shows the SEM images of Mg-4Zn- x Ca-0.3Zr ($x=0, 0.5, 1, 1.5$, and 2, wt.%) alloys. It is observed that the matrix phase in all five investigated alloys exists in the form of coarse dendrites. With the increase in Ca addition, the dendrite size decreases significantly. In addition, as Ca addition gradually increases, the number of eutectic phases in the alloys gradually increases; meanwhile, the content of eutectic phases within grains decreases gradually, while that at grain boundaries increases gradually.

The mapping scanning results shown in Fig. 8 indicate that Zn in all five alloys distributes in the matrix and at grain boundaries. Zn within grains mainly exist in solid solution state, while a small amount of Zn combines with Mg to form secondary phases. In addition, partial Zn reacts with Mg to

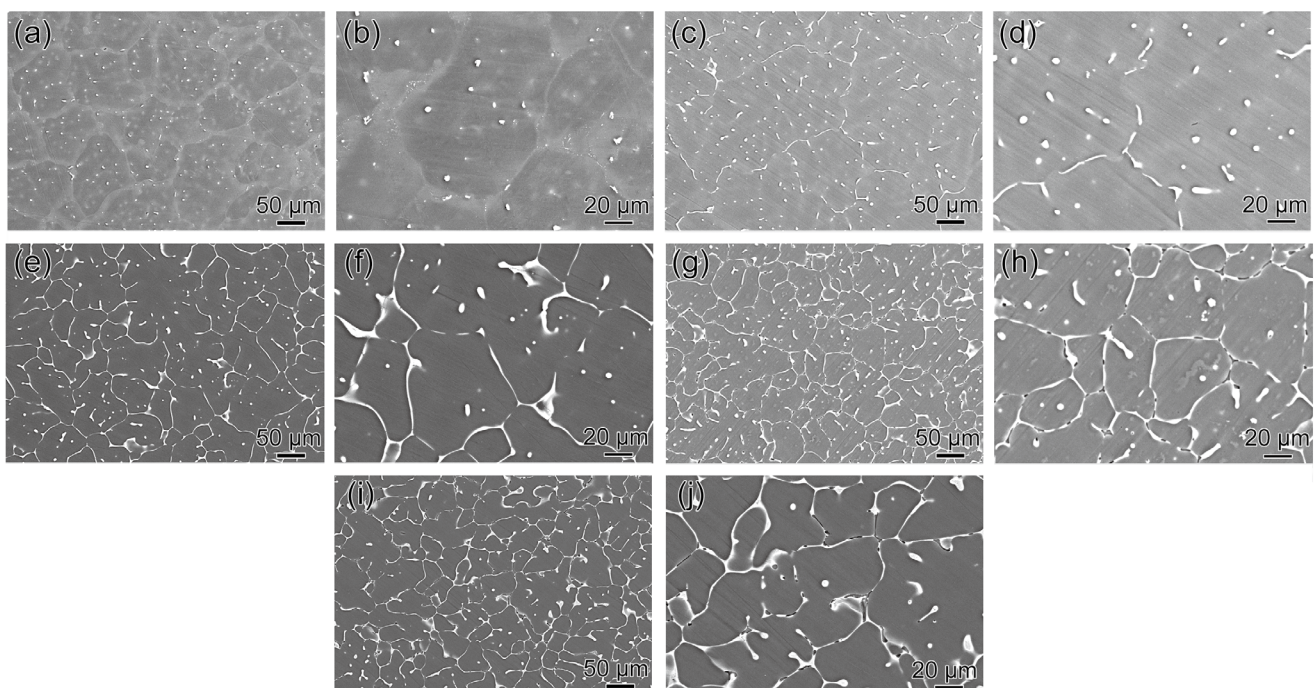


Fig. 7: SEM results of investigated alloys: (a, b) Mg-4Zn-0.3Zr; (c, d) Mg-4Zn-0.5Ca-0.3Zr; (e, f) Mg-4Zn-1Ca-0.3Zr; (g, h) Mg-4Zn-1.5Ca-0.3Zr; (i, j) Mg-4Zn-2Ca-0.3Zr

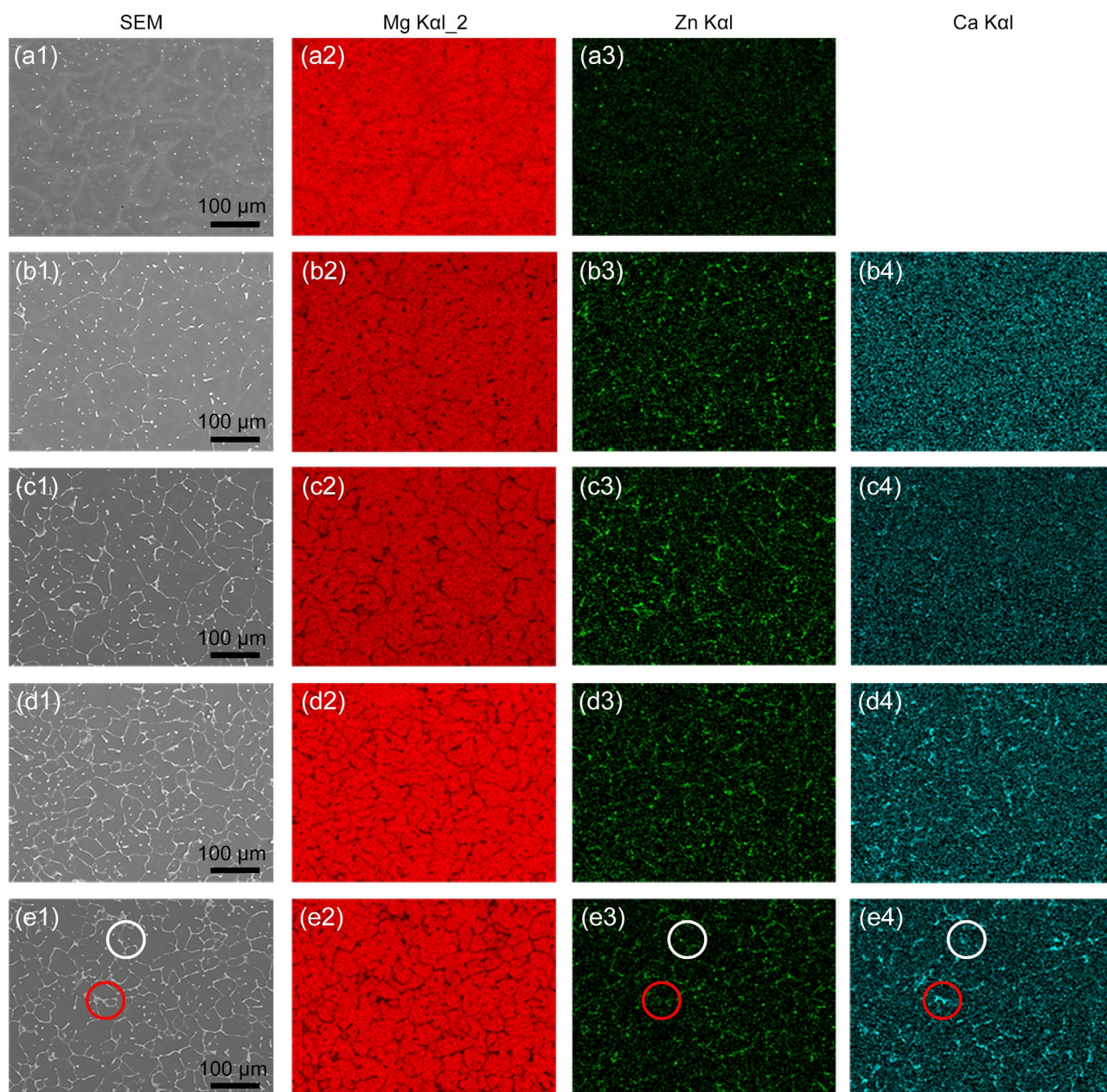


Fig. 8: Elemental distribution mapping of investigated alloys: (a1–a3) Mg-4Zn-0.3Zr; (b1–b4) Mg-4Zn-0.5Ca-0.3Zr; (c1–c4) Mg-4Zn-1Ca-0.3Zr; (d1–d4) Mg-4Zn-1.5Ca-0.3Zr; (e1–e4) Mg-4Zn-2Ca-0.3Zr

form dot-like secondary phase precipitates that are uniformly distributed along grain boundaries. EDS analysis reveals that the Zn/Mg atomic ratio is consistent with that of the MgZn phase [Fig. 9(a)]. After adding Ca, the number of MgZn binary phases at grain boundaries decreases, and instead, MgZnCa ternary phases form. These MgZnCa ternary phases distribute as strip-like structures at grain boundaries, with a small amount present within grains. As the Ca addition increases, the quantity of MgZnCa ternary phases at grain boundaries gradually increases, and their distribution transforms from semi-continuous to continuous networks; meanwhile, the number of MgZn binary phases within grains decreases gradually. The atomic ratio of Zn, Ca, and Mg in MgZnCa ternary phases is close to the stoichiometric composition of the $\text{Ca}_2\text{Mg}_6\text{Zn}_3$ phase [Points B and C in Fig. 9(b), Point E in Fig. 9(c)]. Moreover, in the Mg-4Zn-2Ca-0.3Zr alloy, a

compound composed solely of Mg and Ca is observed, which is mainly distributed at triple grain junctions and in shrinkage porosity-like cavities [as circled in Figs. 8(e1)–(e4)]. Based on previous studies^[27, 34, 35] and EDS results [Point D in Fig. 9(c)], this compound is identified as the brittle Mg_2Ca phase, which fragments during mechanical polishing.

3.1.3 Grain size and secondary phase content

In addition, EBSD results in Fig. 10 show that under the action of the constitutional supercooling effect at the solid-liquid interface, Ca restricts grain growth, thereby reducing the grain size of the alloys with the increase in Ca addition. Specifically, it decreases from 258.37 μm in the Mg-4Zn-0.3Zr alloy to 64.75 μm in the Mg-4Zn-1.5Ca-0.3Zr alloy. However, when the Ca addition reaches 2wt.%, the grain size slightly increases to 98.80 μm .

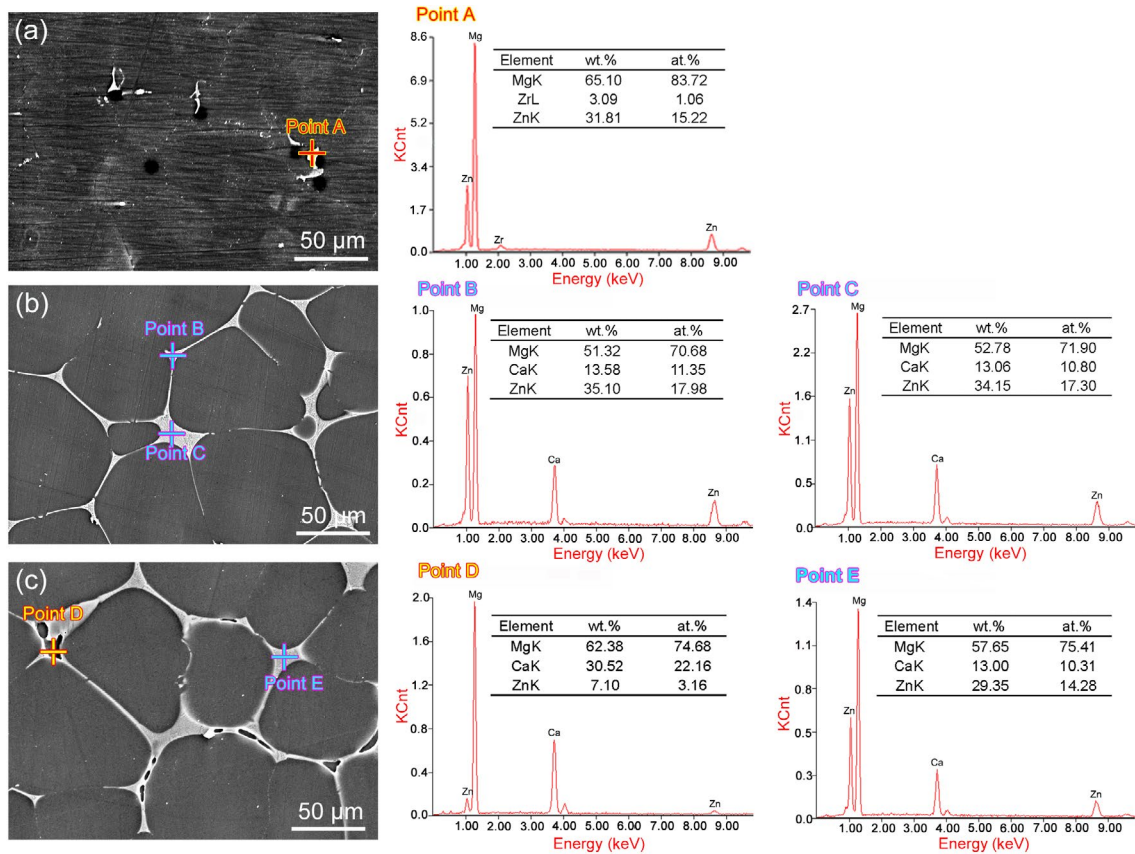


Fig. 9: SEM and EDS results of investigated alloys: (a) Mg-4Zn-0.3Zr; (b) Mg-4Zn-1.5Ca-0.3Zr; (c) Mg-4Zn-2Ca-0.3Zr

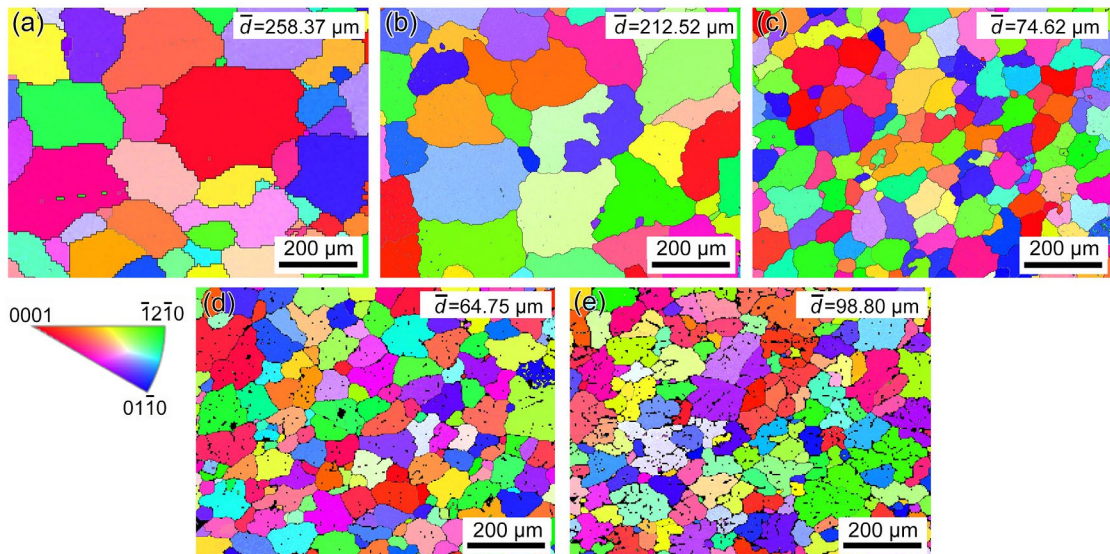


Fig. 10: EBSD results of investigated alloys: (a) Mg-4Zn-0.3Zr; (b) Mg-4Zn-0.5Ca-0.3Zr; (c) Mg-4Zn-1Ca-0.3Zr; (d) Mg-4Zn-1.5Ca-0.3Zr; (e) Mg-4Zn-2Ca-0.3Zr

Furthermore, to characterize the secondary phase content in the investigated alloys with different Ca additions, the Image-Pro Plus software was employed to measure the volume fraction of eutectic phases observed in multiple SEM micrographs. The calculation results indicate that the secondary phase content in the Mg-4Zn-0.3Zr alloy is 4.52%. With the addition of Ca, the secondary phase contents in the alloys are 9.02%, 10.55%, 11.48%, and 12.53%, respectively, i.e., the volume fraction of eutectic phases in the alloys increases significantly with the increase in Ca addition.

3.2 Mechanical properties and fracture morphologies

Figure 11 shows the mechanical property testing results of as-cast Mg-4Zn-xCa-0.3Zr ($x=0, 0.5, 1, 1.5, 2$, wt.%) alloys. With the increase in Ca content, the UTS, YS, and EL of the investigated alloys all exhibit a decreasing trend. Among them, the Mg-4Zn-0.3Zr alloy has the best comprehensive mechanical properties, with UTS, YS, and EL of 261.7 MPa, 147.0 MPa, and 8.8%, respectively. When the Ca content increases to 2wt.%, the UTS of the alloy decreases to 132.0 MPa,

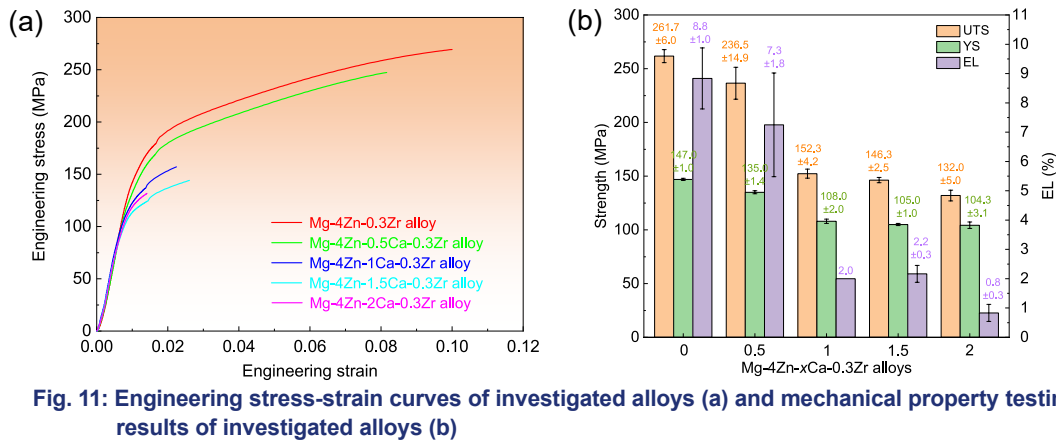


Fig. 11: Engineering stress-strain curves of investigated alloys (a) and mechanical property testing results of investigated alloys (b)

the YS drops to 104.3 MPa, and the EL is only 0.8%. These values represent a decrease of 49.6%, 29.0%, and 90.9% compared with the base alloy, respectively, exhibiting a significantly remarkable deterioration in mechanical properties.

To further clarify the effect of Ca on the fracture behavior of the alloys, the tensile fractures of the five investigated alloys were observed via SEM at low magnification (Fig. 12) and high magnification (Fig. 13). Low-magnification SEM observation reveals that the tensile fracture of the Mg-4Zn-0.3Zr alloy contains numerous cleavage planes and cleavage steps [Fig. 12(a)], while a small number of tear ridges are observed under high magnification [Fig. 13(a)], indicating that the fracture mode of the Mg-4Zn-0.3Zr alloy at room temperature is quasi-cleavage fracture. At this point, the fracture mainly originates from the cleavage cracking of the α -Mg matrix; meanwhile, the small amount of MgZn phase in the alloy is dispersedly distributed without forming a continuous network structure, and its hindering effect on the fracture process is limited, thus, the alloy retains a certain degree of ductility (EL=8.8%). After the addition of 0.5wt.% Ca, the intergranular fracture characteristics of the alloy gradually

become prominent [the area marked by blue circles in Fig. 12(b)], but the overall fracture mode of the alloy remains quasi-cleavage fracture [Figs. 12(b) and 13(b)]. With the further increases in Ca addition, the proportion of cleavage steps in the alloy increases sharply [Fig. 12(c)], and no tear ridges are observed [Fig. 13(c)]. Meanwhile, the fracture surface is covered by large areas of flat cleavage planes, and the intergranular fracture characteristics increase significantly. The fracture mechanism of the alloy transforms from quasi-cleavage fracture to cleavage fracture, resulting in a significant decrease in ductility (with EL dropping to 2.0%) and a further reduction in strength (with UTS decreasing to 152.3 MPa). When the Ca addition reaches 1.5wt.%, the intergranular fracture characteristics of the fracture are further enhanced [Fig. 12(d)], and the fracture exhibits a distinct sugar-candy-like morphology. Secondary cracks are clearly observed in the magnified image [as indicated by the yellow boxes in Fig. 12(d) and red ellipse in Fig. 13(d)], which is one of the reasons for the further deterioration of the alloy's mechanical properties. When the Ca addition reaches 2wt.%, the brittle fracture characteristics are further strengthened, the

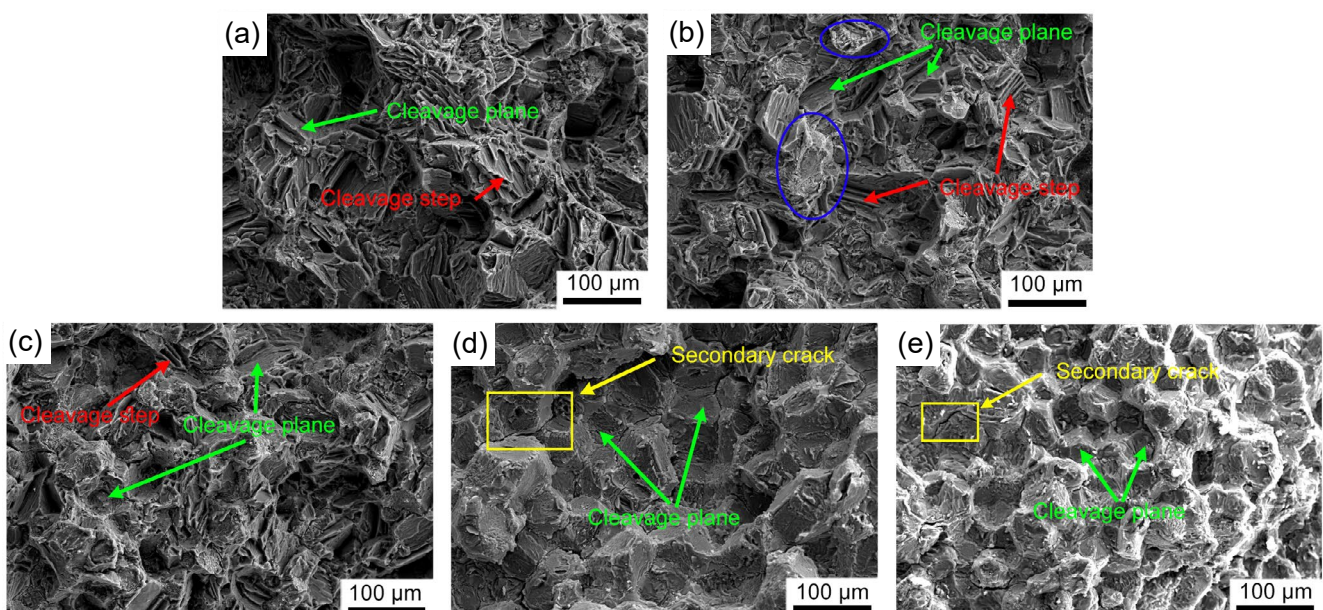


Fig. 12: SEM images of fracture surfaces of investigated alloys: (a) Mg-4Zn-0.3Zr; (b) Mg-4Zn-0.5Ca-0.3Zr; (c) Mg-4Zn-1Ca-0.3Zr; (d) Mg-4Zn-1.5Ca-0.3Zr; (e) Mg-4Zn-2Ca-0.3Zr

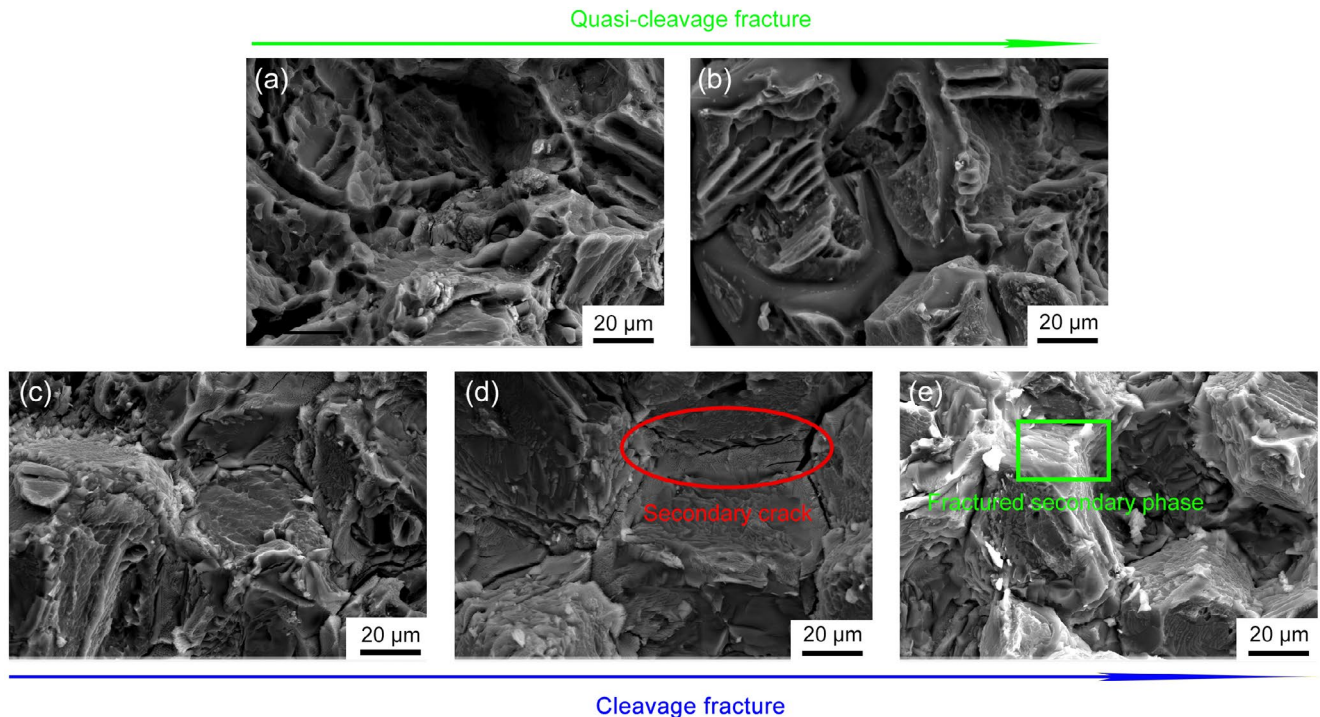


Fig. 13: High-magnification SEM images of fracture surfaces of investigated alloys: (a) Mg-4Zn-0.3Zr; (b) Mg-4Zn-0.5Ca-0.3Zr; (c) Mg-4Zn-1Ca-0.3Zr; (d) Mg-4Zn-1.5Ca-0.3Zr; (e) Mg-4Zn-2Ca-0.3Zr

number of secondary phases surrounding the grains increases significantly, and the fracture of the secondary phases is clearly observed at the fracture surface [Figs. 12(e) and 13(e)].

Based on the mechanical property testing results and fracture morphology results of the investigated alloys, it can be concluded that with the addition of Ca, the fracture mechanism of the alloys gradually transforms from quasi-cleavage fracture to cleavage fracture. To clarify the effect of Ca addition on the ductile-brittle transition mechanism of the investigated alloys, microstructure observation and elemental distribution scanning analysis were conducted on the longitudinal sections of the tensile fractures of the alloys with different Ca additions, the results are shown in Fig. 14. The fracture microstructure results are consistent with those shown in Fig. 7. With the increase in Ca addition, the secondary phases precipitate at grain boundaries gradually increase and form a network structure. In addition, it can be clearly observed that the grains near the fracture do not undergo significant plastic deformation due to tensile loading; instead, grain boundary cracking initiates and ultimately causes material fracture during tensile loading.

To characterize the effect mechanism of the secondary phase on the mechanical properties of the investigated alloys, TEM observation was performed on the fracture microstructure. The results indicate that during tensile deformation, the $\text{Ca}_2\text{Mg}_6\text{Zn}_3$ phase effectively hinders dislocation slip [Fig. 15(a)].

Previous studies have shown that the microstrain and dislocation density are also key factors influencing the mechanical properties of the materials^[36]. Lattice distortion induced by defects, the presence of solute atoms, and microscopic strain caused by residual stress are expected to strengthen the alloy by hindering dislocation motion^[37].

Meanwhile, as a key indicator characterizing plastic deformation and defect structure, dislocation density directly affects the yield strength of the alloy. A higher dislocation density indicates an increased resistance to dislocation motion within the alloy, thereby enhancing the alloy's YS. To further reveal the effect of Ca addition on the ductile-brittle transition mechanism of the investigated alloys, the microstrain and dislocation density of the alloys with varying Ca contents were estimated via the Williamson-Hall relationship based on XRD data^[38]. The calculation methods are shown in Eq. (2)^[38] and Eq. (3)^[39].

$$\beta \cos \theta = \frac{K\lambda}{D} + 4\varepsilon \sin \theta \quad (2)$$

$$DD_{\text{XRD}} = \frac{k\varepsilon}{b^2} \quad (3)$$

Among them, β is the full width at half maximum (FWHM); λ is the wavelength of Cu K α radiation, with a value of 0.15406 nm in this study; K is the shape factor, with a value of 0.9 in this study; D is the grain size; ε is the lattice microstrain; k is a constant related to dislocation type, distribution, and calculation method, with a value of 1 in this study; b is the Burgers vector (unit: nm). The microstrain and dislocation density estimated by Eqs. (2) and (3) are shown in Figs. 16(a) and (b). The negative values originate from the fact that the atomic radius of Zn atoms is smaller than that of Mg atoms, resulting in the microstrain of the alloy being compressive strain. With the increase in Ca addition, the absolute value of the microstrain in the investigated alloys gradually increases, and the dislocation density increases synchronously, which means the resistance to dislocation motion within the alloy is further enhanced. However, the experimental results show

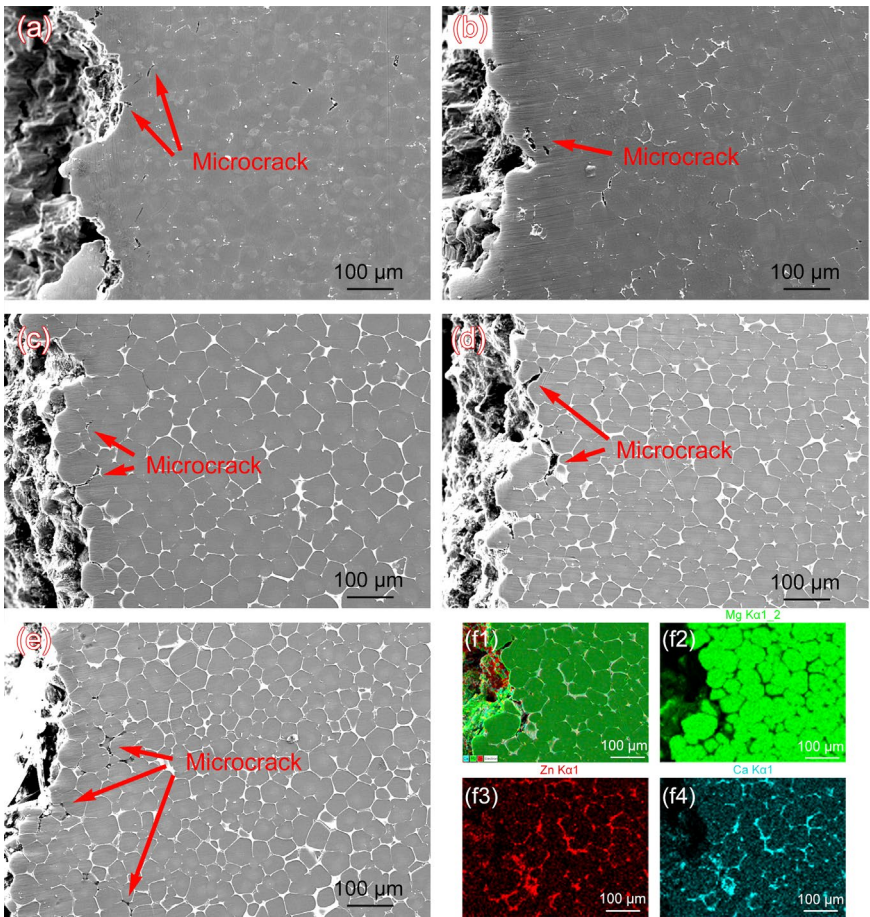


Fig. 14: Microstructure on longitudinal section of investigated alloys after tensile fracture: (a) Mg-4Zn-0.3Zr; (b) Mg-4Zn-0.5Ca-0.3Zr; (c) Mg-4Zn-1Ca-0.3Zr; (d) Mg-4Zn-1.5Ca-0.3Zr; (e) Mg-4Zn-2Ca-0.3Zr alloy; (f1-f4) element mapping scanning results of Mg-4Zn-1.5Ca-0.3Zr

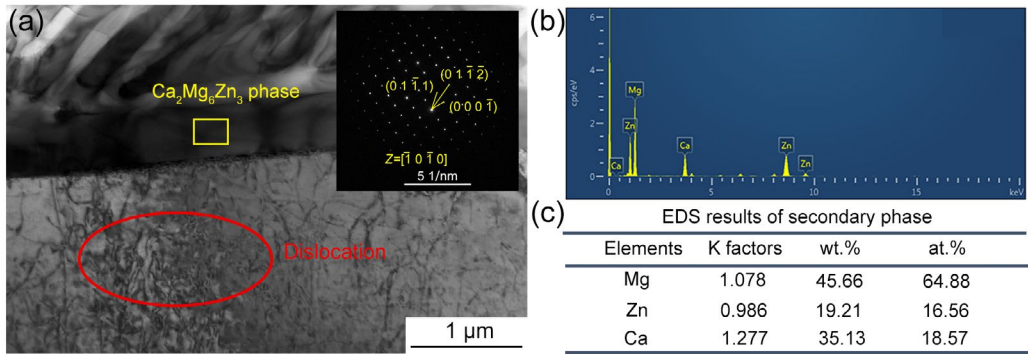


Fig. 15: TEM images of Mg-4Zn-1.5Ca-0.3Zr alloy: (a) bright-field image and SAED spots of secondary phase; (b) and (c) EDS results of secondary phase

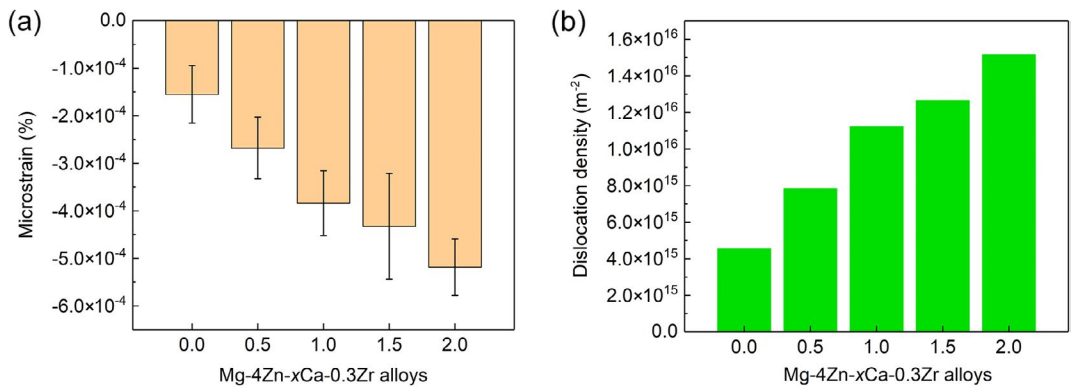


Fig. 16: Estimation results of microstrain (a) and dislocation density (b)

that with the increases in Ca addition, the UTS, YS, and EL of the alloys all gradually decrease. This phenomenon further confirms that the weakening of intergranular bonding strength induced by the formation of brittle secondary phases at grain boundaries exerts a far more significant negative effect than the positive effect of increased dislocation motion resistance on mechanical properties, thereby resulting in a decrease in the comprehensive mechanical properties of the alloys.

3.3 Solidification path and fluidity of investigated alloys

3.3.1 Thermal analysis results of investigated alloys

The solidification process has a significant impact on the casting properties of the alloy. The thermal analysis results of the investigated alloys are shown in Fig. 17. The peaks in thermal analysis curves correspond to the crystallization of the matrix phase and precipitation reactions of secondary phases. As shown in Fig. 17(a), only one type of secondary phase precipitates in the Mg-4Zn-0.3Zr alloy. Combined with its precipitation temperature (350 ± 8 °C) and XRD results [Fig. 6],

Peak B is confirmed to correspond to the precipitation reaction of the MgZn phase. After adding 0.5wt.% Ca, a weak peak (Peak C) appears on the thermal analysis curve of the alloy. Based on its precipitation temperature (405 ± 5 °C) and XRD results [Fig. 6], Peak C is identified as the precipitation reaction of the $\text{Ca}_2\text{Mg}_6\text{Zn}_3$ phase. With further addition of Ca, Peak B disappears while the area of Peak C increases, which further verifies that the amount of secondary phases in the alloy rises with increasing Ca content. When the Ca addition reaches 2wt.%, a new Peak D emerges on the thermal analysis curve. Combined with its precipitation temperature (420 ± 4.5 °C) and XRD results [Fig. 6], Peak D is attributed to the precipitation reaction of the Mg_2Ca phase.

Figure 18 shows the calculation results of the solidification temperature ranges of the investigated alloys. As can be seen, the addition of Ca changes the phase constitution of the alloys, thereby affecting the solidification temperature ranges of the alloys. With the increase in Ca addition, the solidification temperature range first shortens significantly and then remains almost unchanged.

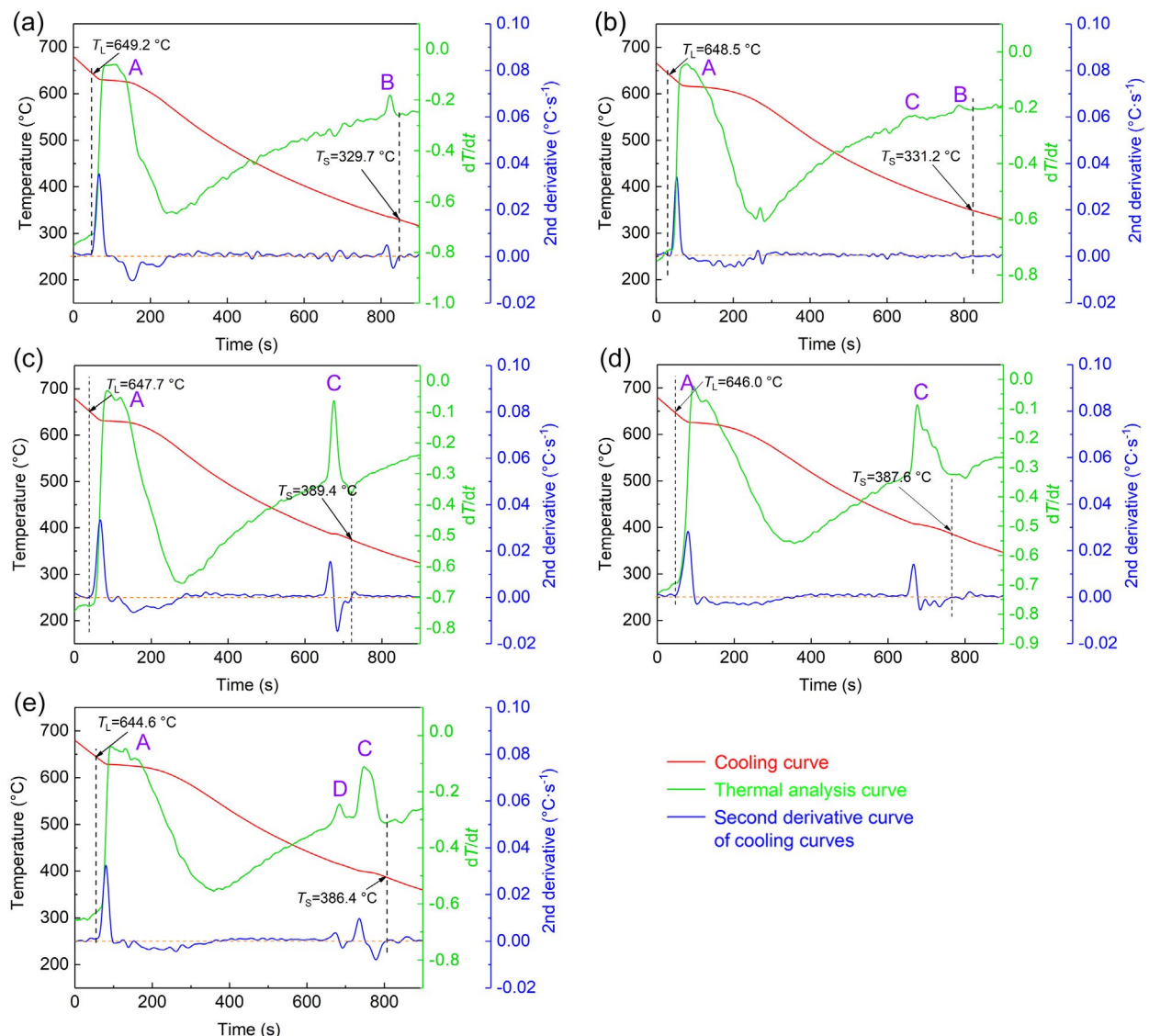


Fig. 17: Thermal analysis results of investigated alloys: (a) Mg-4Zn-0.3Zr; (b) Mg-4Zn-0.5Ca-0.3Zr; (c) Mg-4Zn-1Ca-0.3Zr; (d) Mg-4Zn-1.5Ca-0.3Zr; (e) Mg-4Zn-2Ca-0.3Zr

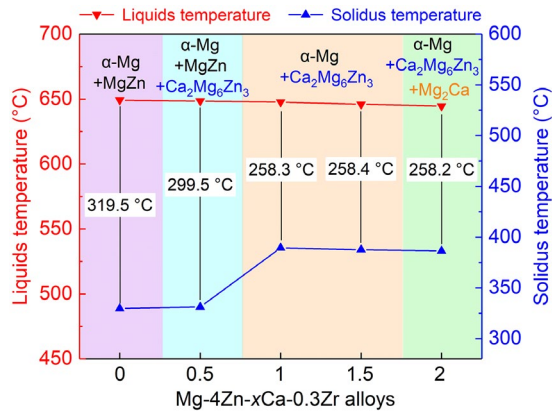


Fig. 18: Liquids and solidus temperature of investigated alloys

3.3.2 Fluidity testing results of investigated alloys

In the process of metal casting and solidification, fluidity is a key indicator for evaluating the mold filling ability of alloy melts, which directly determines whether shrinkage porosity, shrinkage cavities and other defects occur in castings^[40]. The fluidity testing results of Mg-4Zn-xCa-0.3Zr ($x=0, 0.5, 1, 1.5, 2$, wt.%) alloys are shown in Fig. 19 and Table 2. It can be seen that the addition of Ca significantly improves the fluidity of the Mg-4Zn-0.3Zr alloy. Moreover, with the increase in Ca addition, the length of the alloy fluidity samples gradually increases, from 256.0 mm of the Mg-4Zn-0.3Zr alloy to 373.7 mm of the Mg-4Zn-2Ca-0.3Zr alloy.

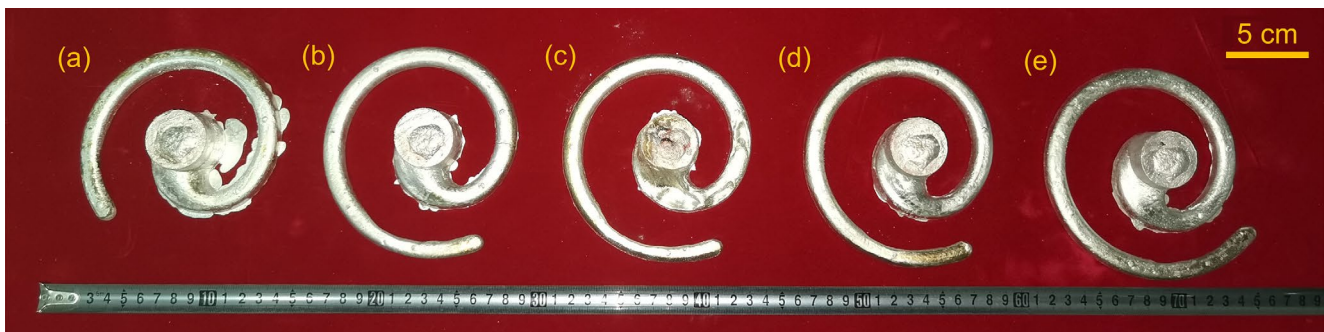


Fig. 19: Fluidity test results of investigated alloys: (a) Mg-4Zn-0.3Zr; (b) Mg-4Zn-0.5Ca-0.3Zr; (c) Mg-4Zn-1Ca-0.3Zr; (d) Mg-4Zn-1.5Ca-0.3Zr; (e) Mg-4Zn-2Ca-0.3Zr

Table 2: Fluidity test results of investigated alloys

Alloys	Mg-4Zn-0.3Zr alloy	Mg-4Zn-0.5Ca-0.3Zr alloy	Mg-4Zn-1Ca-0.3Zr alloy	Mg-4Zn-1.5Ca-0.3Zr alloy	Mg-4Zn-2Ca-0.3Zr alloy
Fluidity length (mm)	256.0±1.6	326.3±2.3	336.5±2.1	344.5±2.4	373.7±2.0

Figure 20 shows the statistical diagrams of the percentage changes in mechanical properties and fluidity length of the investigated alloys with different Ca additions. Negative values represent a decrease, and positive values represent an increase. Based on the mechanical properties and fluidity data of all investigated alloys, when the Ca addition is 0.5wt.%, the UTS, YS, and EL are only decreased by 9.6%, 8.2%, and 17%,

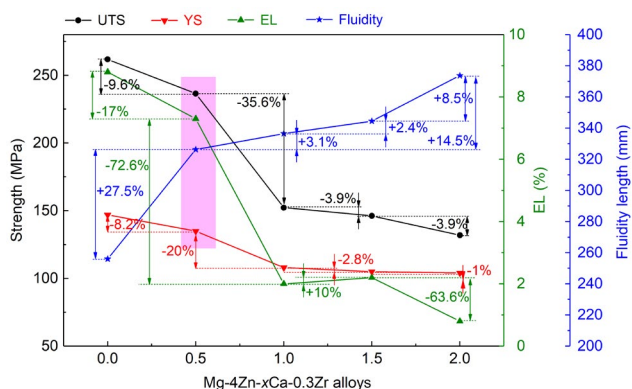


Fig. 20: Variation ranges of mechanical properties and fluidity length of experimental alloys with various Ca additions

respectively, compared with the Mg-4Zn-0.3Zr alloy (which has the highest values). Meanwhile, its fluidity specimen length is increased by 27.5% relative to the Mg-4Zn-0.3Zr alloy. With a further increase in Ca content to 2wt.%, the fluidity gradually improves; however, the mechanical properties decrease significantly once the Ca addition exceeds 0.5wt.% (the UTS, YS, and EL of the Mg-4Zn-1Ca-0.3Zr alloy are reduced by 35.6%, 20%, and 17%, respectively, compared with the Mg-4Zn-0.5Ca-0.5Zr alloy). Therefore, considering both formability and mechanical properties, the Mg-4Zn-0.5Ca-0.3Zr alloy exhibits the optimal comprehensive performance among all investigated alloys.

4 Discussion

4.1 Effect of Ca addition on ductile-brittle transition mechanism of Mg-4Zn-xCa-0.3Zr alloys

According to the experimental results, with the addition of Ca, the alloy exhibits a series of changes in the microstructure and solidification process parameters that are theoretically

beneficial to its mechanical properties: (1) the grain size firstly decreases and then slightly increases; (2) the degree of lattice distortion induced by Ca elements dissolved in the matrix increases, leading to an enhancement in the absolute value of the alloy's microstrain; (3) the ability of the secondary phases at grain boundaries to pin dislocations during tensile deformation is improved; (4) the solidification temperature range significantly shortens; and (5) the fluidity continuously improves. However, the actual mechanical property tests indicate that the UTS, YS, and EL of the alloy all decrease monotonically with the increase in Ca content.

To clarify this discrepancy, an analysis is carried out from the following aspects: From the perspective of phase nature, previous studies via first-principles calculations have revealed that the MgZn phase exhibits good ductility, whereas both the $\text{Ca}_2\text{Mg}_6\text{Zn}_3$ and Mg_2Ca phases are classified as brittle intermetallic compounds^[41, 42]. When the alloy is subjected to tensile stress, these brittle secondary phases cannot accommodate stress through plastic deformation, and stress concentration is prone to occur inside the phases, eventually leading to the formation of initial microcracks and cracking. Meanwhile, with the increase in Ca content, the $\text{Ca}_2\text{Mg}_6\text{Zn}_3$ phase at the grain boundaries gradually transforms from a semi-continuous distribution to a continuous network structure (Figs. 7 and 14), while the Mg_2Ca phase preferentially accumulates at triple grain junctions and near shrinkage porosity defects. The continuously distributed brittle $\text{Ca}_2\text{Mg}_6\text{Zn}_3$ and Mg_2Ca phases at the grain boundaries also destroy the continuity of the metallurgical bonding between the α -Mg matrix. In addition, the continuous network of brittle secondary phases divides the α -Mg matrix into isolated regions, forming "brittle skeletons". The deterioration of this grain boundary structure significantly reduces the energy barrier for crack initiation, i.e., under low stress, the secondary phases at the grain boundaries will also crack preferentially, generating intergranular microcracks. Furthermore, it can be observed that the cracks in the samples with Ca content less than 1.5wt.% all originate from the interface between the matrix and the secondary phases, and the cracks propagate along the grain boundaries. However, the cracks in the Mg-4Zn-2Ca-0.3Zr alloy sample tend to propagate transgranularly. The study on the effect of the Mg_2Ca phase on the deformation and failure mechanisms of magnesium alloys shows that plastic incompatibility exists between the Mg matrix and Mg_2Ca phase, which sharply amplifies local stress. Triple junctions readily act as preferential initiation sites for microcracks. Subsequently, the cracks propagate along grain boundaries, leading to material fracture^[43].

According to the Hall-Petch relationship^[44], grain refinement should theoretically enhance the strength and ductility of the alloy by increasing the resistance to dislocation slip and coordinating plastic deformation. However, this strengthening effect is not observed in the present study. The underlying reason may lie in the fact that grain refinement is premised on grain boundaries serving as strong bonding interfaces. With

the addition of Ca, brittle secondary phases with a continuous network gradually form at the grain boundaries, which destroy the continuity of the metallurgical bonding between α -Mg matrix grains. Under such circumstances, the grain boundaries no longer act as strengthening sites that impede dislocation slip; instead, they become weakened channels for crack initiation and propagation. Meanwhile, refined grains not only increase the grain boundary resistance to dislocation slip but also enlarge the grain boundary area, which imply more sites for crack initiation. Consequently, the dislocation strengthening effect induced by grain refinement is far outweighed by the crack degradation effect triggered by brittle secondary phases. In addition, although the increase in dislocation density enhances the resistance to dislocation slip, it also leads to dislocation pile-up adjacent to the secondary phases. The stress concentration caused by dislocation pile-up further exacerbates the cracking tendency of the secondary phases, thereby resulting in the deterioration of the comprehensive mechanical properties of the alloys.

Results of thermal analysis and fluidity testing indicate that the addition of Ca shortens the solidification temperature range and improves the fluidity of the alloy. These changes are theoretically conducive to enhancing the casting quality of the alloy, but their effect on improving mechanical properties is relatively limited. A shortened solidification temperature range reduces the solid-liquid coexistence region, promotes the planar advancement of the solidification front, mitigates the formation of shrinkage porosity defects inside the castings, and reduces the macroscopic and microscopic segregation of the castings, thereby improves their mechanical properties. Meanwhile, the improved fluidity indirectly enhances the mechanical properties of castings by reduces filling defects and decreases the sources of stress concentration in the castings. However, even for the Mg-4Zn-2Ca-0.3Zr alloy with the optimal fluidity, its fracture is still characterized primarily by brittle secondary phase fracture and microcrack propagation [Figs. 13(e) and 14(e)], rather than failure dominated by casting defects. This indicates that when brittle secondary phases of the alloy become the primary limiting factor for mechanical properties, the benefits brought by the improvement of casting quality cannot offset the negative effects caused by internal microstructural degradation.

In summary, although the addition of Ca induces a series of theoretically beneficial microstructural changes for mechanical properties, including grain refinement, reduction in the solidification temperature range, and enhancement in fluidity, all these beneficial effects are offset by the dominant factor of the formation and aggregation of brittle secondary phases ($\text{Ca}_2\text{Mg}_6\text{Zn}_3$ and Mg_2Ca). By inducing microcracks, weakening grain boundaries, and accelerating crack propagation, the brittle secondary phases directly determine the evolution trend of the alloy's mechanical properties, eventually resulting in a continuous decrease in the mechanical properties with increasing Ca content. This mechanism is also consistent with the research results of Li et al.^[13] on Mg-2Zn-xCa alloys.

4.2 Effect of Ca addition on solidification behavior and fluidity of Mg-4Zn-xCa-0.3Zr alloys

4.2.1 Solidification temperature range

According to the thermal analysis results, the liquidus temperature gradually decreases with the increase in Ca addition. However, regarding the solidus temperature, the addition of Ca and its gradual increase leads to a transformation in the alloy's phase constitution. The Mg-4Zn-0.3Zr alloy exhibits a lower solidus temperature due to the precipitation of the MgZn phase. In the Mg-4Zn-0.5Ca-0.3Zr alloy, the precipitation of the $\text{Ca}_2\text{Mg}_6\text{Zn}_3$ phase consumes Zn elements in the alloy, thereby reduces the precipitation content of the MgZn phase. In addition, the precipitation temperature of the $\text{Ca}_2\text{Mg}_6\text{Zn}_3$ phase is higher than that of the MgZn phase, so the solidus temperature of the alloy increases slightly from 329.7 °C to 331.2 °C. When the Ca addition continues to increase, the quantity of the $\text{Ca}_2\text{Mg}_6\text{Zn}_3$ phase increases continuously and the precipitation time of the phase gradually prolongs, which not only consumes a large amount of Zn elements, leading to a gradual decrease or even disappearance of the MgZn phase, but also results in a slight decrease in the solidus temperature of the alloy. When the Ca addition reaches 2wt.%, the Mg_2Ca phase forms, which only has a slightly higher precipitation temperature than the $\text{Ca}_2\text{Mg}_6\text{Zn}_3$ phase, thus not significantly changing the solidification temperature range of the alloy.

4.2.2 Effect of Ca addition on fluidity of Mg-4Zn-xCa-0.3Zr alloys

It is well known that the viscosity of an alloy is the core intrinsic factor governing its fluidity. The lower the viscosity of the alloy melt, the smaller the internal friction force impeding flow within it, the weaker the flow resistance, and the better the fluidity, with a significant negative correlation observed between the two. Figure 21 presents the temperature evolution curves of the liquid viscosity [Fig. 21(a)] and total viscosity [Fig. 21(b)] of the alloys with different Ca additions, calculated via the JMatePro software. When the temperature of the molten alloy is above the liquidus, the total viscosity of the alloy is approximately equal to the liquid viscosity. When the

molten alloy solidifies below the liquidus, the formation of the mushy zone endows the alloy melt system with a multiphase characteristic. At this stage, the liquid viscosity specifically refers to the viscosity of the “remaining liquid phase”, while the total viscosity denotes the overall viscosity of the “liquid phase+solid particles/free crystals/dispersed phases”. Notably, the total viscosity is not a simple superposition of the liquid viscosity and the viscosities of other phases: solid particles, free crystals, and dispersed phases themselves possess no “fluidity”; what they provide is “additional resistance hindering liquid flow” rather than “superposition of their own viscosities”. It can be seen from Fig. 21 that with the increase in Ca addition, the total viscosity of the investigated alloys exhibits a slight downward trend, corresponding to an improvement in the alloy's fluidity. When the alloy solidifies into the mushy zone, the liquid viscosity reflects the flow capacity of the residual Mg-Zn-Ca-Zr liquid phase, indicating that the fluidity of the residual liquid phase of the alloy at the same temperature is enhanced after Ca addition.

In addition, Cong^[45] and Zhou^[46] et al. indicated that the fluidity of an alloy is not only affected by the viscosity, but also significantly influenced by the change in solidification path caused by the variation of the alloy system resulting from the adjustment of alloying elements. Among these factors, the growth behavior of dendrites in the alloy remarkably affects the flow characteristics and path of the residual liquid phase. Researchers have divided the solidification process into four stages: free feeding stage, interdendritic feeding stage, dendrite separation stage, and dendrite bridging stage^[2]. Before the alloy melt solidifies to the dendrite coherency state, the interdendritic liquid phase flows freely. However, once dendrite coherency is achieved, a complex dendritic interdendritic network is formed, resulting in the liquid phase being divided into multiple isolated molten pools. These isolated molten pools are separated from each other, and the flow path of the liquid phase is severely blocked, ultimately exerting a significant impact on the alloys' fluidity.

Therefore, based on the principle of differential scanning calorimetry, thermocouples were placed at the edge and the center of the melt, and the solidification process and temperature changes at both locations were simultaneously

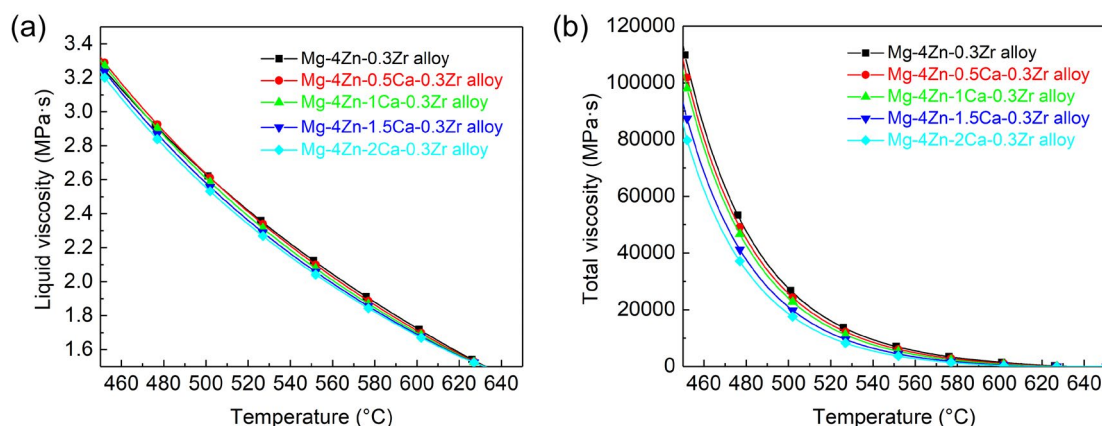


Fig. 21: Temperature-liquid viscosity (a) and temperature-total viscosity (b) relationship curves of investigated alloys

measured in this study. During solidification, the edge exchanges heat directly with the air, so its cooling rate is significantly faster than that at the center of the crucible, resulting in a temperature difference between the two positions before dendrite coherency. Meanwhile, since the thermal conductivity of the solid phase is superior to that of the liquid phase, the temperature difference gradually increases as solidification proceeds. When the melt solidifies to the dendrite coherency state point, the heat from the center and edge of the melt is rapidly conducted outward through the solid dendrites, and the temperature difference then gradually decreases. When the temperature difference reaches its maximum value, dendrite coherency occurs exactly. The temperature corresponding to this state is defined as the dendrite coherency temperature (T_{coh}). Figure 22 shows the measurement results of the T_{coh} of the investigated alloys. It can be seen that the T_{coh} of the alloys gradually decreases with the increase in Ca addition. Among them, the Mg-4Zn-0.3Zr alloy has the highest T_{coh} , reaching 624.3 °C. This indicates that dendrite coherency occurs in the alloy at a relatively low

solid fraction, which severely restricts the flow of the liquid phase in the melt. With the increase in Ca addition, the T_{coh} of the alloys gradually decreases, indicating that the addition of Ca can delay the dendrite coherency process of the alloys. Figure 23 is the schematic diagram of the feeding channels in the alloys under different dendrite coherency states during solidification. When the alloy completes dendrite coherency at a higher temperature/lower solid fraction, the dendritic network in the melt forms prematurely, significantly hindering the flow of the residual liquid phase. In contrast, when the alloy has a lower dendrite coherency temperature/higher solid fraction, the feeding channels in the melt are more abundant, allowing the residual liquid phase to flow for a longer time with higher efficiency. Meanwhile, the calculation results from JMatePro show that with the increase in Ca addition, the liquid viscosity of the residual liquid phase in the alloys gradually decreases after the alloys solidify into the mushy zone. Under the combined effect of the above two factors, the fluidity of the alloys is gradually enhanced with the addition of Ca.

Furthermore, Kou et al.^[47] indicated that the solid-liquid

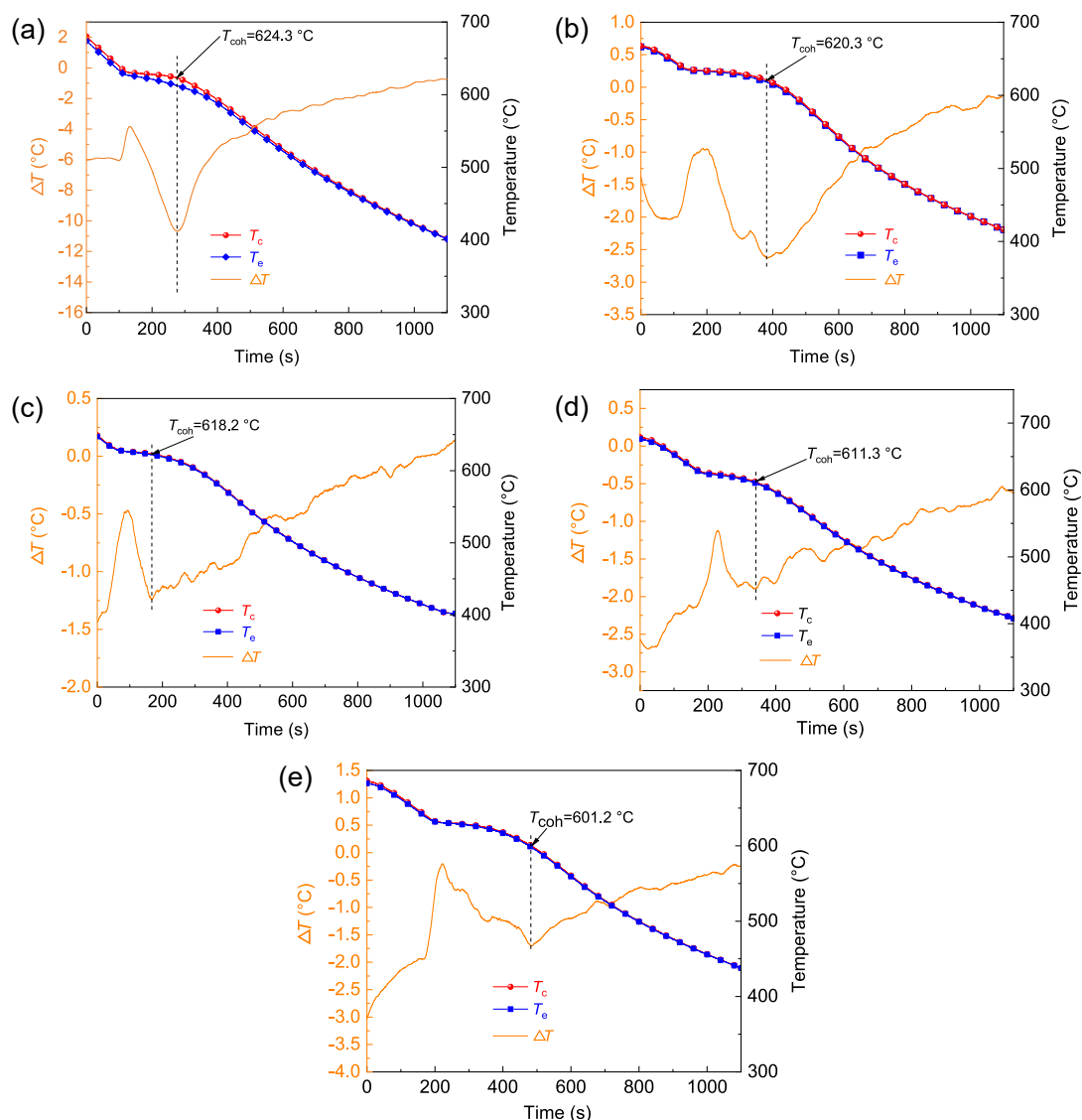


Fig. 22: Dendrite coherence temperature measurement results of investigated alloys: (a) Mg-4Zn-0.3Zr; (b) Mg-4Zn-0.5Ca-0.3Zr; (c) Mg-4Zn-1Ca-0.3Zr; (d) Mg-4Zn-1.5Ca-0.3Zr; (e) Mg-4Zn-2Ca-0.3Zr

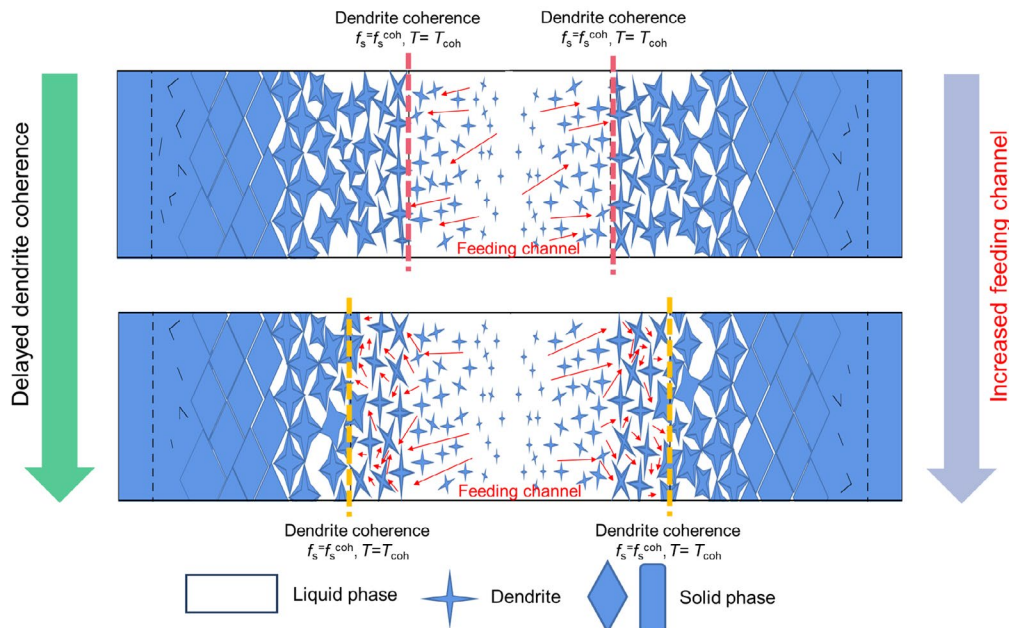


Fig. 23: Schematic diagram of feeding channel conditions in alloys when reaching dendrite coherence state point under different melt states

(S/L) interface near the grain boundaries approximately corresponds to the $T-(f_s)^{1/2}$ relationship curve [where $(f_s)^{1/2} \rightarrow 1$]. Figure 24 presents the $T-(f_s)^{1/2}$ relationship curves of the Mg-4Zn- x Ca-0.3Zr alloys with different Ca additions. With the increase in Ca addition, the spacing of the S/L interface front of the investigated alloys shortens, and the sharp angle at the front of the interface gradually increases. This indicates that the addition of Ca improves the morphology of the interdendritic feeding channels in the alloys: based on the Hagen-Poiseuille criterion^[32], the volumetric flow rate of the liquid phase through the channels decreases with the increase in channel length, a phenomenon caused by the flow resistance induced by liquid viscosity. Combined with the previous experimental results on dendrite coherency temperature, liquid

viscosity, and total viscosity, the following conclusions can be drawn. With the addition of Ca, the dendrite coherency behavior of the alloys is delayed, prolonging the free flow time of the residual liquid phases between dendrites; both the total viscosity of the alloys and the viscosity of the residual liquid phases decrease, and this enhances the flow capacity of the liquid phases; meanwhile, the improvement of the S/L interface morphology reduces the flow resistance of the residual liquid phases at the S/L interface front. Under the synergistic effect of the above multiple factors, the fluidity of the alloys is significantly improved.

5 Conclusions

The study systematically investigated the regulation mechanisms of Ca addition on the phase constitution, microstructure, mechanical properties, solidification behavior, and fluidity of cast Mg-4Zn- x Ca-0.3Zr ($x=0, 0.5, 1, 1.5, 2$, wt.%) alloys. The specific conclusions are as follows:

(1) With the Ca addition from 0 to 2 wt.%, the phase constitution undergoes a regular transformation. The eutectic phase distribution shifts from intragranular-dominated to grain boundary-dominated. Meanwhile, Ca exerts a regulatory effect on grain size that firstly refines and then slightly increases.

(2) The addition of Ca has a significant negative impact on the comprehensive mechanical properties of the alloy. The core reason for the deterioration of mechanical properties is the destructive effect of brittle secondary phases at grain boundaries.

(3) By altering the phase precipitation sequence ($x=0$ wt.%: $\alpha\text{-Mg}+\text{MgZn} \rightarrow x=0.5$ wt.%: $\alpha\text{-Mg}+\text{MgZn}+\text{Ca}_2\text{Mg}_6\text{Zn}_3 \rightarrow x=1$ wt.%, 1.5 wt.%: $\alpha\text{-Mg}+\text{Ca}_2\text{Mg}_6\text{Zn}_3 \rightarrow x=2$ wt.%: $\alpha\text{-Mg}+\text{Ca}_2\text{Mg}_6\text{Zn}_3+\text{Mg}_2\text{Ca}$), Ca significantly affects the solidification path and solidification temperature range of the alloy.

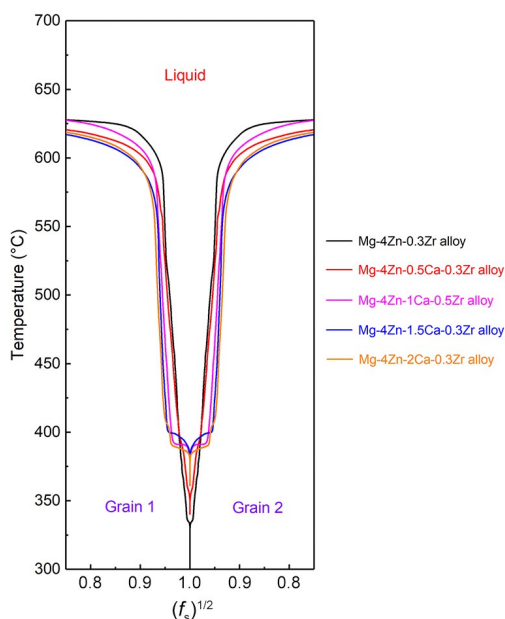


Fig. 24: $T-(f_s)^{1/2}$ relationship curves of investigated alloys with different Ca addition

(4) The addition of Ca significantly improves the fluidity of the alloy, and its enhancement mechanism stems from the synergistic effect of three factors: Delaying dendrite coherency, reducing the viscosity of the alloy, and reducing the flow resistance of the liquid phase between dendrites.

Conflict of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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