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The Effect of High-Temperature Heat Treatment on the Precipitation Behavior and Mechanical Properties of Mg-Al-Zn-Ca Alloys

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Abstract

This study first involves the melting of Mg-xAl-(8-x)Zn-(2-3)Ca (wt%, where unspecified refers to weight percentage) magnesium alloys with various compositions. The microstructure of the alloys is investigated using techniques such as OM, SEM, and XRD. It is found that variations in the Al/Zn ratio and Ca content significantly affect the composition and quantity of the second phase within the Mg-Al-Zn-Ca alloy system. Through tensile tests on five different alloys, it is observed that the Mg-3Al-5Zn-3Ca alloy exhibits relatively good comprehensive mechanical properties, achieving a tensile strength, yield strength, and elongation of 149 MPa, 99 MPa, and 3.1%, respectively. The precipitation behavior of the five alloys is studied, revealing that the Mg-3Al-5Zn-3Ca alloy, when heat-treated at 350℃ for 60 hours, precipitates a high-density rod-like phase with a density of approximately 0.14N/μm^2 and an average size of 1.21μm. Under the influence of precipitation strengthening, the comprehensive mechanical properties of the alloy are enhanced.

Keywords

Magnesium Alloys; Precipitation Behavior; Mechanical Properties.

1. Introduction

Magnesium alloys are considered to be highly promising alternative materials due to their significant advantages such as low density, high specific strength, and good damping capacity[1]. In the aerospace field, magnesium alloys are widely used in the production of key components for aircraft, missiles, spacecraft, and satellites because of their unique properties, aiming to reduce component weight, enhance the maneuverability of aircraft, and lower the cost of space vehicle launches[2]. However, during use, magnesium alloy components can generate excessive heat, leading to material failure due to overheating or deformation. As a result, there is a growing demand for materials that possess both excellent thermal management and outstanding mechanical properties.

Compared to rare earth elements, alkaline earth metal calcium (Ca) is more cost-effective and is widely used as an alloying element, aimed at enhancing the high-temperature performance of alloys[3, 4]. The introduction of Ca into Mg-Al based alloys can particularly promote the formation of thermally stable Laves phases, specifically including C14-Mg_2Ca (hexagonal structure), C15-Al_2Ca (cubic structure), C36-$(Mg, Al)_2Ca$ (dihydral hexagonal structure), and single-layer G.P. zones[5, 6].This addition strategy significantly optimizes the high-temperature performance of alloy materials, highlighting the key role of the element Ca in the science of alloy materials. Pan conducted an in-depth investigation of the thermal conductivity of binary magnesium alloys and found that the alloying elements can be arranged in the following order: Zn, Al, Ca, Sn, Mn, and Zr[7]. Accordingly, Zn is considered suitable for the preparation of high thermal conductivity magnesium alloys. Among the various magnesium alloys, Mg-Zn alloys exhibit excellent aging response, primarily attributed to the maximum solubility of Zn in the magnesium matrix, which is approximately 6.2 wt%. This property allows for the precipitation of a substantial amount of precipitate phase during the aging process[8]. Further research reveals that the addition of calcium (Ca) elements can enhance the aging response of Mg-Zn alloys. Therefore, Mg-Zn-Ca is widely regarded as a magnesium alloy whose performance can be improved through precipitation hardening[9]. By comprehensively utilizing the advantages of these two alloys, we have developed a novel Mg-Al-Zn-Ca heat-resistant alloy and studied its precipitation behavior and its influence on mechanical properties.

2. Experimental

Using a resistance melting furnace to produce Mg-Al-Zn-Ca system alloys, the raw materials include commercially pure Mg, Al, and Zn (≥99.9%) as well as Mg-20wt%Ca intermediate alloy. The melt is protected by covering it with a salt mixture and refined using BaCl2 refining agent. Prior to casting, the melt is held at 740°C for 20 minutes to purify it, and then cast into steel molds preheated to approximately 250°C at a temperature of 720°C.

Test pieces were cut from the castings, and all surfaces of the samples were polished. The samples were then placed in a muffle furnace for heat treatment experiments, with sufficient air in the furnace. Samples were taken out at different exposure temperatures and times, followed by water quenching for analysis. The morphology of the heat-treated samples was observed using a field emission SEM(Zeiss Gemini 300), and the chemical composition of different reaction products was analyzed using the equipped EDS. Samples were observed for precipitate phases using a Talos F200X field emission transmission electron microscope (TEM). Samples for scanning electron microscopy (SEM) observation were prepared using standard grinding and polishing methods. The samples for TEM observation were ground to a thickness of approximately 80μm, and discs with a diameter of 3mm were punched out, followed by milling with a PIPSion milling machine. Phase identification was conducted using XRD (D8ADVANCE-A25) under Cu Kα radiation. Phase transition analysis was performed using Diamond TG/DTA apparatus.

Flat dog-bone specimens with a gauge length of 15mm and a cross-sectional area of 6mm×2mm were machined from the same position of each ingot using a wire cutting machine. The tensile tests were conducted at room temperature using a MTS CMT5105 universal testing machine, with the extensometer removed after the material yielded. The tensile strain rate was set at $0.000167s^{-1}$. At least three specimens of each alloy condition were prepared for testing.

3. Results

3.1. Microstructure of Alloy Castings

Figure 1 presents optical microscope images of cast magnesium alloys with different compositions. It can be observed that the second phase content is relatively high in all five magnesium alloy samples, and a substantial amount of the second phase forms a dense, continuous network structure, which can contribute to the enhancement of the alloy's properties. With changes in alloy composition, the density of the second phase exhibits an increasing trend in Figure 2 (a-e), and the network structure becomes more continuous. Figure 2 shows the XRD patterns of the cast samples. It is evident that variations in the Al/Zn ratio and Ca content significantly affect the phase composition of Mg-Al-Zn-Ca based alloys. Three high-intensity characteristic diffraction peaks are clearly visible in the XRD curves, corresponding to the hexagonal phase α-Mg at 2θ=31.9°, 34.4°, and 36.6°, which correspond to the (100), (002), and (101) crystal planes, respectively. Additionally, distinct characteristic peaks of $Ca_2Mg_6Zn_3$ and Al_2Ca phases are present in the five Mg-Al-Zn-Ca based alloys.

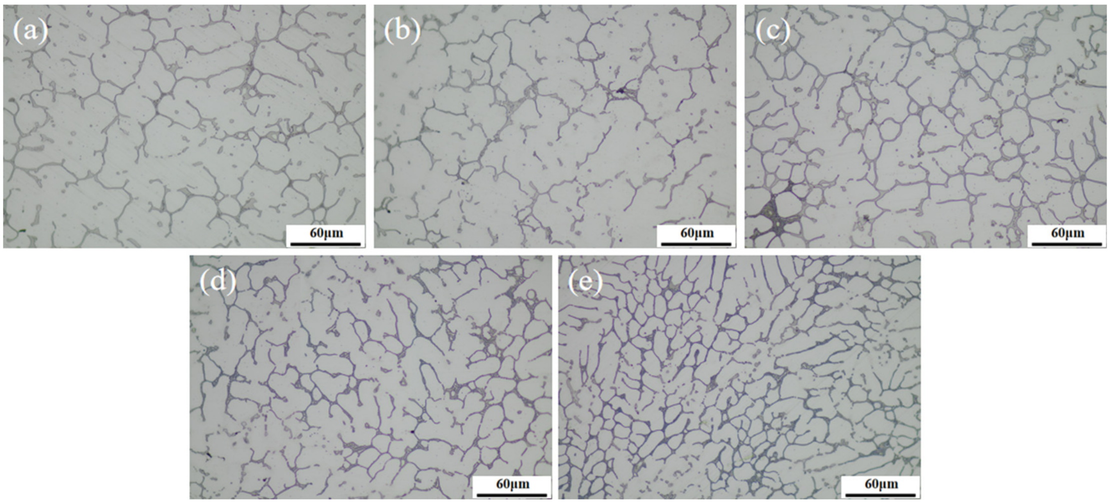

Fig 1. OM images of as-cast magnesium alloys with different compositions: (a)AZX262; (b)AZX352; (c)AZX353; (d)AZX623; (e)AZX624

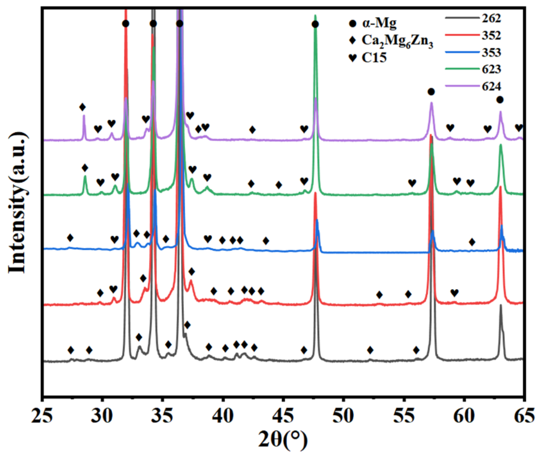

Fig 2. XRD patterns of as-cast alloy samples

Figure 3 shows the secondary electron images of cast magnesium alloys with different compositions. From these images, the distribution and morphology of the various secondary phases in the alloy can be observed. The α-Mg matrix is widely distributed throughout the alloy, while the $Ca_2Mg_6Zn_3$ phase forms a coarse network structure during the solidification process. In contrast, the C15-Al_2Ca phase mainly exhibits a fine skeletal and lamellar structure.The compositions of the second phase in different component alloys are summarized in Table 1 for reference. Combining Figures 2 and 3, we can observe that with a fixed $Ca_2Mg_6Zn_3$ content of 2wt.% and a total Al+Zn content of 8wt.%, when the Al/Zn ratio is 0.33, the second phase in the alloy is only the $Ca_2Mg_6Zn_3$ phase. As the Al/Zn ratio increases to 0.6, the second phases become both $Ca_2Mg_6Zn_3$ and C15-Al_2Ca. Increasing the Ca content to 3wt.% while maintaining the Al/Zn ratio at 0.6 results in the second phases remaining as $Ca_2Mg_6Zn_3$ and C15-Al_2Ca. When the Al/Zn ratio rises to 3, the second phases present in the alloy are C15-Al_2Ca and $Ca_2Mg_6Zn_3$, with the area fraction of the C15-Al_2Ca phase significantly exceeding that of the $Ca_2Mg_6Zn_3$ phase. When the $Ca_2Mg_6Zn_3$ content is increased to 4wt.% and the Al/Zn ratio is still maintained at 3, the second phases remain as C15-Al_2Ca and $Ca_2Mg_6Zn_3$, with a slight increase in the fraction of the $Ca_2Mg_6Zn_3$ phase.

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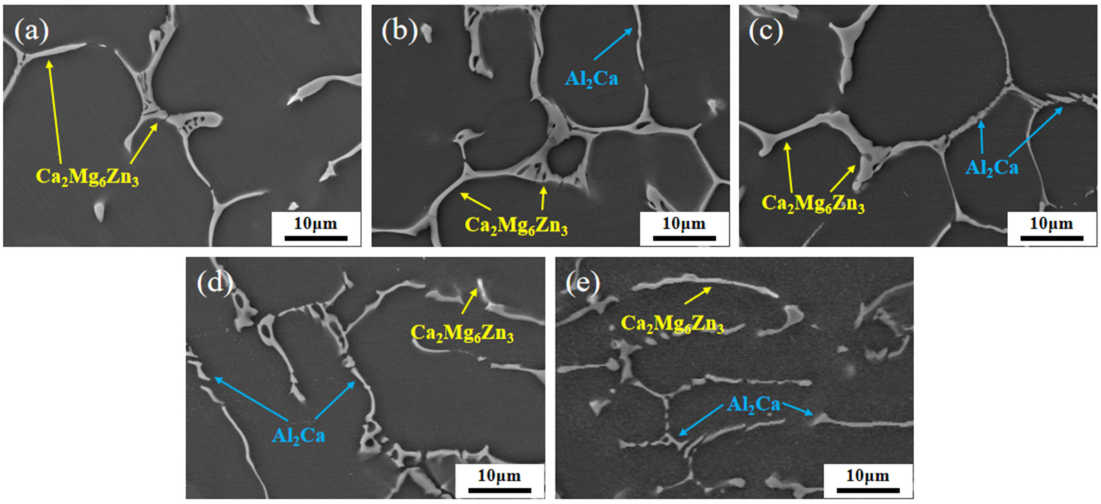

Fig 3. SEM secondary electron images of as-cast magnesium alloys with different compositions: (a)262; (b)352; (c)353; (d)623; (e)624

Table 1. EDS results of solidified second phase in as-cast alloy

		The element content of the three phases (at%)			
		Mg	Al	Zn	Ca
AZX262	$Ca_2Mg_6Zn_3$	56.18	26.30	3.30	14.21
AZX352	$Ca_2Mg_6Zn_3$	62.1	7.72	20.43	9.75
	Al_2Ca	61.75	17.61	10.06	10.59
AZX353	$Ca_2Mg_6Zn_3$	62.1	7.72	20.43	9.75
	Al_2Ca	56.18	26.30	3.30	14.21
AZX623	$Ca_2Mg_6Zn_3$	73.81	11.51	12.12	2.56
	Al_2Ca	63.66	24.37	0.56	11.41
AZX624	$Ca_2Mg_6Zn_3$	67.77	10.55	13.16	8.53
	Al_2Ca	58.5	26.72	1.35	13.43

3.2. Microstructure of the Alloy After Heat Preservation

Figure 4 presents the optical microscopy (OM) images of the Mg-Al-Zn-Ca alloy system after holding at 400℃. From images 4a-e, it can be observed that the secondary phase solidified in the alloy has experienced varying degrees of melting and even spheroidization. Compared to the other four alloys, the second-phase skeleton at the grain boundaries of the AZX353 alloy still maintains good continuity, indicating that this alloy exhibits better thermal resistance. By examining the intragranular changes in the alloy, we found that after the 400℃ holding, only the AZX353 alloy showed a significant amount of precipitate phases, most of which are elongated and rod-like, with a small amount appearing as short rods.However, as the holding time was extended to 20 hours, the precipitates within the grains of the AZX353 alloy significantly decreased, indicating that the stability of these precipitates at the high temperature of 400℃ is poor. By reducing the holding temperature to 350℃ and observing the optical microscopy images of the Mg-Al-Zn-Ca alloy after 60 hours of holding at 350℃ (as shown in Figure 5), we found that, except for the AZX353 alloy which maintained good continuity of the second phase after heat treatment, the second phase at the grain boundaries in the other four alloys exhibited varying degrees of melting and even spheroidization.By observing the intra-crystalline changes in the alloy, we found that after a heat treatment at 350°C for 60 hours, the AZX353 alloy still exhibited a substantial amount of precipitate phase, with a density of approximately 0.14N/μm^2 and an average size of 1.21μm. This indicates that the precipitate phase has good stability at the high temperature of 350°C.

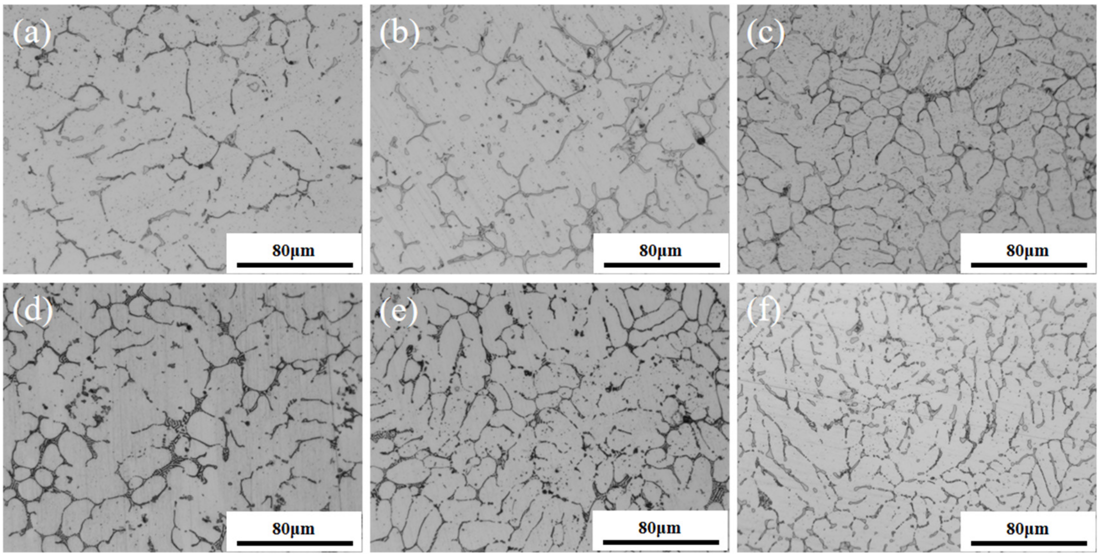

Fig 4. The OM images of magnesium alloy after holding at 400°C for 10h: (a)AZX262; (b)AZX352; (c)AZX353; (d)AZX623; (e)AZX624; (f)AZX353 after holding at 400°C for 20h

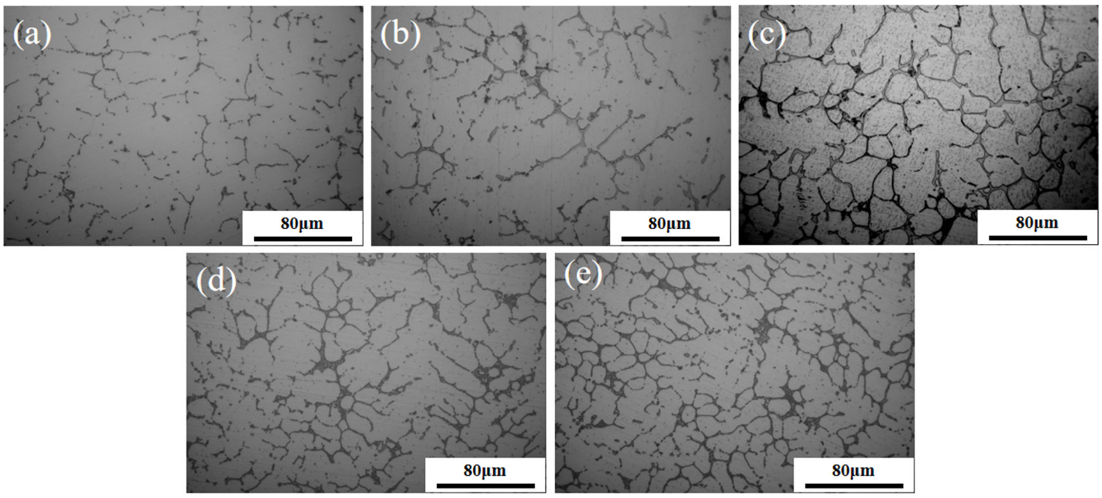

Fig 5. The OM images of magnesium alloy after holding at 350°C for 60h: (a)AZX262; (b)AZX352; (c)AZX353; (d)AZX623; (e)AZX624

Figure 6 presents the secondary electron images obtained from the SEM analysis of different alloy compositions after being held at 350°C for 60 hours. It is evident from the figure that, compared to the other four alloys, the AZX262 alloy exhibits the most severe melting and spheroidization of the second phase at the grain boundaries. The solidifying second phase in this alloy is primarily composed of the $Ca_2Mg_6Zn_3$ phase, which incorporates a certain amount of Al, consistent with reported literature [10]. Therefore, the thermal stability of the $Ca_2Mg_6Zn_3$

phase at 350°C is relatively poor, leading to its susceptibility to decomposition, a phenomenon also mentioned in the literature[11].

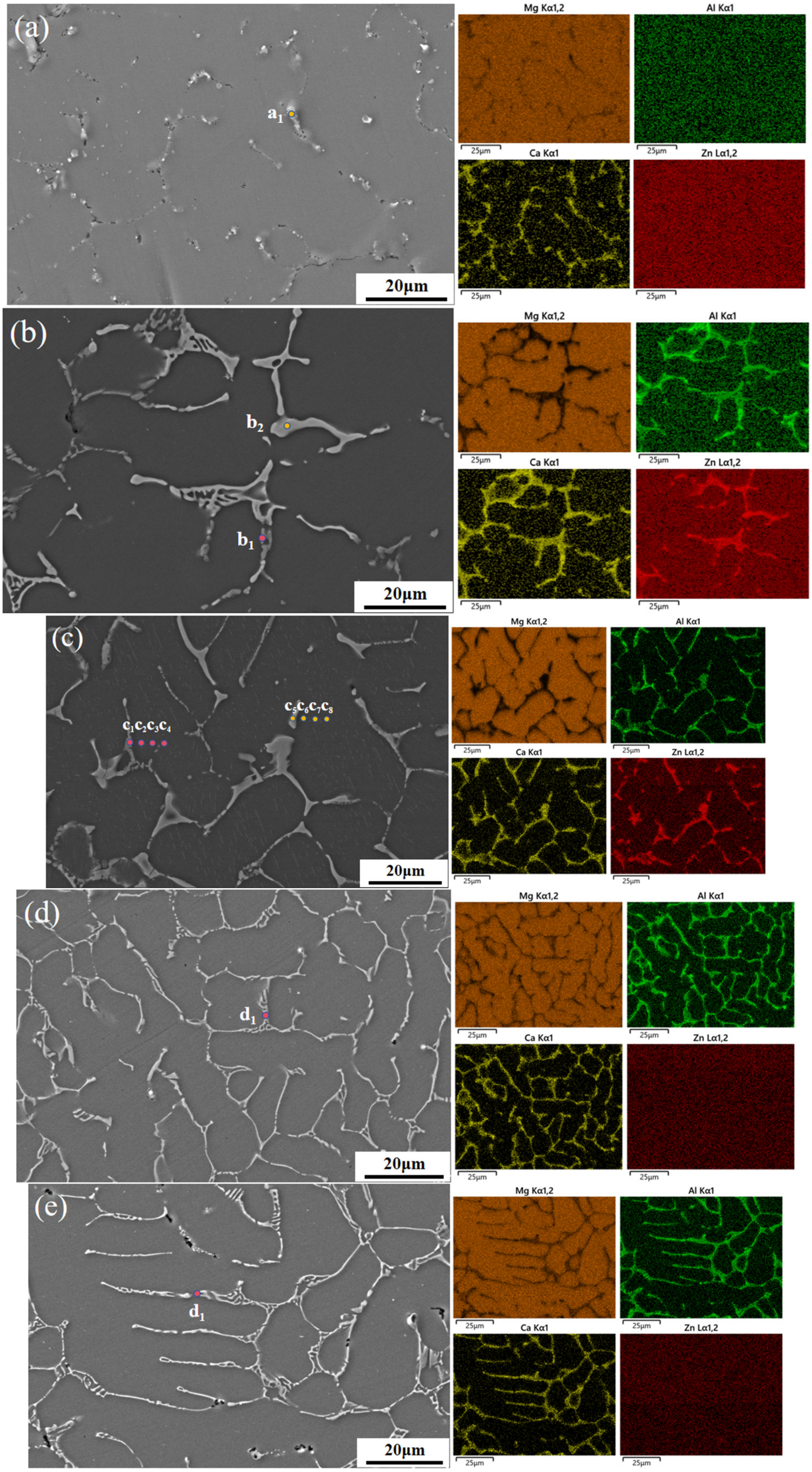

Fig 6. SEM secondary electron images of magnesium alloys with different compositions after holding at 350°C for 60h: (a)AZX262; (b)AZX352; (c) AZX353; (d) AZX623; (e)AZX624

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Based on the EDS layered images of the alloy, it can be seen that after being held at 350°C for 60 hours, the Al and Zn elements, which were originally enriched in the solidified second phase of the AZX262 alloy, have uniformly dissolved into the α-Mg matrix. In contrast, in the AZX623 and AZX624 alloys, the Zn elements are uniformly distributed within the α-Mg matrix after the same heat treatment, which indirectly reflects the dissolution of the $Ca_2Mg_6Zn_3$ phase within the alloy. Conversely, the Al and Ca elements in the AZX623 and AZX624 alloys remain enriched in the second phase at the grain boundaries, composed of the Al_2Ca phase. Therefore, the thermal stability of the Al_2Ca phase is more exceptional at 350°C. With the increase in the Al/Zn ratio and Ca content, the proportion of the Al_2Ca phase in the Mg-Al-Zn-Ca alloy system gradually increases. When the Al/Zn ratio reaches 0.6 and the Ca content increases to 3 wt.%, the distribution of the Al_2Ca phase and the $Ca_2Mg_6Zn_3$ phase in the AZX353 alloy is of significant reference value for the enhancement of the thermal resistance of the Mg-Al-Zn-Ca alloy system. However, further increasing the Al/Zn ratio and Ca content in an effort to augment the proportion of the Al_2Ca phase in the alloy yields minimal improvements in the thermal resistance of the Mg-Al-Zn-Ca alloy system. The composition of the second phase at the grain boundaries in five different Mg-Al-Zn-Ca alloys is summarized in Table 2 for the reader's reference.

Table 2. EDS Results of Intermetallic Compounds in Alloys after Holding Different Magnesium Alloys at 350°C for 60 Hours

		The element content of the three phases (at%)			
		Mg	Al	Zn	Ca
262	a_1	74.3	11.58	2.68	11.44
352	b_1	84.23	6.35	6.24	3.18
	b_2	43.72	19.74	22.66	13.89
353	c_1	53.52	29.55	2.23	14.71
	c_2	88.15	5.9	4.02	1.93
	c_3	93.28	3.36	1.37	1.99
	c_4	96.74	1.38	1.03	0.85
	c_5	51.71	16.48	18.59	13.22
	c_6	88.11	3.98	4.01	3.83
	c_7	95.42	1.58	1.62	1.38
	c_8	97.42	0.88	1.36	0.34
623	d_1	80.76	15.02	0.84	3.38
624	e_1	55.48	30.07	1.42	13.02

3.3. Mechanical Properties of Insulated Alloys

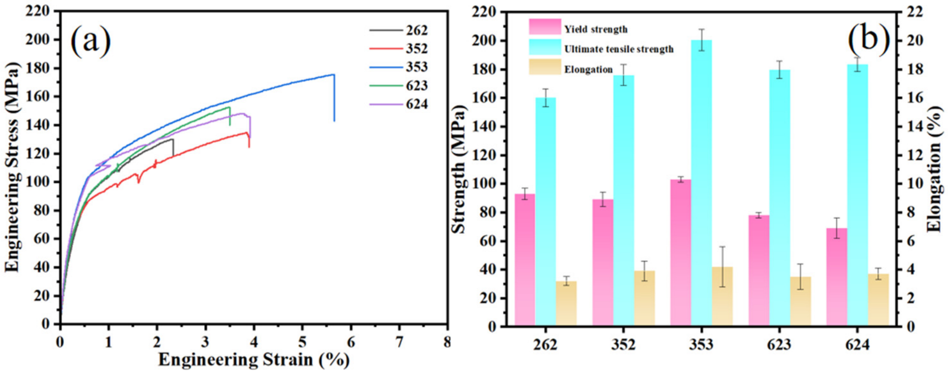

Fig 7. Tensile curves of magnesium alloys with different compositions at room temperature at 350℃ for 60h

Table 3. Mechanical properties of as-cast and heat-treated magnesium alloys with different compositions at room temperature.

Alloy	YS(MPa)	UTS(MPa)	EL(%)
262(AC)	90±4	113±6	1.3±0.2
262(350℃ 60h)	89±6	129±4	3.2±0.3
352(AC)	85±5	125±4	2.6±0.6
352(350℃ 60h)	81±4	139±7	3.9±0.7
353(AC)	99±3	149±3	3.1±0.5
353(350℃ 60h)	103±2	164±6	4.2±1.4
623(AC)	96±1	129±5	1.1±0.2
623(350℃ 60h)	78±6	149±4	3.5±0.9
624(AC)	97±2	129±1	1.81±0.2
624(350℃ 60h)	99±7	147±3	3.7±0.4

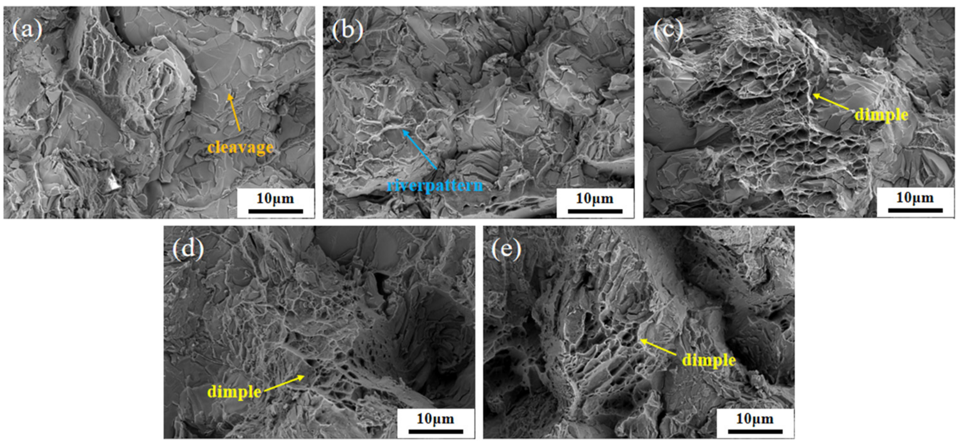

Fig 8. SEM images of tensile fracture surfaces tested at room temperature after heat preservation at 350℃ for 60h: (a)262; (b) 352; (c) 353; (d) 624

Figure 7 shows the room temperature tensile curves of different component magnesium alloys after holding at 350°C for 60 hours. The mechanical properties of both cast and heat-treated alloys are summarized in Table 3 for reference. Among the Mg-Al-Zn-Ca system cast alloys, the AZX262 alloy exhibits poor overall mechanical properties, with yield strength, tensile strength, and elongation only reaching 90 MPa, 113 MPa, and 1.3%, respectively. In contrast, as the Al/Zn ratio and Ca content increase, the overall mechanical properties of the AZX353 alloy achieve optimal performance, with yield strength, tensile strength, and elongation reaching 99 MPa, 149 MPa, and 3.1%, respectively. After being held at 350°C for 60 hours, the mechanical properties of the Mg-Al-Zn-Ca alloy system are significantly enhanced. Among them, the AZX353 alloy, which exhibits precipitate behavior within the grains, demonstrates the most remarkable overall mechanical performance, with the tensile strength increasing from 149MPa in the as-cast state to 164MPa after 60 hours of heat treatment, and the elongation increasing from 3.1% to 4.2%. Compared to the $Ca_2Mg_6Zn_3$ phase, the finer structure of the Al_2Ca framework is more beneficial for the alloy to achieve plasticity[10]. Thus, the partial melting of the $Ca_2Mg_6Zn_3$ phase contributes to the improvement of the alloy's plasticity. At the same time, the dense precipitate phase generated within the crystal has an effective blocking effect on dislocations[12], thereby enhancing the mechanical properties of the alloy. Figure 8 shows the SEM images of the room temperature tensile fracture surfaces after being held at 350°C for 60 hours. The fracture of the AZX262 alloy primarily features cleavage facets with poor plasticity, while the AZX352 alloy shows a river-like pattern, indicating improved plasticity. Noticeable dimples can be observed in the AZX353, AZX623, and AZX624 alloys, suggesting that these three heat-treated alloys exhibit good plasticity, with the AZX353 alloy achieving the best elongation rate of 35.5%.

4. Summary

In this study, we conducted high-temperature heat treatment on cast Mg-Al-Zn-Ca alloys to investigate the precipitation behavior of the alloys under this treatment and its effects on tensile mechanical properties. The results are as follows:

(1) In cast Mg-Al-Zn-Ca alloys, the primary phases consist of α-Mg, C15-Al_2Ca, and $Ca_2Mg_6Zn_3$. With the increasing Al//Zn ratio and Ca content, the C15-Al_2Ca content in the Mg-Al-Zn-Ca alloys gradually rises.

(2) At a heat treatment temperature of 350℃ the C15-Al_2Ca phase exhibits higher thermal stability compared to the $Ca_2Mg_6Zn_3$ phase. Microstructurally, the AZX353 alloy demonstrates superior heat resistance compared to other Mg--Al-Zn-Ca alloys.

(3) After a heat treatment at 350°C for 60 hours, a large amount of precipitated phase was found in the AZX353 alloy, with a density of approximately 0.14 N/μm^2 and an average size of 1.21 μm. Under the strengthening effect of the precipitates, the comprehensive mechanical properties of the alloy were improved, with yield strength, tensile strength, and elongation being 103 MPa, 164MPa, 4.2% respectively.

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