Effect of Ca on microstructure and high temperature creep properties of AM60-1Ce alloy

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Abstract: A series of AM60-1Ce-xCa ($x=0, 0.5, 1.5, 2.5$) magnesium alloys were prepared by gravity casting method and analyzed by means of XRD, DSC and SEM. The effects of Ca on normal temperature mechanical properties and high temperature creep behavior of alloys were characterized by tensile and constant creep test. Microstructure analysis indicated that Ca was preferentially combined with Al in the alloy to form the high melting point Al_2Ca phase at the grain boundary. The addition of Ca can refine the crystal grains and reduces the content of $\beta-Mg_{17}Al_{12}$ phase. With the increase of Ca content in the alloy, Al_2Ca phases at the grain boundary gradually changed to the network of lamellar structure, and replaced the $\beta-Mg_{17}Al_{12}$ phase as the main strengthening phase gradually. The creep resistance of the alloy continuously increases because the high-temperature stable phase Al_2Ca firmly nailed at grain boundaries impedes the sliding of grain boundaries. However, when the addition of Ca was more than 1.5%, mechanical properties of the alloy started to decrease, which was probably due to the large amount of irregularly shaped Al_2Ca phases at the grain boundary. Experimental results show that the optimal addition amount of Ca is 1.5wt. %.

Key words: as-cast magnesium alloy; Al_2Ca hard phase; mechanical properties; high temperature creep properties

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As green engineering materials of the twenty-first century, magnesium alloys have many advantages, such as a high specific strength and stiffness, high vibration absorption, a strong electromagnetic shielding and radiation resistance, and being easy to process and recycle^[1]. Magnesium alloys have important applications in the automobile, communications, and aerospace fields. AM60 magnesium alloy has become one of the most commonly used cast magnesium alloys because of its good mechanical properties, corrosion resistance, and casting properties. Manganese is one of the most important alloying elements in magnesium alloys, which can form a high-melting-point compound with impurity-element iron, and can be excluded as slag, such that the harmful effect of iron on the corrosion resistance

of magnesium alloy is eliminated. The aluminum-manganese phase with a high melting point precipitates preferentially during solidification, which hinders the alloy grain growth^[2]. However, when the temperature exceeds 398 K, the strength and creep resistance of the AM60 magnesium alloy decrease significantly. Thus, it is difficult for the AM60 magnesium alloy to be used widely as a component in power systems, such as engine parts, in the automobile industry^[3-5].

The creep-failure modes of magnesium-aluminum alloys at high temperature are mainly intergranular fractures. The crack initiates at the protruding part of the grain boundary and the boundary of the strengthening phase/matrix. Grain boundary sliding expands the crack gradually into a hole. Under stress, the hole propagates along the grain boundary perpendicular to the stress direction, which leads to sample fracture. Discontinuous precipitation and decomposition of intermetallic compounds are the main factors that lead to a decrease in creep resistance at high temperature^[6]. The β phase ($Mg_{17}Al_{12}$) is the main strengthening phase at room temperature, but the melting point of the β phase is low

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(≤ 710 K), and the β phase is unstable at high temperature. The grain boundary is weakened at high temperature, and slip occurs easily along the grain boundary during the deformation, which leads to crack formation. The interface between the coarse lamellar discontinuous β -phase layers that precipitate along the grain boundaries in the microstructure is close to the atomic compact plane, and most of the interfaces are perpendicular to the grain boundaries, which is equivalent to providing additional sliding planes near the grain boundaries. Under stress, these interlaminar interfaces, which are approximately perpendicular to the grain boundaries, provide additional deformable degrees of freedom for structures near the grain boundaries in the three-dimensional space, to facilitate the sliding of grain boundaries [7]. Therefore, the β phase tends to be considered as the main factor to reduce the creep resistance of the magnesium–aluminum alloy, especially in discontinuous precipitation during creep at a high temperature, which significantly reduces the high-temperature strength and creep resistance of the magnesium alloy.

The main directions of magnesium-alloy development in the use of microalloying elements are to inhibit β -phase formation and to develop low-cost heat-resistant magnesium alloys with excellent comprehensive properties. The main alloying elements that are used to improve the creep resistance of magnesium alloys include rare-earth elements cerium and yttrium [8]; alkali-earth elements calcium and strontium; and the IV and V group elements, such as Si, Sn, and Sb. The experimental results of Lu et al. [9] showed that the $\text{Al}_{11}\text{Ce}_3$ precipitated phase that was formed by adding rare-earth cerium into magnesium–aluminum alloy had a high hardness, a high melting point (1,508 K), a high thermal stability, and a slow rare-earth element diffusion rate, which improved the high-temperature properties of the alloy. However, the costs of rare-earth elements are high and an excessive amount of cerium may result in $\text{Al}_{11}\text{Ce}_3$ coarsening into strips, which leads to matrix cleavage and a decrease in mechanical properties [10].

Calcium can refine the grain size and improve the high-temperature performance of the magnesium alloy [11]. However, when only calcium is added, magnesium alloys, such as AZ91, are prone to heat cracking and exhibit a poor plasticity [12]. Therefore, many researchers have added calcium and rare-earth elements into magnesium alloys to enhance the room-temperature and high-temperature performances [11–14]. However, insufficient data can be obtained to understand the mechanism of why calcium enhances the room-temperature mechanical properties and high-temperature creep properties of magnesium alloys containing rare-earth elements. In this study, AM60-1Ce was selected as the magnesium alloy matrix. The effect of calcium on the microstructure, room-temperature mechanical properties, and high-temperature creep properties of the AM60-1Ce magnesium alloy was studied.

1 Experimental procedure

Commercial AM60 alloy was used as raw material, and magnesium–cerium and magnesium–calcium alloys were

used as intermediate alloys. The AM60 alloy was melted in a crucible resistance furnace followed by the addition of Mg-1%Ce and Mg-30%Ca intermediate alloys, and then solution treated at 750 °C and stirred to ensure that the intermediate alloys were dissolved completely. The molten alloy was held at 720 °C for 30 min, and poured into a mold at 710 °C. The mold (12 mm $\times$ 100 mm $\times$ 200 mm) was pre-heated to 180–200 °C. Melting and stirring were carried out under argon to avoid magnesium-alloy oxidation. The chemical compositions of the four studied alloys are listed in Table 1.

Table 1: Chemical composition of tested alloys (mass%)

Alloys	Al	Mn	Ce	Ca	Mg
AM60-1Ce	5.7	0.27	0.82	-	Bal.
AM60-1Ce-0.5Ca	5.7	0.24	0.77	0.39	Bal.
AM60-1Ce-1.5Ca	5.8	0.23	0.74	1.34	Bal.
AM60-1Ce-2.5Ca	5.7	0.24	0.73	2.19	Bal.

The cast metallographic specimens were cut from the bottom of the ingots, and the specimen surfaces were etched with 5% nitric-acid solution after being ground and polished. The microstructures were characterized using a ZEISS (AXIO-Imager.A2m) optical microscope (OM) and a ZEISS (EVO 18) scanning-electron microscope (SEM). X-ray diffraction (XRD) analysis was carried out to identify the phase constitutions in the microstructure. Differential scanning calorimetry (DSC, Netzsch DSC 404C) was used to study the austenizing process where the samples were machined into 2.0 mm-diameter cylinders with length of 0.5 mm. DSC scans were carried out in a protective atmosphere of high-purity flowing argon (50 mL·min⁻¹). Samples were heated from room temperature to 1,373 K at 10 K·min⁻¹ before being cooled to room temperature at 40 K·min⁻¹.

Microhardness tests were performed using a 1600-5122VD microhardness tester. Specimens that were used in the tensile test and tensile creep test were cut from the cast ingots, and machined to the dimensions shown in Fig. 1. Tensile tests were performed using a universal testing machine (CMT1505) at ambient temperature and a strain rate of 1 mm·min⁻¹. Creep tests were performed at 175 °C with a 100 MPa load. During the test, alloys were placed in a protective dried atmosphere and the temperature was kept constant. The sensitivity of the elongation measurement was better than 10⁻⁵.

Fig. 1: Shape and dimension of specimens for tensile test and tensile creep test

2 Results and discussion

2.1 Effect of Ca on microstructure of AM60-1Ce alloy

The optical images of the AM60-1Ce-*x*Ca alloy microstructure are shown in Fig. 2. Figure 2(a) shows that the microstructure of the as-cast AM60-1Ce magnesium alloy has a typical dendritic morphology, which is composed of the Mg matrix, a dendritic

β -Mg₁₇Al₁₂ phase at the grain boundary, a eutectic phase with a lamellar shape (α -Mg+ β -Mg₁₇Al₁₂), a fine needle-like rare-earth phase Al₁₁Ce₃, and a small amount of granular Al₈Mn₅ phase. With calcium addition [0.5%, 1.5% and 2.5%, Fig. 2(b–d)], the second alloy phase has been refined significantly. The lamellar eutectic phase (α -Mg+ β -Mg₁₇Al₁₂) of the alloys substantially decreases and almost disappear, whereas new compound Al₂Ca is found at the grain boundary.

Fig. 2: Optical images of as-cast AM60-1Ce (a), AM60-1Ce-0.5Ca (b), AM60-1Ce-1.5Ca (c) and AM60-1Ce-2.5Ca (d)

To characterize the grain size, a grain map of the EBSD results for the AM60-1Ce and AM60-1Ce-2.5Ca alloys is shown in Fig. 3. The average grain size of the α -Mg phase decreases from ~151 μ m to 115 μ m as the calcium content increases from 1% to 2.5%. Similar conclusions have been found in previous studies [13–16].

Figure 4(a) shows that the AM60-1Ce alloy is mainly composed of a magnesium matrix, a dendritic β -Mg₁₇Al₁₂ phase at the grain boundary, a eutectic phase with a lamellar shape (α -Mg+ β -Mg₁₇Al₁₂), a fine needle-like rare-earth phase Al₁₁Ce₃, and a small amount of granular Al₈Mn₅ phase. When 0.5% calcium was added [Fig. 4(b)], the laminar eutectic phase of the alloy decreased significantly, and the size of the dendritic phase β -Mg₁₇Al₁₂ that had precipitated at the grain boundary decreased. Simultaneously, a small amount of bright-white new phases appeared. When the calcium addition was increased to 1.5% [Fig. 4(c)], the number of β -Mg₁₇Al₁₂ phases and the fine needle-like rare-earth phase Al₁₁Ce₃ at the grain boundary decreased significantly, whereas the bright-white new dendritic phase increased. It can be seen in Fig. 4(d), when calcium

reached 2.5%, the β -Mg₁₇Al₁₂ phase disappeared. Except for a small amount of island-shaped Al₁₁Ce₃ phase, the second phase was replaced by a bright-white new phase at the grain boundary, and showed a reticular structure.

Figure 5 shows the XRD pattern of the as-cast AM60-1Ce-*x*Ca alloy. The AM60-1Ce magnesium alloy is mainly composed of α -Mg, β -Mg₁₇Al₁₂, Al₁₁Ce₃, and Al₈Mn₅ in trace amounts. Figure 5(b–d) shows that, with calcium addition, a new Al₂Ca phase appears in the alloy. Moreover, with an increase in calcium content, the diffraction peak of the Al₂Ca phase in the alloy increases, whereas the diffraction peak of the β -Mg₁₇Al₁₂ phase decreases and almost disappears.

In the magnesium–aluminum–calcium ternary alloy, aluminum can affect the dissolution of calcium in the solid solution, which makes it difficult for calcium to be dissolved in the α -magnesium matrix [17]. Calcium can dissolve in β -Mg₁₇Al₁₂ at less than 1.0%. It is easier for calcium to combine with aluminum and magnesium compared with other elements to produce intermetallics when the calcium content exceeds 1.0%. The phenomenon is related to the electronegativity difference [18–19]. Usually, electronegativity is

Fig. 3: Grain map of EBSD results for AM60-1Ce (a) and AM60-1Ce-2.5Ca (b) alloys

Fig. 4: SEM images of as-cast AM60-1Ce-xCa alloys: (a) AM60-1Ce, (b) AM60-1Ce-0.5Ca, (c) AM60-1Ce-1.5Ca and (d) AM60-1Ce-2.5Ca

used to measure the chemical affinity. A higher electronegativity difference between two elements results in a stronger chemical affinity between them, and a more stable generated compound^[20]. Table 2 shows the electronegativity difference between the main elements in the alloy (Pauling's Electronegativity)^[21]. The electronegativity difference between elements is $\Delta P_{\text{Al-Ca}} = 0.6 > \Delta P_{\text{Mg-Ca}} = \Delta P_{\text{Al-Mg}} = 0.3$, which indicates that the stability of Al_2Ca exceeds that of Mg_2Ca or $\text{Mg}_{17}\text{Al}_{12}$. The stability of the compound can be assessed from its formation enthalpy or melting point. The ΔH of the three compounds Al_2Ca , Mg_2Ca , and $\text{Mg}_{17}\text{Al}_{12}$ were

$-217 \text{ kJ}\cdot\text{mol}^{-1}$ ^[22], $-39.3 \text{ kJ}\cdot\text{mol}^{-1}$ ^[23], and $-1.09 \text{ kJ}\cdot\text{mol}^{-1}$ ^[24], and the melting points were 1,352 K, 988 K, and 710 K, respectively. The melting point of Al_2Ca is the highest, thus, it is the easiest to form and is the most stable, followed by Mg_2Ca . The most difficult to form and the least stable compound was $\text{Mg}_{17}\text{Al}_{12}$. The mass ratio of Ca/Al in the magnesium–aluminum–calcium series of alloys determines the compound type^[25]. When the mass percentage ratio of Ca/Al is less than 0.8, an Mg_2Ca compound cannot be obtained and only an Al_2Ca compound formed. The mass ratio of Ca/Al in the AM60-1Ce-xCa series

Fig. 5: XRD patterns of as-cast AM60-1Ce (a), AM60-1Ce-0.5Ca (b), AM60-1Ce-1.5Ca (c) and AM60-1Ce-2.5Ca (d)

Table 2: Electro negativity values and difference of elements ^[27]

Element	Electronegativity (P)	$\Delta P/[P_A - P_B]$			
		Mg	Al	Ce	Ca
Mg	1.31	0	0.3	0.19	0.3
Al	1.61	0.3	0	0.49	0.6
Ce	1.12	0.19	0.49	0	0.11
Ca	1.01	0.3	0.6	0.11	0

alloys in this experiment were less than 0.8, so it was difficult to obtain Mg_2Ca compound. In contrast, the study of AZ31 magnesium alloys with calcium, strontium and cerium at the trace level (approximately 0.2wt.% per element) showed the existence of phases other than $Mg_{17}(Al, Zn)_{12}$ and Al_8Mn_5 , namely: Al_2Ca , Al_2Sr , $Al_{11}Ce_3$, et al ^[26].

Figure 6 shows the DSC curve of the AM60-1Ce-xCa alloy during cooling. Figure 6(a) shows that two exothermic peaks appeared at ~887 K and 712 K during alloy cooling, and these correspond to the primary α -Mg and the eutectic β - $Mg_{17}Al_{12}$, respectively. Therefore, the solidification of primary α -Mg occurred at 887 K, and the eutectic transformation ($L \rightarrow \alpha$ -Mg + β - $Mg_{17}Al_{12}$) occurred at 712 K, whereas the exothermic peak of $Al_{11}Ce_3$ cannot be detected because it exists as a minor phase.

Fig. 6: DSC curves of as-cast AM60-1Ce-xCa alloys: (a) $x=0$; (b) $x=0.5$; (c) $x=1.5$; (d) $x=2.5$

Figure 6(b) shows that most of the 0.5% calcium dissolved in the α -Mg and β - $Mg_{17}Al_{12}$ matrix, and the content of Al_2Ca was so low that the exothermic Al_2Ca peak could not be detected. When the calcium addition increased to 1.5% [Fig. 6(c)], the exothermic peak of the β - $Mg_{17}Al_{12}$ phase was not detected near 712 K, the exothermic peak of α -Mg appeared near 883 K, and a new exothermic peak appeared at 801 K, which corresponds to Al_2Ca . This result indicates that calcium and aluminum in the alloy could form the Al_2Ca phase at 801 K, which consumed

a large amount of aluminum in the alloy and significantly reduced the $\beta\text{-Mg}_{17}\text{Al}_{12}$ phase in the alloy. When the calcium addition increased to 2.5% [Fig. 6(d)], the exothermic peak of the $\beta\text{-Mg}_{17}\text{Al}_{12}$ phase was still not detected near 712 K; the exothermic peak of $\alpha\text{-Mg}$ appeared near 882 K, and the height of the exothermic peak decreased significantly, whereas the exothermic peak of Al_2Ca increased significantly to near 817 K. Therefore, when the calcium addition increased to 2.5%, extensive Al_2Ca phase formed in the alloy.

Some studies^[12] indicate that a grain refinement of the AZ91 alloy resulted from the increase in grain nucleation rate and the inhibition of grain-boundary movement by calcium-containing second phases. Calcium, as a surface-active element adsorbed on the grain boundary, decreased the nucleation energy required to form a critical nucleus size, and increased the heterogeneous core at crystallization simultaneously. Calcium has a high growth-restriction factor, which is quantified by the Q -value^[13]. In a binary system, $Q = mC_0(k-1)$, where m is the slope of the liquidus line, C_0 is the initial alloy composition, and k is the equilibrium partition coefficient for the element^[28]. Because of the presence of calcium solute ($Q_{\text{Ca}} = 11.94$ ^[29]), the grain size of the quaternary alloy is refined. Moreover, because the affinity of aluminum–calcium is the highest (the difference in electronegativity is largest) and the enthalpy of formation of Al_2Ca is the lowest, calcium is able to form the most stable Al_2Ca with aluminum in the alloy in preference and inhibit the formation of the $\beta\text{-Mg}_{17}\text{Al}_{12}$ phase.

2.2 Effect of Ca addition on mechanical properties of AM60-1Ce alloy

The hardness of the AM60-1Ce- $x\text{Ca}$ series alloy is shown in Fig. 7. Most calcium was dissolved in the matrix and a $\beta\text{-Mg}_{17}\text{Al}_{12}$ phase formed when 0.5% calcium was added to the alloy, which increased the hardness of the AM60-1Ce-0.5Ca from 55.36 HB to 56.28 HB. When the calcium content increased to 1.5%, the hard eutectic-phase Al_2Ca at the grain boundary replaced the $\beta\text{-Mg}_{17}\text{Al}_{12}$ phase as the main strengthening phase, which enhanced the hardness of the AM60-1Ce-1.5Ca to 59.54 HB. When the calcium content increased to 2.5%, a large amount of Al_2Ca at the grain boundary improved the hardness of the AM60-1Ce-2.5Ca to 61.48 HB.

Fig. 7: Hardness and tensile strength of as-cast AM60-1Ce- $x\text{Ca}$ alloys

The room-temperature tensile strengths of the AM60-1Ce- $x\text{Ca}$ alloys are also shown in Fig. 7. The room-temperature tensile strength increased from 177 MPa to 180 MPa by adding 0.5% Ca to the AM60-1Ce alloy. When the calcium content increased to 1.5%, the tensile strength of the AM60-1Ce-1.5Ca reached 205 MPa, which resulted mainly because of the change in enhanced phase from the $\beta\text{-Mg}_{17}\text{Al}_{12}$ phase to the eutectic-phase Al_2Ca dispersed at the grain boundary, which strengthened the grain boundary and hindered the dislocation motion. When the calcium addition was increased to 2.5%, a large number of Al_2Ca phases formed a network structure at the grain boundary, which increased the alloy brittleness, and cracks initiate because of the stress concentration. Thus, the tensile strength of the alloy decreased significantly to 159 MPa.

Figure 8 shows the room-temperature yield strength and elongation of the AM60-1Ce- $x\text{Ca}$ alloys. The yield strength increased from 98 MPa to 100 MPa by adding 0.5% calcium to the AM60-1Ce alloy. When the calcium content increased to 1.5%, the yield strength reached 123 MPa because eutectic-phase Al_2Ca rather than $\beta\text{-Mg}_{17}\text{Al}_{12}$ phase was dispersed at the grain boundary, and the hard stable Al_2Ca strengthened the grain boundary and retarded the plastic deformation. When the calcium addition was increased to 2.5%, the yield strength decreased significantly to 70 MPa, because the Al_2Ca phases formed a network structure at the grain boundary, which increased the alloy brittleness significantly.

Fig. 8: Yield strength and elongation of as-cast AM60-1Ce- $x\text{Ca}$ alloys

In Fig. 8, the elongation of the AM60-1Ce- $x\text{Ca}$ alloys increased from 7.8% to 15.4% with an increase in calcium content from 0.5% to 1.5%; however, the elongation of the AM60-1Ce-2.5Ca decreased sharply to 5.7%. This result indicates that the alloy plasticity increased with the increase in calcium content (0%–1.5%), whereas the decrease in plasticity of the AM60-1Ce-2.5Ca resulted due to that the Al_2Ca phases formed a network structure at the grain boundary.

The difference in elongation of the experimental alloys can be confirmed from Fig. 9, which shows the presence of a number of cleavage planes and steps, and some small ridges and dimples in the localized areas of the tensile fracture surface, and indicates that all tensile fracture surfaces exhibited a quasi-cleavage fracture. When the calcium content increased from 0% to 1.5% [Fig. 9(a–c)], dimples on the fracture surfaces increased

Fig. 9: SEM images of tensile fractographs for as-cast AM60-1Ce-xCa alloys at room temperature: (a) $x=0$; (b) $x=0.5$; (c) $x=1.5$; (d) $x=2.5$

and the dimple size decreased, which proved that the alloy toughness improved. However, the plasticity of the AM60-1Ce-2.5Ca alloy decreased significantly, because of the occurrence of a number of Al_2Ca phases with a reticular structure at the grain boundary, which was confirmed by the increase in cleavage steps and the decrease in dimples in Fig. 9(d).

In addition to grain refining, the mechanical properties of the AM60-1Ce-xCa alloys at room temperature were affected by the strength and morphology of the second phase at the grain boundary. With a moderate addition of calcium (1.5%), the Al_2Ca phase with a higher hardness and stability replaced the $\beta\text{-Mg}_{17}\text{Al}_{12}$ as the main strengthening phase, which was dispersed at the grain boundary, showed a dendritic distribution, and lead to a strengthening of the grain boundary. The tensile strength of the AM60-1Ce-1.5Ca alloy at room temperature was improved significantly.

2.3 Effect of Ca addition on high temperature creep properties of AM60-1Ce alloy

Figure 10 shows the creep curves of the AM60-1Ce-x%Ca alloy at 423 K and 100 MPa. The 10 h creep of the AM60-1Ce alloy was in the second stage, namely the steady creep stage, and the creep strain (ε) was 5.58%. After 0.5% calcium addition, the creep was also in the steady creep stage, and the ε decreased to 5.06%. When the calcium content was 1.5%, the creep was still in the second stage after 10 h, and the ε was reduced significantly to 3.96%. The AM60-1Ce-2.5Ca alloy was also in the steady creep stage after 10 h, and the ε was reduced to 3.34%.

The curve of the first derivation for creep strain-rate prediction $\dot{\varepsilon}_t$ with time t after creep for 10 h at 423 K and 100 MPa is shown

Fig. 10: Creep strain curves of as-cast AM60-1Ce-xCa alloys

in Fig. 11. The steady creep rate of the AM60-1Ce alloy was $2.12 \times 10^{-6} \text{ s}^{-1}$. With 0.5% calcium addition, the steady-state creep rate of the alloy was reduced significantly to $3.26 \times 10^{-7} \text{ s}^{-1}$, which is 84.6% lower than that of AM60-1Ce, i.e., the creep-resistance performance was improved significantly. When the calcium content reached 1.5%, the steady-state creep rate of the alloy was $1.46 \times 10^{-7} \text{ s}^{-1}$, which was 55.2% lower than the AM60-1Ce-0.5Ca, and the creep resistance also improved significantly. When the calcium content reached 2.5%, the steady creep rate of the alloy was $6.17 \times 10^{-8} \text{ s}^{-1}$, which decreased by 57.7% compared with AM60-1Ce-1.5Ca, and the creep resistance improved. Therefore, it can be concluded that the creep performance of the AM60-1Ce alloy was improved significantly by calcium, and the higher amount of calcium resulted in a higher creep resistance of the AM60-1Ce-xCa alloy.

A large amount of lamellar eutectic phase ($\alpha\text{-Mg}+\beta\text{-Mg}_{17}\text{Al}_{12}$)

Fig. 11: Creep strain rate curves of as-cast AM60-1Ce-xCa alloys

existed at the grain boundaries in the AM60-1Ce alloy [Fig. 4(a)], where the interface was close to the atomically dense surface, and approximately perpendicular to the grain boundary. This is equivalent to a greater reliability of sliding planes near the grain-boundary area, such that the additional degrees of freedom for grain-boundary sliding during creep results in a decrease of creep properties. The precipitated $\beta\text{-Mg}_{17}\text{Al}_{12}$ phase at the grain boundary was very unstable at a high temperature and was prone to cracking during the creep process, which led to a decrease in alloy creep properties. Figure 12(a) shows the SEM micrograph of the AM60-1Ce alloy after creep for 10 h at 423 K and 100 MPa. During the

creep process at a high temperature, the metastable phase $\beta\text{-Mg}_{17}\text{Al}_{12}$ precipitated at the grain boundary and caused microcracks, which reduced the grain-boundary strengthening significantly. The microcracks promoted grain-boundary migration and sliding, and increased the creep deformation of the alloy. Figure 12(b) shows the SEM morphology of the AM60-1Ce-1.5Ca alloy after 10 h of creep at 423 K and 100 MPa. The Al_2Ca phase at the grain boundary was very stable during the high-temperature creep process (no significant change resulted after 10 h of creep) and can prevent the grain boundary sliding, which improves the alloy creep resistance.

Magnesium alloy has a HCP structure, which cannot provide sufficient slip systems during deformation, but grain-boundary sliding can provide additional slip systems to satisfy deformation conditions for magnesium-alloy creep^[30]. Humble^[31] found in an experiment that grain-boundary sliding forms 40%–80% of the total deformation in Mg-0.8Al compared with that less than 10% in pure aluminum. At room temperature, grain-boundary deformation is not obvious and can be neglected. However, the creep failure of magnesium alloy at a high temperature is caused by atomic instability at the grain boundary, easy diffusion, and easy sliding under stress. Thus, grain-boundary sliding at high temperature is one of the main reasons for increasing creep deformation^[32]. With an increase in calcium addition, the high-temperature stable Al_2Ca phases at the grain boundaries increased gradually and were nailed firmly at the grain boundaries to improve the alloy creep properties.

Fig. 12: SEM images of as-cast alloys after 10 h's creep (432 K, 100 MPa) for AM60-1Ce (a) and AM60-1Ce-1.5Ca (b)

3 Conclusions

The influence of alloying element, calcium, on the mechanical and creep properties of the AM60-1Ce alloy at room and high temperatures was explored, and the following conclusions were made:

- (1) When calcium is added to the AM60-1Ce alloy, it combines with aluminum to form a more stable Al_2Ca phase with dendrite morphology at the grain boundary as the main reinforcing phase, which strongly inhibits the formation of the $\beta\text{-Mg}_{17}\text{Al}_{12}$ phase.
- (2) With an increase in calcium content, the Al_2Ca phase at

the grain boundary with a higher hardness gradually replaces the $\beta\text{-Mg}_{17}\text{Al}_{12}$ phase as the main strengthening phase, which significantly improves the hardness and strength of the AM60-1Ce-xCa alloys. When the calcium content reaches 2.5%, Al_2Ca forms as a network structure at the grain boundary, which makes the matrix brittle and decreases the tensile strength significantly.

- (3) With an increase in calcium addition, the high-temperature stable phase Al_2Ca at the grain boundary instead of the metastable phase $\beta\text{-Mg}_{17}\text{Al}_{12}$ impedes the sliding of the grain boundary, and improves the creep resistance of the AM60-1Ce alloy continuously.

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