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# Effect of $Al_2Ca$ intermetallic compound addition on grain refinement of AZ31 magnesium alloy

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**Abstract:** The $Al_2Ca$ intermetallic compound was prepared by melting process in a vacuum induction furnace. And the $Al_2Ca$ compound was added in as-cast AZ31 alloys for grain refinement. The effect of its additional levels on grain refinement of as-cast AZ31 alloy was investigated and the mechanism of the grain refinement was discussed. The results reveal that the addition of 1.1% $Al_2Ca$ (mass fraction) decreases the average grain size of as-cast AZ31 alloy from 354 to 198 μm. And the thermal stability of the grains refined by $Al_2Ca$ is superior. The grain refining mechanism is attributed to the combined effects of solute and heterogeneous nucleation from the $Al_2Ca$.

**Key words:** AZ31 magnesium alloy; $Al_2Ca$; grain refinement; mechanism

## 1 Introduction

Recently, magnesium alloys have been widely concerned in applications for the automobile and aerospace industries as a structure material due to their low specific strength and energy consumption [1,2]. However, for the most commercially and commonly used magnesium alloys, such as AZ31, AZ61 and AZ91, their mechanical properties and performance are relatively low and cannot meet the requirement of many applications [1]. It is well known that the grain size is a very important factor for overcoming this shortcoming of these alloys, and according to Hall−Petch equation, high strength can be attained with fine-grained magnesium alloys [3,4].

In Al-free Mg alloys, Zr is an extremely effective nucleation agent for the solidification of Mg alloys. Unfortunately, in commercially used Al-bearing Mg alloys, no suitable or effective nucleants have yet been found. Nonetheless, several approaches have been developed. These approaches mainly include superheating [5], carbon inoculation [6], adding suitable grain refiners and alloying elements, such as Ca, Sr [7], RE [8,9], Ti−B [10], Mn [11], ZnO [12], AlN [13] and $Al_2Y$ [14]. Due to simplicity and good adaptability to alloy's compositions, the addition of small amount of alloying elements or grain refiner has become more popular in industrial application.

Ca is one of the most important alloying elements for Mg alloys due to low cost and lightness compared with other elements. In recent years, Ca has been used to improve the creep and high temperature performances of the Mg alloys. Mg−Al−Ca alloys revealed excellent creep resistance and elevated temperature properties due to the formation of high melting point Ca-containing

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phases with various sizes located both at the grain boundaries and within grains interior [15]. The addition of Ca to the AZ31 and AZ91 alloys can increase the high temperature properties because of the existence of $(Al,Mg)_2Ca$ phases [16,17]. HOMMA et al [18] reported the precipitation of $Al_2Ca$ plates during the creep test of Mg−Al−Ca−Mn alloys which had better creep properties. Additionally, some investigations reported that the addition of Ca into Mg−Al alloys will produce an effective grain refinement. Obvious microstructure refinement in AZ31 [19], Mg−5%Al [20], AM60 [21] and AZ91D alloys [22] was observed with Ca additions. Some investigators thought about the grain refinement mechanism of addition of Ca into Mg−Al alloys as the higher growth restriction factor (GRF) [23] of Ca in Mg alloy, some thought about it as the heterogeneous nucleation of in situ formed $Al_2Ca$ compounds in Mg alloys [19]. However, the refinement mechanism of Ca in Mg alloys is not fully understood and unfortunately, and the addition of Ca in AZ31 melt tends to increase the viscosity of the melt [13] and leads to the surface defect [24].

Therefore, in this work, in order to study the effect of $Al_2Ca$ compound addition on the grain refinement of Mg−Al alloys, $Al_2Ca$ intermetallic compound was prepared by melting process in a vacuum induction furnace under an argon atmosphere. Then, it was added into AZ31 Mg alloy melt to check the grain refining effects on as-cast AZ31 magnesium alloy and the possible refining mechanism.

## 2 Experimental

The $Al_2Ca$ intermetallic compound was synthesized by pure Al (>99.9%) and pure Ca (>99.9%) through melting reaction process at 1023 K using an alumina crucible in a vacuum induction furnace under an argon atmosphere. The Al/Ca molar ratio was 2:1. After the melting reaction, the products were held for about 10 min, then cooled with furnace and the primary $Al_2Ca$ block was achieved. The agate balls with a diameter of 10 mm were used as the milling media and mixed with the starting material at a ball-to-powder mass ratio of 10:1. The $Al_2Ca$ block and milling balls were put into the agate jar, and then mixed at a speed of 50 r/min for 12 h. Finally, the $Al_2Ca$ powder was obtained.

A commercial AZ31 Mg alloy was melted in a mild steel crucible in an electric resistance furnace under the protection of $CO_2$+0.5% $SF_6$ (volume fraction) mixture gas. Then, 0.5% $Al_2Ca$, 1.1% $Al_2Ca$, 1.7% $Al_2Ca$ and 3.5% $Al_2Ca$ powders were added into the AZ31 Mg alloy melt at about 993 K, respectively. The melt was stirred and held for 10 min and then poured into a steel mold ($d$20 mm × 90 mm) preheated to 473 K in order to obtain a sample ingot. The actual chemical compositions of the experimental alloys were inspected by an XRF 800CCDE X-ray fluorescence spectrometer and results are listed in Table 1. For grain morphology observation, all as-cast samples were cut in the horizontal direction at the location of 15 mm from the bottom of the ingots. Moreover, in order to clearly show the grain boundaries of the samples and estimate the thermal stability of the fine grains, the solid solution treatment of the samples was carried out at 688 K for 10 h and followed by water quenching.

**Table 1** Chemical compositions of alloys studied (mass fraction, %)

| Alloy | Mg | Al | Zn | Mn | Ca |
|---|---|---|---|---|---|
| AZ31 | 96.03 | 2.87 | 0.71 | 0.39 | 0 |
| AZX3105 | 95.45 | 3.19 | 0.72 | 0.38 | 0.26 |
| AZX3110 | 94.97 | 3.47 | 0.74 | 0.36 | 0.46 |
| AZX3115 | 94.45 | 3.76 | 0.72 | 0.35 | 0.72 |
| AZX3130 | 92.52 | 4.85 | 0.73 | 0.38 | 1.52 |

In order to identify the precipitation sequence of the $Al_2Ca$ phase and the $\alpha$-Mg phase, a thermal analysis method was used to detect whether the $Al_2Ca$ precipitates during solidification. Before cooling, a thermocouple was placed at the center of the mild steel crucible with its tip set at 10 mm from the bottom of the crucible. The alloy melt was cooled in the furnace. The cooling curves were recorded by a datalogger and computer. In addition, to study the stability of $Al_2Ca$ in liquid Mg, the $Al_2Ca$/Mg solid−liquid diffusion couple was prepared by traditional method. Pure Mg and $Al_2Ca$ compound block (melting point about 1352 K) were used. A rectangular piece of $Al_2Ca$ compound block was polished with 800-grit SiC paper, and then cleaned with acetone to make sure an oxide-free surface. Pure Mg was melted under a protective atmosphere of $CO_2$+0.5%SF6. $Al_2Ca$ compound block was immediately submerged into the Mg melt, and isothermally held at 993 K for 10 min, and then the samples were quenched in cold water.

These samples were ground, polished and then etched with a solution of 2.5 g picric acid + 45 mL ethanol + 2.5 mL acetic acid + 5 mL distilled water and then the grain size of each sample was examined using polarized light in Olympus optical microscope. The obtained color images were analyzed by Image-Pro Plus 5.0 software. The phase identification was analyzed by a Dimax 2500PC type X-ray diffractometer (XRD) operated at 40 kV and 30 mA. The microstructure was observed by a scanning electron microscope (SEM) with energy dispersive spectrometer (EDS).

## 3 Results and discussion

### 3.1 Characteristics of $Al_2Ca$ intermetallic compound

Figure 1 presents the XRD pattern of the Al−Ca intermetallic compound. It can be seen that the main compound in the product is $Al_2Ca$ and small amount of $Al_4Ca$ phase. In Al−Ca binary phase diagram [25], there have been two compounds, i.e., $Al_2Ca$ and $Al_4Ca$. When the Al/Ca molar ratio is 2:1, the product is $Al_2Ca$. Due to the little burning of Ca under the limited vacuum degree, the $Al_4Ca$ compound is present in the products. Figure 2(a) shows the image of the $Al_2Ca$ block sample. As the compound is very brittle, it is easy to crush and ball-mill into powder, as shown in Fig. 2(b). It can be seen that the powder is composed of anomalous particles with sizes of 5−10 μm.

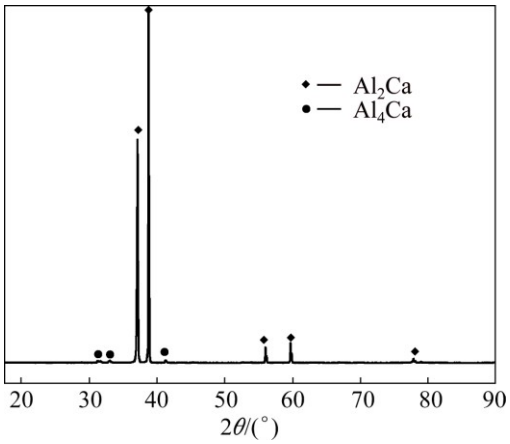


**Fig. 1** XRD pattern of $Al_2Ca$ intermetallic compound

### 3.2 Grain refining performance of $Al_2Ca$ intermetallic compound

In order to identify the phase composition of the alloys, the as-cast alloys were examined by XRD and the patterns are shown in Fig. 3. The AZ31 alloy consists only of $\alpha$-Mg phase. Extra peak was reproducibly identified to be the $Al_2Ca$ phase in the spectra in the AZX3110, AZX3115 and AZX3130 alloys, respectively. The absence of the $Al_2Ca$ phase in the AZX3105 alloy is presumably due to the relatively small addition amount of the $Al_2Ca$ compound. Figure 4 shows the typical as-cast microstructures of the AZ31 alloys and Fig. 5 illustrates the variation of the average grain size with different addition levels of $Al_2Ca$. Without any $Al_2Ca$ addition, the average grain size of AZ31 alloy is about 354 μm (Fig. 4(a)). With the increase of addition level of $Al_2Ca$ powder, the average grain size is remarkably reduced. When the addition of the $Al_2Ca$ is 1.1% (mass fraction), the average grain size decreases to 198 μm (Fig. 4(c)), i.e., the smallest grain size. However, with the further increase of $Al_2Ca$ addition level from 1.1% to

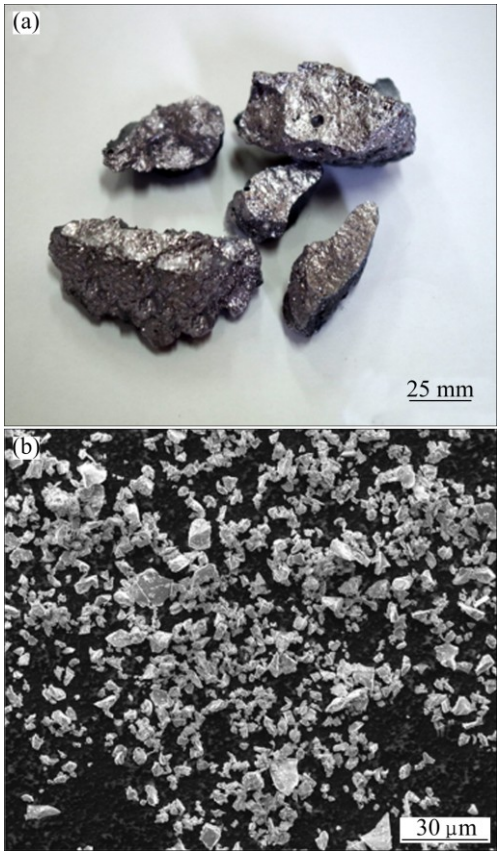


**Fig. 2** SEM images of $Al_2Ca$ intermetallic compound obtained by casting: (a) Raw; (b) Ball-milling

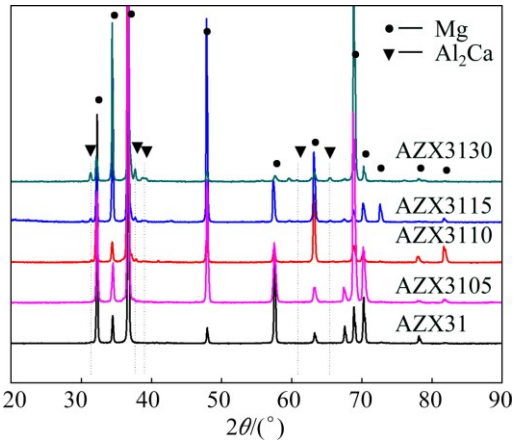


**Fig. 3** XRD patterns of as-cast alloys

3.5% (mass fraction), the average grain size has a trend to increase (Figs. 4(d) and (e)). Therefore, it is clear that the $Al_2Ca$ compound can efficiently refine the as-cast AZ31 Mg alloy.

In order to clearly reveal the grain boundaries and distribution of the second phases, the as-cast samples of the experimental alloys were subjected to a solution heat treatment. The optical micrographs of the alloys after solution heat treatment are shown in Fig. 6. And the corresponding variation of the average grain sizes with

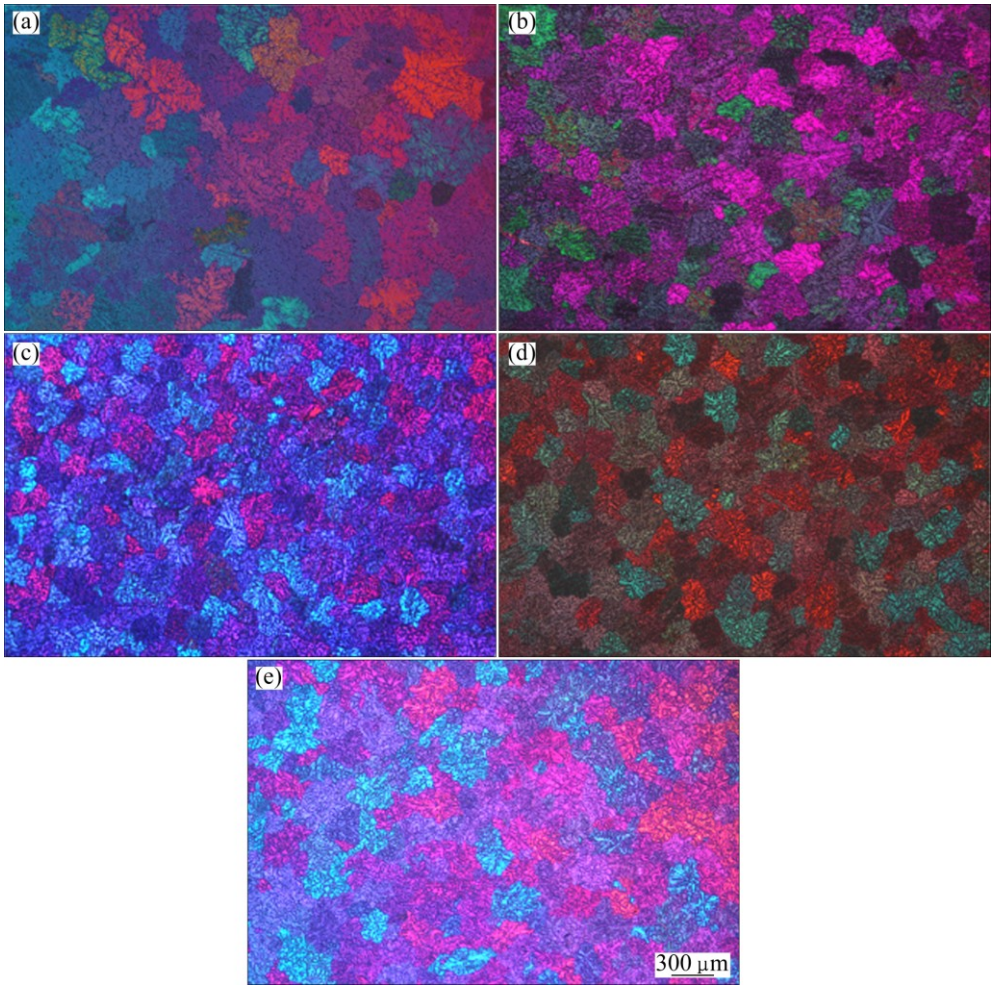


**Fig. 4** Optical micrographs of as-cast AZ31 alloys with different addition levels (mass fraction) of $Al_2Ca$: (a) 0; (b) 0.5%; (c) 1.1%; (d) 1.7%; (e) 3.5%

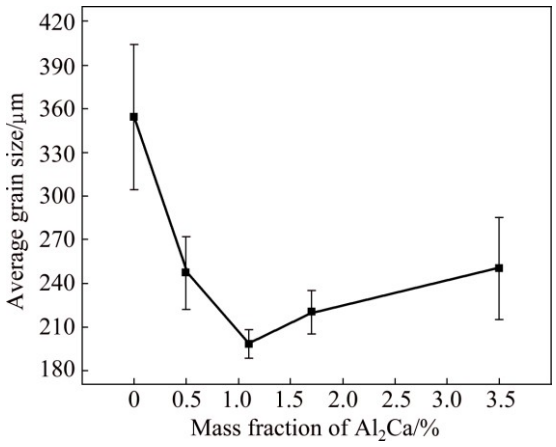


**Fig. 5** Grain size variation of as-cast AZ31 magnesium alloys with addition level of $Al_2Ca$

different additions of $Al_2Ca$ is shown in Fig. 7. It is obvious that the change trend of grain size of solution-treated alloys with the increase of $Al_2Ca$ is the same as that of the as-cast alloys, similar to Fig. 5. However, after solution treatment at 688 K for 10 h, the average grain size without addition of $Al_2Ca$ alloy increases to 400 μm, as shown in Fig. 6(a). When $Al_2Ca$ contents are 1.1% and 1.7%, the average grain sizes are 200 and 223 μm, respectively, which is almost the same as that of the as-cast one. This indicates that the refined grains have high thermal stability. Next, it is worth noting that the grain boundaries of AZ31 alloy with addition of 3.5% $Al_2Ca$ are not be revealed, due to too many second phases distributed at the grain boundary. In order to observe the grain size, polarization images should be used again, as shown in Fig. 6(e), meanwhile, optical micrograph contained a grain (marked in red) in Fig. 6(e) is also overlapped.

Figure 8 presents the microstructures of the solution-treated AZ31 Mg alloy with different levels of $Al_2Ca$ addition. LIU et al [26] reported that the dissolution of $Al_2Ca$ into the Mg matrix is difficult during the solution treatment of alloys at 688 K. It is found that the alloying phases exist in the matrix of heat-treated alloys, shown as the bright parts in Fig. 8. The granular and irregular mass alloying phases may be

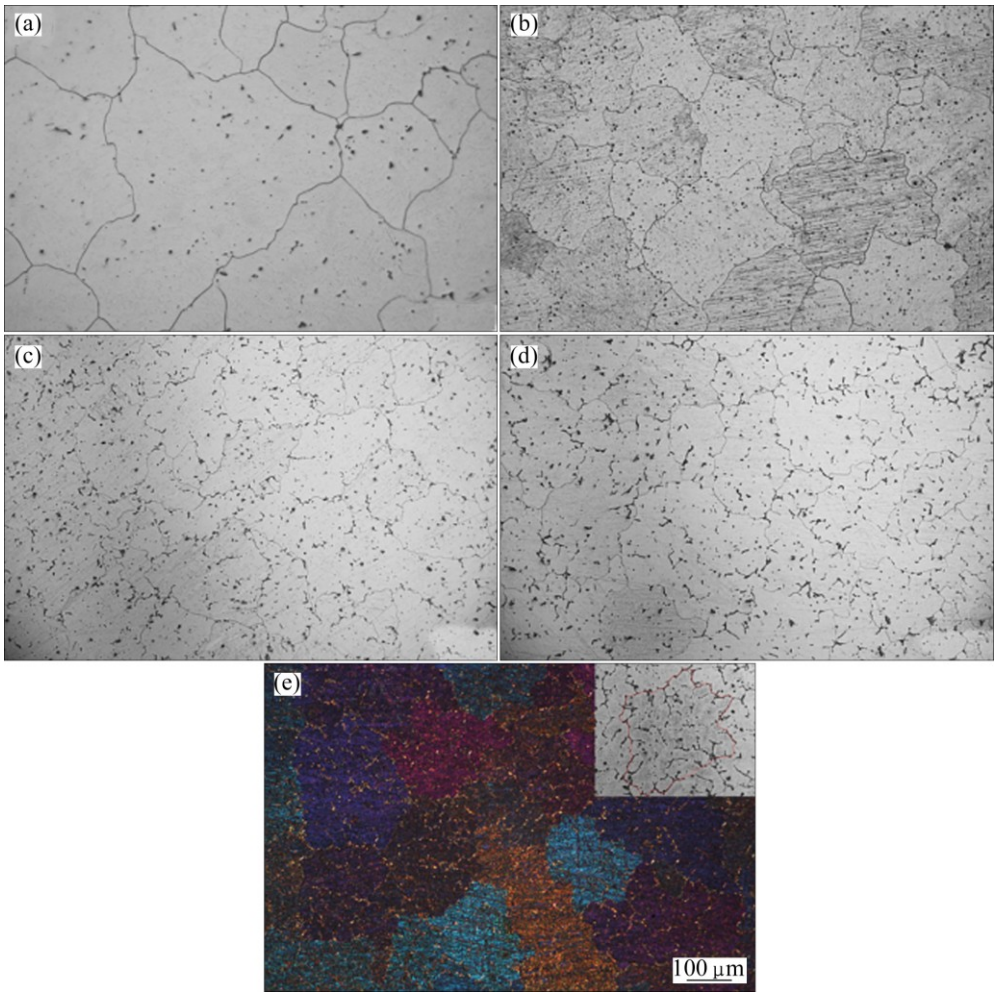


**Fig. 6** Optical micrographs of AZ31 alloys after solution heat treatment with different amounts of $Al_2Ca$: (a) 0; (b) 0.5%; (c) 1.1%; (d) 1.7%; (e) 3.5%

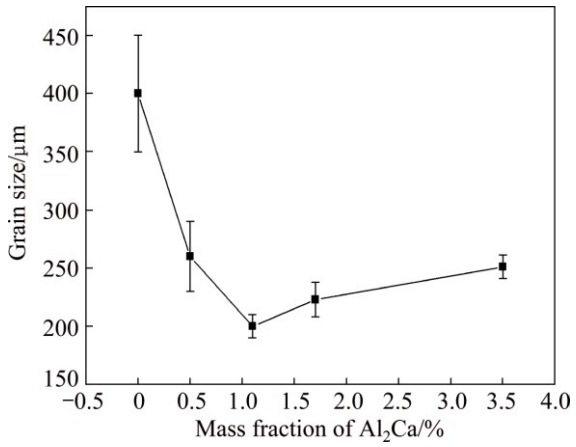


**Fig. 7** Grain size variation of AZ31 alloys after solution heat treatment with different addition levels of $Al_2Ca$

Al−Mn intermetallic compound in the heat-treated AZ31 alloy without addition of $Al_2Ca$ compound, as shown in Fig. 8(a). In general, the $Mg_{17}Al_{12}$ and Al−Mn phases may exist in the as-cast AZ31 alloy. But, after solution treatment at 688 K for 10 h, $Mg_{17}Al_{12}$ phase is dissolved in the matrix. Besides, after the addition of the $Al_2Ca$ powders, the volume fraction of the bright parts rises with the increase of addition content of $Al_2Ca$. For AZ31 alloy with 1.1% $Al_2Ca$ powder, the irregular shaped alloying phases are distributed not only inside the grains, but also along the grain boundary, as shown in Fig. 8(c). The distribution and morphology of alloying phases are almost no changed, but the size of the second phase is larger, compared with Figs. 8(c) and (d). As the $Al_2Ca$ content increases to 3.5%, semi-continuous alloying phases are so thick that it is difficult to identify grain boundaries of alloys, as shown in Fig. 8(e).

Meanwhile, it also reveals that the semi-continuous alloying phase forms probably during the eutectic solidification process and has a lamella-type morphology (the enlarged image in the upper right corner of Fig. 8(e)).

### 3.3 Grain refinement mechanism

Figure 9 shows SEM image and EDS analysis of AZ31 alloy with the addition of 1.1% $Al_2Ca$ powder. The

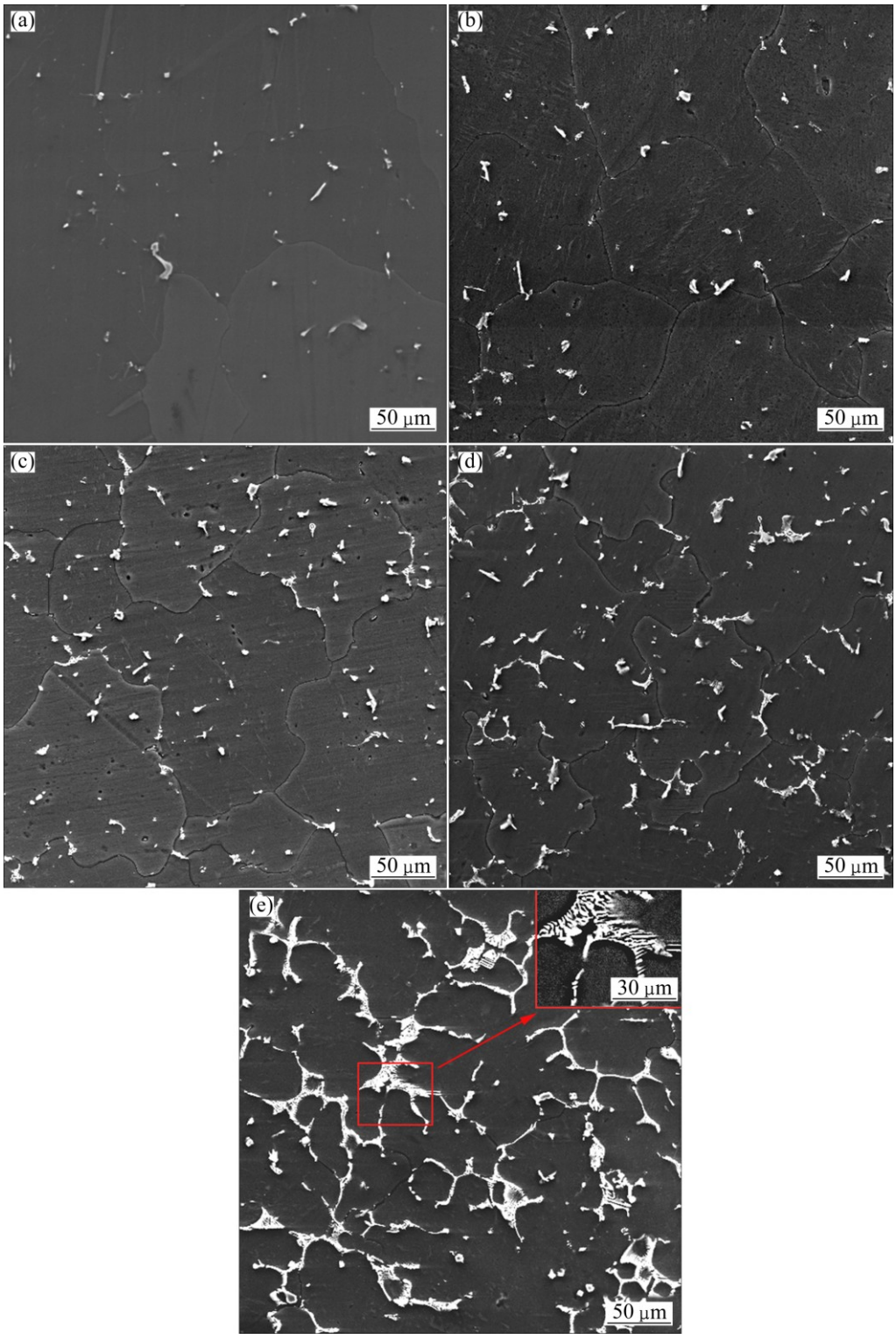


**Fig. 8** Microstructures of heat-treated AZ31 alloys with different additions of $Al_2Ca$: (a) 0; (b) 0.5%; (c) 1.1%; (d) 1.7%; (e) 3.5%

chain-like and granular shape $Al_2Ca$ compound is distributed along the grain boundary and inside grains, respectively, such as points *A* and *B*. In addition, there also exists irregular massive Al−Mn compound within grains and Al−Mn−Ca compound near the grain boundary. In this work, the notable grain refinement of the AZ31 alloy is obtained by adding 1.1% $Al_2Ca$ compound (Fig. 4(c)). Although a small number of Al−Mn−Ca compounds (like point *C* in Fig. 9) exist in the alloy, the Mn content is the consistent as well as its contribution to grain refinement. So, the $Al_2Ca$ compound in the melt and solidification process plays a decisive role in the grain refinement of the AZ31 alloy.

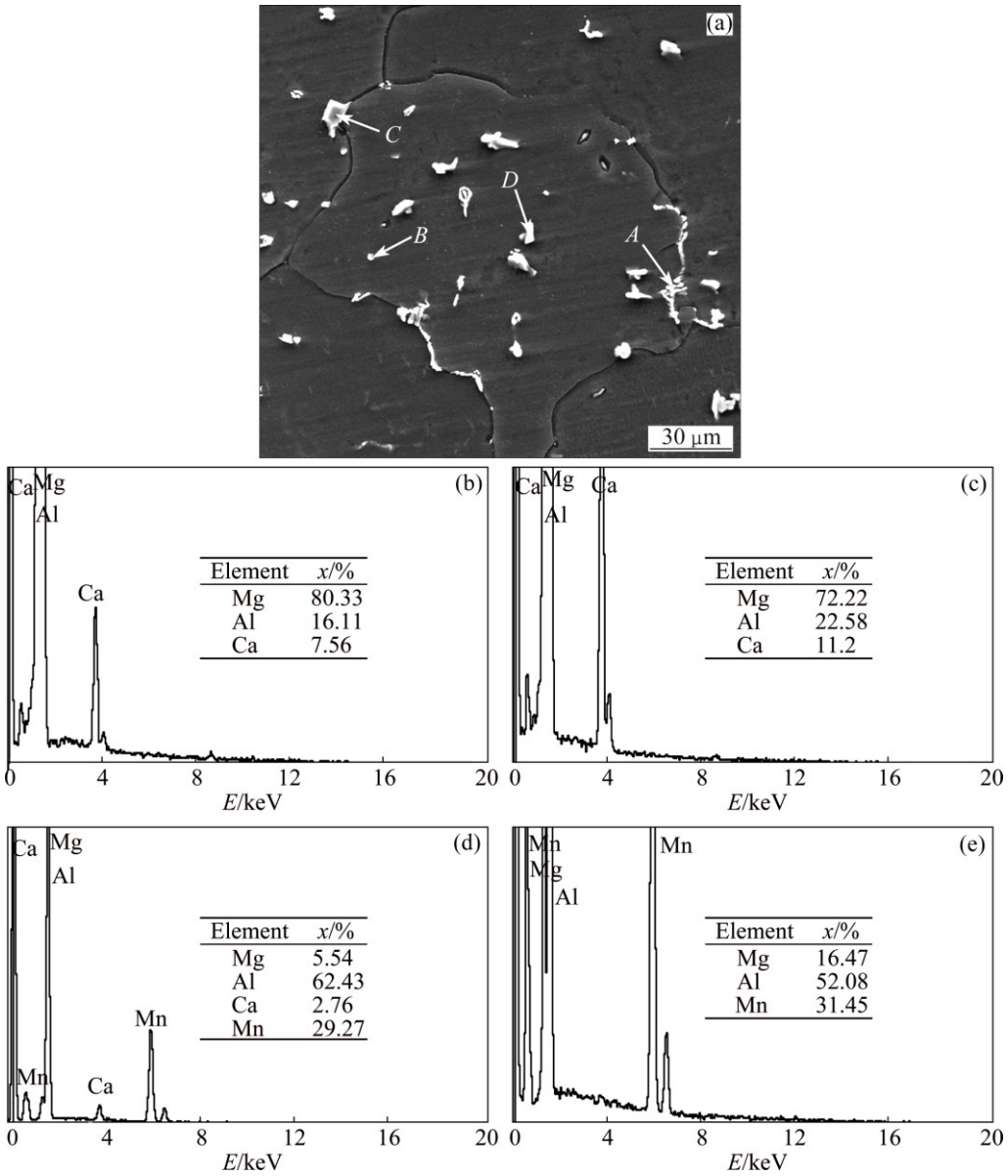


**Fig. 9** SEM image (a) and EDS analysis of points *A* (b), *B* (c), *C* (d) and *D* (e) of AZ31 alloy with addition of 1.1% $Al_2Ca$

In general, the grain refinement of polycrystalline materials is mainly determined by enhancing the nucleation rate in the melt and/or reducing the growth of grains [27,28]. So, the main approaches of grain refinement are adding potent nucleating agent, increasing undercooling and holding back grain boundary sliding. In this work, $Al_2Ca$ compound is adopted directly rather than Ca. So, the grain refinement of the AZ31 alloy obtained by adding $Al_2Ca$ seems to be the heterogeneous nucleation of primary $\alpha$-Mg on the $Al_2Ca$ particles. In fact, some $Al_2Ca$ particles are often found in the central region of $\alpha$-Mg grains (as shown in Figs. 8 and 9). In addition, the early study [19] found that the grain refinement through addition of Ca in the AZ31 alloy is attributed to the inoculation effect of $Al_2Ca$ particles formed in the melts, and crystallographic examination of relationship between $Al_2Ca$ and Mg using the edge-to-edge matching model indicates that $Al_2Ca$ particles are effective inoculants for heterogeneous nucleation of Mg. However, the solid particles for heterogeneous nucleation not only need to have a good lattice matching, but also need to be good stability in the liquid phase.

From Figs. 8 and 9, it is obvious that the morphology of the $Al_2Ca$ phase in the alloys is extremely different from pre-added particles of $Al_2Ca$ (as shown in Fig. 2(b)). It can presume that the $Al_2Ca$ compound can dissolve into AZ31 alloy melt, and subsequently precipitate during solidification, although the melting point of $Al_2Ca$ (1079 °C) is higher than 720 °C of the melt temperature. ROKHLIN et al [29,30] reported that the $Al_2Ca$ phase soluble in solid Mg is in equilibrium

with the Mg solid solution in the Mg−Al−Ca system.

In order to validate the idea, the Mg/$Al_2Ca$ liquid−solid diffusion couple was prepared in Mg melt at 720 °C. Line scanning can characterize the diffusion of elements near the interface. The result of line scan (Fig. 10) obviously shows the mutual diffusion for Mg, Al and Ca elements. It can also show the possibility of the formation of intermetallic compounds. The compositions of these compounds were analyzed by the EDS. The compositions of the lamella-type phase (labeled as *A*) were found to be 64.6% Mg, 25.2% Al and 11.2% Ca (mole fraction). The compositions of the irregular bulk phase (labeled as *B*) was found to be 16.6% Mg, 56.1% Al and 27.3% Ca (mole fraction). And the composition of another lamella-type phase (labeled as *C*) was found to be 81.9% Mg, 12.3% Al and 5.8% Ca (mole fraction). This indicates that the mole ratios of Al to Ca in those compounds (labeled as *A*, *B* and *C* in Fig. 10) are all close to 2:1. Those compounds should be identified as $Al_2Ca$. Besides, as shown in Fig. 10, there are two diffusion zones formed between $Al_2Ca$ and Mg alloys. Zone *a* represents the mixture of (Mg−$Al_2Ca$) eutectic (labeled as *A*) with $Al_2Ca$ dendrites (labeled as *B*), and zone *b* represents the mixture of (Mg−$Al_2Ca$) eutectic (labeled as *C*) with Mg dendrites. Only Mg and $Al_2Ca$ phases were found in this diffusion couple. This means that lamella-type eutectic $Al_2Ca$ was formed from the diffusion of Ca along with Al in Mg. Figure 11 shows the thermal analysis results for the investigated alloys, showing both the cooling curve and the variation of cooling rate with cooling time during solidification. The only one peak, can be clearly observed on the cooling rate curve (Fig. 11(a)), indicating the $\alpha$-Mg phase nucleated at 627.8 °C in the AZ31 alloy, while the nucleation temperature of $\alpha$-Mg phase is 623.7 °C in the AZX3110 alloy. Another peak at 516.8 °C (Fig. 11(b)) corresponds to $Al_2Ca$ phase precipitation in the AZX3110 alloy. That is close to precipitation temperature of the $Al_2Ca$ in the Mg−Al−Ca alloy [31].

Based on the above discussion and experimental data, we suggest that $Al_2Ca$ compound can dissolve into the Mg melt and subsequently re-precipitate during solidification under the condition of casting of the metal mould. So, at the initial stage of solidification, the solute segregation of Ca along with Al at solid/liquid interface can provide stronger constitutional undercooling for nucleation [32]. In addition, under the non-equilibrium solidification, it is possible that some $Al_2Ca$ precipitates firstly due to the limited solubility of $Al_2Ca$ [29]. This part of $Al_2Ca$ (point *B* in Fig. 9) was present in the undercooled layer and was activated as the potent nucleating agents of $\alpha$-Mg. Therefore, this part of $Al_2Ca$ was observed in the center of the grains. The other $Al_2Ca$ was pushed to the grain boundaries and solidification end. As is known in Ref. [32], the grain refinement of Mg−Al by Ca addition can be improved further in the presence of potent nucleants.

It can be seen that grain refinement of AZ31 alloy by the $Al_2Ca$ compounds was mainly attributed to the combined effects of solute and heterogeneous nucleation. It can be seen from Fig. 5 that the grain size of AZ31 Mg alloy is minimum when the addition amount of $Al_2Ca$ is 1.1%. Combined with Fig. 8(c), $Al_2Ca$ particles are distributed not only inside the grains but also along the grain boundary with fine and dispersed granular. But excessive addition of $Al_2Ca$ powders is prone to

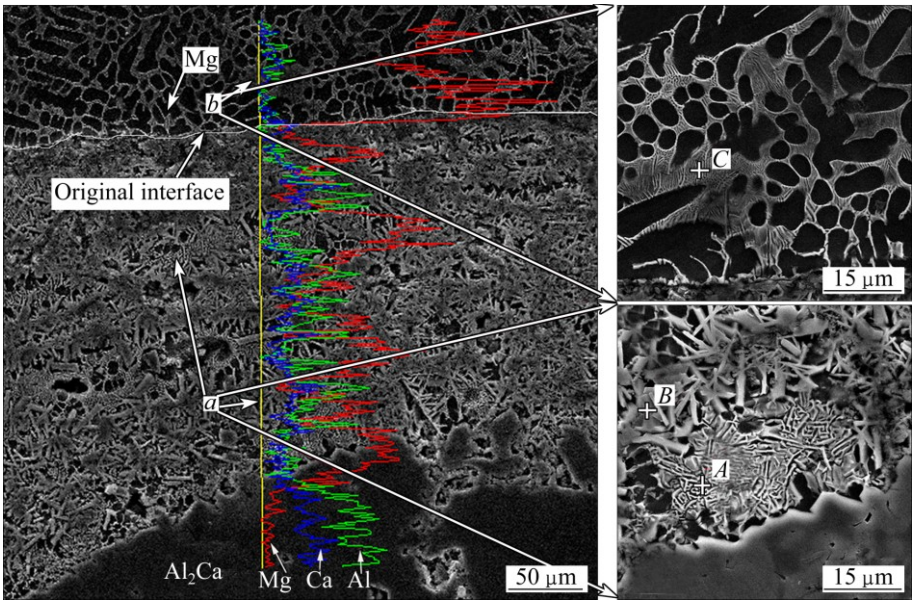


**Fig. 10** Microstructures of liquid−solid Mg−$Al_2Ca$ diffusion couple at 720 °C with SEM−EDS line scanning: *a*—$Al_2Ca$ dendrites + (Mg−$Al_2Ca$) eutectic; *b*—Mg dendrites + (Mg−$Al_2Ca$) eutectic

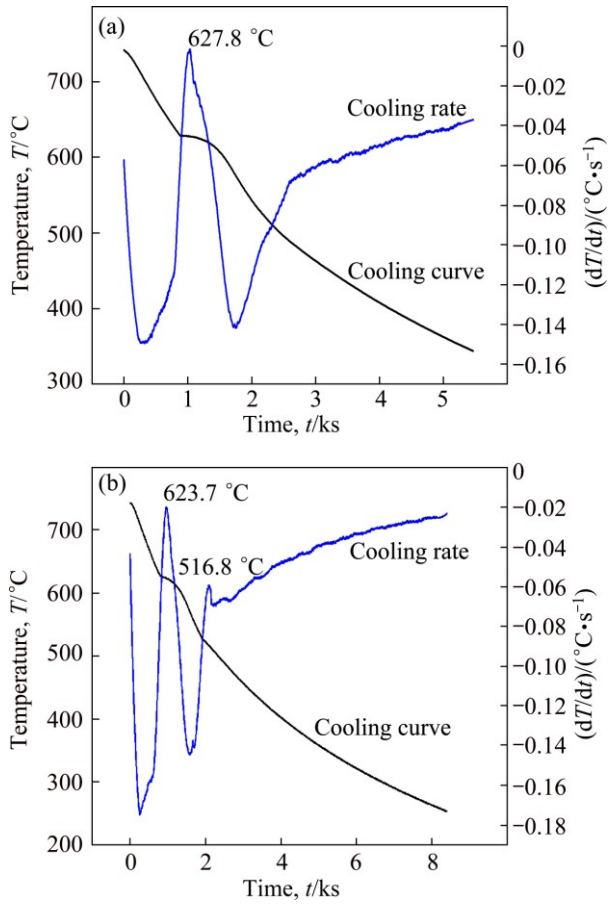


**Fig. 11** Cooling curves and rate curves determined from thermal analysis: (a) AZ31; (b) AZX3110

aggregate to form clusters (Figs. 8(d) and (e)) and the nucleating particles are difficult to disperse. Correspondingly, the number of effective heterogeneous nuclei decreases, which decreases the grain refining efficiency of $Al_2Ca$ on AZ31 Mg alloy. A similar phenomenon has been reported in Ref. [33].

## 4 Conclusions

1) The $Al_2Ca$ intermetallic compound was prepared by pure metal melting process in a vacuum induction furnace under an argon atmosphere. This shows perfect grain refining effect for AZ31 alloy.

2) The $Al_2Ca$ compounds can be dissolved into the AZ31 alloy melt, subsequently re-precipitate during solidification under the non-equilibrium rapid solidification, and provide stronger constitutional undercooling for the grain refinement process.

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# $Al_2Ca$ 金属间化合物对 AZ31 镁合金晶粒细化的影响

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**摘 要**：采用真空熔炼方法制备 $Al_2Ca$ 金属间化合物并将其添加到 AZ31 镁合金中，研究其添加量对铸态 AZ31 镁合金晶粒细化的影响，同时讨论其晶粒细化机理。结果表明：添加 1.1% $Al_2Ca$(质量分数)可使得铸态 AZ31 镁合金晶粒尺寸从 354 μm 细化到 198 μm，且经 $Al_2Ca$ 细化后，合金晶粒的热稳定性良好。晶粒细化的机理是溶质效应和 $Al_2Ca$ 的异质形核协同作用。

**关键词**：AZ31 镁合金；$Al_2Ca$；晶粒细化；机理

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