

An investigation on hot-crack mechanism of Ca addition into AZ91D alloy

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In automotive components, there is a significant weight saving potential in converting to magnesium alloys. Adding Ca element is one of the most effective ways to improve the temperature and mechanical properties of magnesium alloy. However, as hot-cracks often appear in such materials, Ca addition will thus encumber the development of this magnesium alloy. There are few reports on the hot-crack mechanism of magnesium alloy with Ca. This paper focused on the investigations as why to results in the hot-crack phenomenon of Ca addition. These results indicated that Ca addition affects the solidification process of AZ91D alloy, such as elevating the tendency of divorce eutectic and forming the new temperature of Al₂Ca phase. In addition, the Ca-contained phase distributed as the net-shape forms on grain boundary and results in lower boundary strength of the liquid film. Both of the above reasons would deteriorate filling capacity of the melt and the hot-crack resistance during solidification stage, resulting in the worst hot-crack property of this alloy. © 2005 Springer Science + Business Media, Inc.

1. Introduction

Attractive high temperature and mechanical properties of light materials, such as magnesium alloys have increased in the scope of their use in the transportation industry. Some of magnesium alloy's applications (for example, for gear box housing, oil pan, transfer case, crankcase, tank coves etc.) require a good creep or good mechanical resistance. Some cast magnesium alloys were tested for stress corrosion, and demonstrated a high sensitivity to this kind of degradation [1–4]. In addition, the strength and toughness of magnesium alloys, especially the fatigue property of these alloys (due to the lower reduction ratio of cross-section [5–9]), did not satisfy the requirement during their service. For example, weight reduction for automobile fuel economy has spurred the growth of magnesium consumption over the last decade at an annual rate of 15%. However, its

use is limited to certain parts of the vehicle compartment because the creep strength or toughness of conventional Mg-Al alloy is poor [10]. These applications of magnesium alloys in the engine compartments which require high creep resistances are necessary for further weight reduction. Recent efforts to develop creep-resistant magnesium alloys for such applications have resulted in a number of experimental alloys [11–14].

One important research orientation is to add Ca, RE, Si, or Sr elements into magnesium alloys. Since Ca is a relatively inexpensive element, its addition into magnesium alloy will improve the mechanical properties of magnesium alloys at room or high temperatures [15, 16]. The magnesium alloy with Ca exhibits an evident increase in both ambient strength and compressive yield strength. As well, the creep strength above at 150°C for equal weight compared with Sr and RE

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element addition into magnesium alloys has been reported in many references. However, the cast defects, such as a hot-crack, obviously limited the application of Ca addition into magnesium alloys. At the same time, it consequently restricted the development of magnesium alloys with Ca at higher temperatures. Few references have focused on the corresponding mechanism of how to improve the hot-crack resistance of the magnesium with Ca. Extensive comprehension of the hot-crack mechanism of Ca addition into the magnesium alloys will help to accelerate the research and development of Ca-contained elevated temperature alloy. This article is mainly concerned with the variation on alloy structure, hot-crack resistant property and solidification characterization of Ca-contained alloy, consequently providing the hot-crack mechanism of Ca addition into AZ91D alloy.

2. Experimental method

The raw materials for the tests include commercial grade AZ91D ingot and Mg-30 wt%Ca master alloy. The protect gas chosen is 0.5 wt%SF₆/CO₂. The AZ91D alloy ingots were melted in an electrical resistance furnace using a mild steel crucible under the protection of the mixed gas of CO₂/0.5 wt%SF₆. Mg-30 wt%Ca master alloys were added to the melt at about 730°C. After holding for 10 min, the melt was poured at about 730°C.

Optical microscopy and samples were etched with a solution of 4 vol% nitric acid + ethyl alcohol to demonstrate its microstructure. The SEM images of samples were examined in a Philip-505 scanning electron microscope (SEM) with an energy dispersive X-ray spectrometer (EDS) in order to investigate the microstructures and second phases in the alloy. Chemical analysis of the cast experimental alloys was performed by inductively coupled plasma (ICP). The solidification curve was obtained by *in-situ* detect of temperature automatic recorder on sand mould sample. The testing method of hot-crack property is a critical diameter method. The diagrammatic sketch of the hot-crack die is schematically shown in Fig. 1. The material of hot-crack mould is a steel of 0.4 wt% carbon. The most probable site for a hot-crack to occur in the mould is the area between the upper and middle column, which endures a maximum amount of stress during the solidification of this alloy. The hot-crack property of each alloy is evaluated by the

hot-crack grade standard, which is the square valuation of maximal diameter of the middle column caused by a hot-crack phenomenology and is the average value of two experimental results. The higher the hot-crack grade standard, the worse the hot-crack property of the alloy.

3. Results

Fig. 2 indicates the influence of different quantities of Ca addition into AZ91D alloy on the hot-crack property. It clearly shows that as the quantity of Ca added into AZ91D alloy increases, the hot-crack grade value of AZ91D alloy also increases. This means that the hot-crack property of AZ91D alloy becomes poor or decreases. The hot-crack grade of the alloy increases from 82 to 256 when the quantity of Ca added increases from 0 to 1.0 wt% Ca, respectively.

Fig. 3 is the morphogenesis of AZ91D alloy with Ca addition. The hot-crack phenomenon on this surface is clearly shown. The characterization may easily fracture under applied loading. Therefore, we should overcome this defect in the process although it improves the strength of AZ91D alloy with Ca addition because of the refinement of α -Mg grains. In addition, the fracture surface of the cracks in AZ91D alloy displayed a highly dendritic structure. These cracks are accompanied by intergranular boundaries and smooth dendrites, where the interdendritic liquid had withdrawn. In addition, no indication of direct fracture of the dendrites would be observed. These phenomena indicate that hot-crack is vital to the solidification process of AZ91D, especially in the terminal stage of solidification.

X-ray diffraction (XRD) pattern taken from AZ91D containing 1.0 wt%Ca alloy is shown in Fig. 4, in which peaks can be indexed as arising from three phases, the α -Mg phase, the β (Mg₁₇Al₁₂) phase and the Al₂Ca phase. The new phase of Al₂Ca has a similar microstructure of thin strip. It mainly plays a role in the α -Mg grain refinement, as its addition can improve the strength of this alloy. That is, in increasing the amount of Ca added into AZ91D alloy, the α -Mg grain refinement becomes higher. This is because of the synergistic effect of both nucleation and growth rate of α -Mg grain. Therefore, adding Ca into AZ91D alloy assists the original nucleation but defers or limits the growth of the α -Mg grain [17].

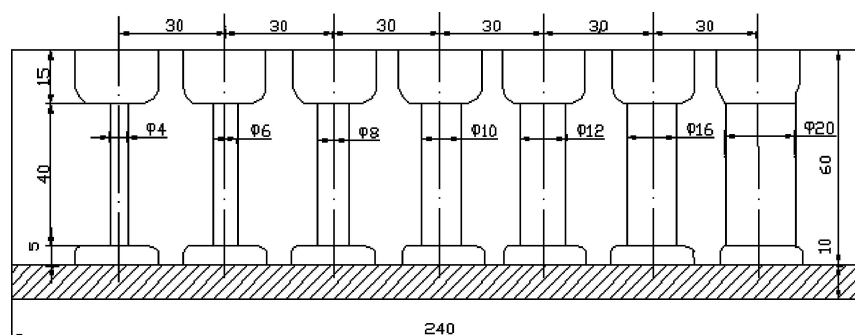


Figure 1 Schematic drawing of the hot-crack die mould.

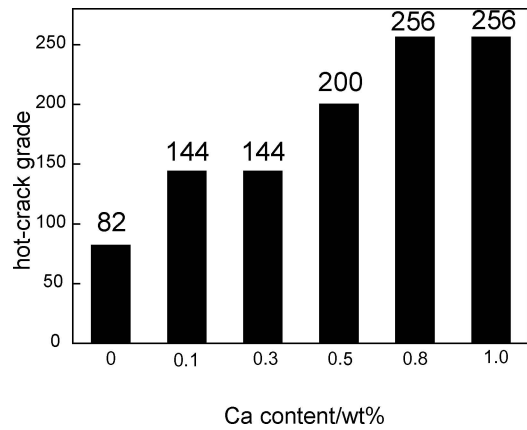


Figure 2 Effect of Ca on hot-crack-resistant property of AZ91D.

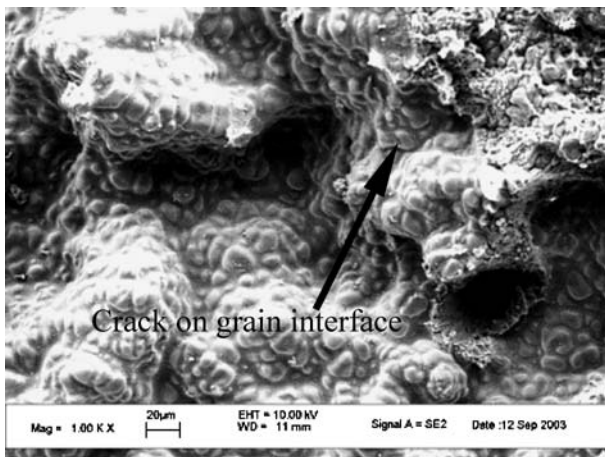


Figure 3 The morphology of hot-crack.

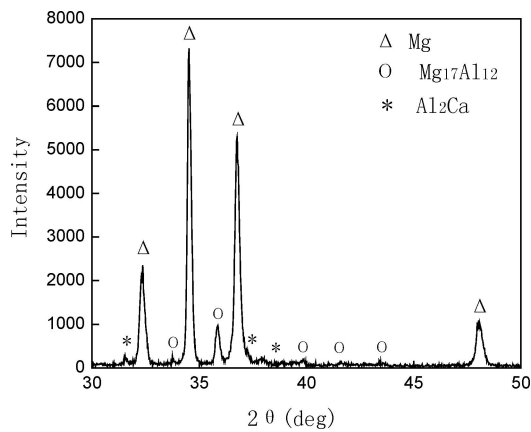
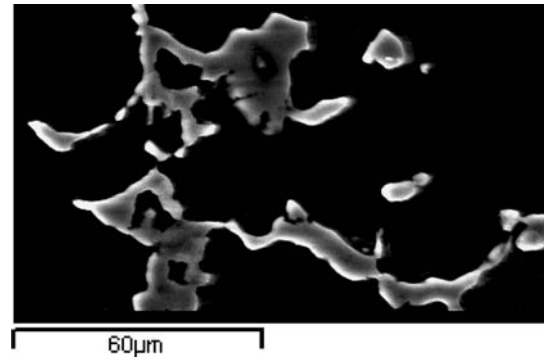


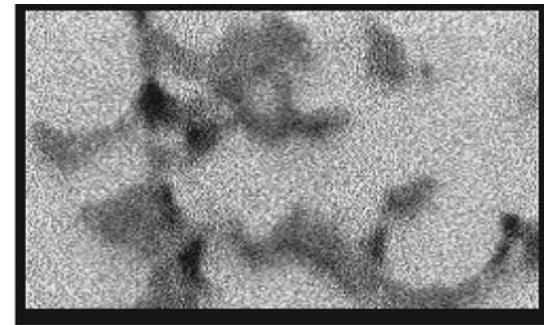
Figure 4 X-ray diffraction pattern of 1.0 wt%Ca + AZ91D alloy.

Fig. 5 is the element surface composition distribution of AZ91D with 0.4 wt%Ca. It is clearly seen that the Ca element segregates to the α -Mg grain boundary. Some of the Ca-contained phase is dispersed along the grain boundary as a homogeneous net shape to improve the phase microstructure of AZ91D alloy, simultaneously, the other Ca element is concentrated excessively with Al as the form of the Al_2Ca phase aggregate on the grain boundary.

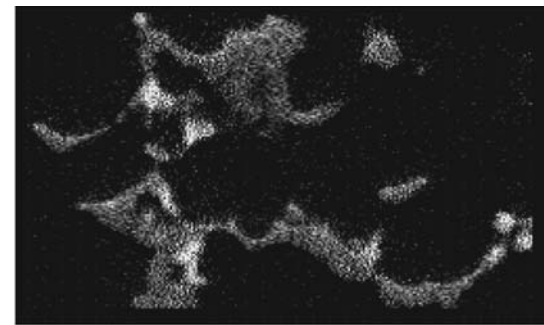
Fig. 6 is the optical micrograph of AZ91D alloy with different amounts of Ca additions. The grey zone on the grain boundary is the main α -Mg phase of the eu-



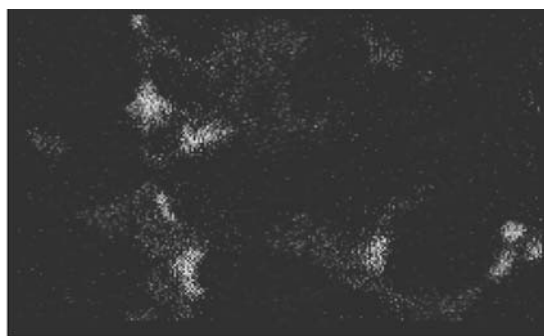
(a)



(b)



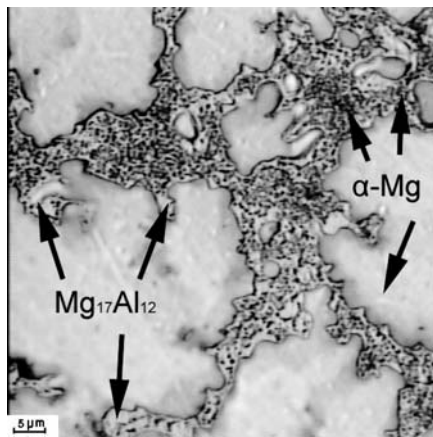
(c)



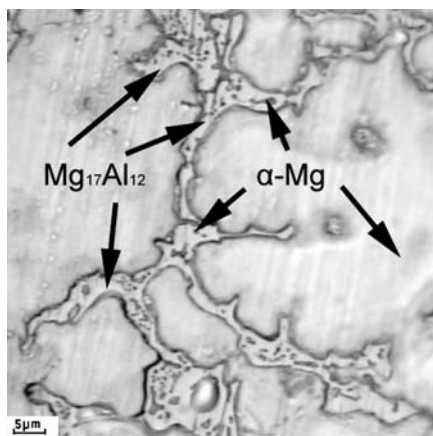
(d)

Figure 5 Surface composition analysis of 0.4 wt%Ca + AZ91D alloy: (a) Morphology, (b) Mg, (c) Al, and (d) Ca.

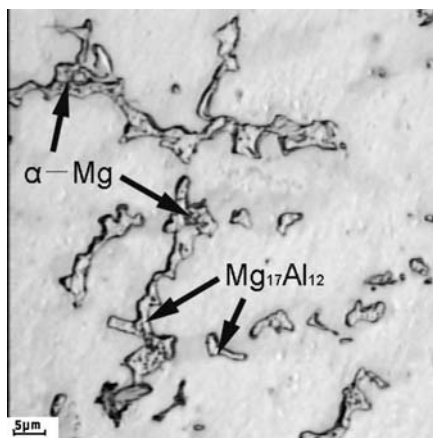
tectic, as shown in Fig. 6. As the quantity of Ca added increased, the dimension of the eutectic on the grain boundary obviously decreased and the quantity of the α -Mg phase of the eutectic on the grain boundary reduced visibly. This means that the β -Mg₁₇Al₁₂ phase of the eutectic on the boundary had to nucleate and



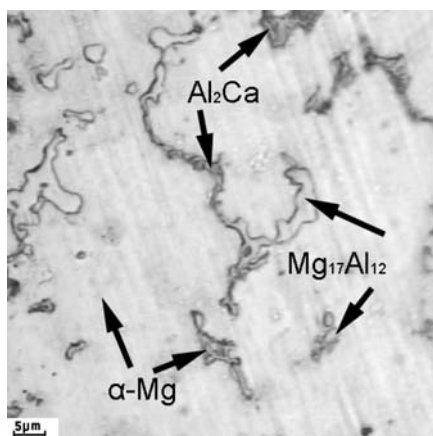
(a)



(b)



(c)



(d)

Figure 6 Effects of Ca on eutectic structure morphology of AZ91D: (a) 0, (b) 0.2%Ca, (c) 0.4%Ca, and (d) 1.0%Ca.

grow independently during the solidification process. When the amount of the Ca addition reached 1 wt%, the dimension of the eutectic was minimal. This therefore results in a beneficial influence on improving the mechanical properties, such that the yield stress and ultimate tensile strength are over the base alloy, but the elongation and apparent fracture toughness are below the base alloy at room temperature. It seems that it is necessary to add the other element into AZ91D alloy in order to obtain the good strength and toughness properties, as adding Ca only elevates these properties by grain-refinement. One of the authors reported that the fatigue microcracks initiation and growth behaviors of the cast magnesium alloys occurred mainly on the boundary of the α -Mg grain at room temperature [5, 6]. At the same time, the phenomenon of the microcrack propagated along the boundary and cleaved partly by the α -Mg grain at high temperature was found by *in-situ* observation with SEM [18]. Therefore, improving the second phase of magnesium alloy is very important in order to elevate the resistance of fatigue damage of magnesium alloys. Moreover, the Al_2Ca phase could be easily seen as the thin strip shape on the boundary and the eutectic phase mainly existed as the form of divorce eutectic as shown in Fig. 6d.

Fig. 7 is the differential solidification curves of the different amount of Ca added into AZ91D alloy. The ratio of $dT/dt-T$ varied with the temperature of the eutectic reaction, which represented the solidification characterization of AZ91D alloy with different Ca additions. These results show that the temperature peaks of the eutectic reaction have an approximate scope from 420°C to 450°C with different amount of Ca addition into AZ91D alloy, and that the formed relative curves about the temperature and dT/dt of the Al_2Ca phase varied with the amount of Ca added into AZ91D alloy. In addition, for comparison convenience, the dT/dt curves would descend about 0, 0.5, 1.0 and 1.5°C , respectively, according to the different amounts of Ca addition as shown in Fig. 7. We also see that the curve of AZ91D with no Ca addition had two evident peaks, which represented the primary α -Mg phase emanation reaction and the eutectic reaction as shown in curve 1 in Fig. 7. As the amount of the Ca addition increased, the new

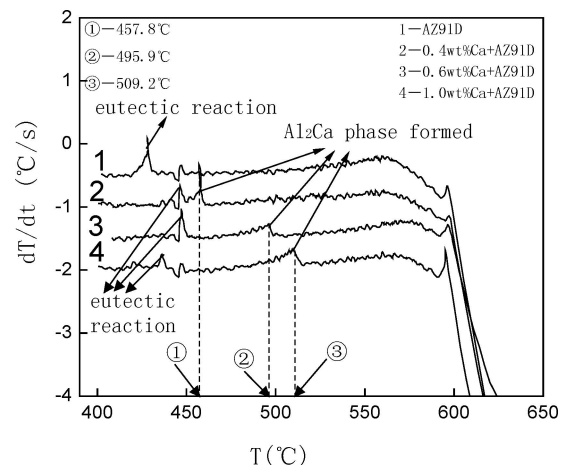


Figure 7 Effect of Ca on the formation temperature of Al_2Ca phase.

peak prior to the eutectic reaction peak occurs on the differential curve as shown in Fig. 7. The temperature according to the new peak also rose as the quantity of the Ca addition increased. Based on the microstructure and phase analysis mentioned above, the new peak that occurred on the curve represented the Al_2Ca phase precipitation on the grain boundary. The temperature of the Al_2Ca phase precipitation elevated increased from 457.8 to 509.2°C, as the amount of the Ca addition increased from 0.4 wt% and 1.0 wt%. In addition, as the temperature of the Al_2Ca phase precipitation rose, the earlier the time of that Al_2Ca phase precipitation, and the more sufficient the growth of the Al_2Ca phase precipitation on the grain boundary. It can also be seen in Fig. 7 that the temperature of the eutectic reaction increased with the Ca addition into AZ91D alloy.

4. Discussions

Previous research has not explained the hot-crack mechanism of Ca addition systematically. Some of these researchers thought that the crack was initiated by the thermal stress because there is a difference in the shrinkage rate between the second phase and the magnesium matrix during solidification [19]. Micromechanics analysis [20–23] based on the couple stress theory has demonstrated that high stress concentration and microcracking damage may be caused due to the effect of boundary layers at the interfaces of two dissimilar materials. For the problem of current interest, the boundary layers with high concentration are caused by the thermal mismatch of the constituent phases. It has been thought that the large amount of the reticular Ca-contained phase was formed along grain boundary, which harmed the hot-crack property [24]. Thus, these previous assertions lacked sufficient experimental evidence and profound analyses. Based on the authors' experimental results, more sufficient explanations will be proposed. Except for those reasons mentioned above, Ca addition into AZ91D alloy not only promotes the tendency of the divorce eutectic, but also elevates the formation temperature of the Al_2Ca phase as well as debasing the filling capacity of the melt, all of which are important reasons to deteriorate the hot-crack property.

The main reasons are: firstly, since the hot-crack phenomenon is closely connected with the solidification process of AZ91D alloy, the eutectic reaction mode

during the critical last stages of solidification is a rather important influence on the filling capacity of the melt, which directly contributes to the tendency of the hot-crack property of AZ91D alloy. If the tendency of divorce eutectic is lower, the form of the eutectic reaction is mainly synergistic nucleation and growth both $\beta\text{-Mg}_{17}\text{Al}_{12}$ and $\alpha\text{-Mg}$ of eutectic. Subsequently they grow in the coupled growth way. Therefore, they grow mutually towards the centre of the interdendritic channels, which allows the feeding paths to remain open for longer and to facilitate the fill behavior of their boundaries. The results are quite different when Ca is added into AZ91D alloy, which leads to an increase in the tendency of the divorce eutectic. If the tendency of the divorce eutectic were higher, the $\alpha\text{-Mg}$ phase of the eutectic would occur prior to the nucleation and growth on the primary $\alpha\text{-Mg}$ phase. Therefore, this reaction would inhibit the other eutectic phase (the $\beta\text{-Mg}_{17}\text{Al}_{12}$ phase), which was nucleating and propagating simultaneously. These results reveal that the nucleation and growth of the $\beta\text{-Mg}_{17}\text{Al}_{12}$ phase in the interdendritic liquid during the terminal solidification stage are likely to significantly increase. At the same time, it can elevate the surface area to volume ratio of the feeding channels and result in a greater resistance to the feed ability. Moreover, as the quantity of Ca added increases, the tendency of the divorce eutectic rose and the feeding capacity of the alloy reduced, leading to the worst hot-crack property of magnesium alloys.

Secondly, by increasing the quantity of Ca added, the temperature of the Al_2Ca phase precipitation increases. When the alloy melts and forms the interdendritic frameworks during the solidification terminal stage, the Al_2Ca phase is precipitated and developed at higher temperatures. This phase would conduct the more effective blocked function in the feeding channel. This phase deteriorates the hot-crack property of the alloy.

Thirdly, as Ca is one of the surface activity elements, it mainly aggregates and distributes as a net shape on the $\alpha\text{-Mg}$ grain boundary as shown in Fig. 5. This results in the lower boundary tension of the liquid film during solidification process. Therefore, the net shape characterization of the Ca-contained phase distribution can elevate the hot-crack tendency of magnesium alloys.

Based on the above discussion, the hot-crack mechanism of Ca addition into AZ91D alloy as it would be schematically shown in Fig. 8. That is, Ca addition can

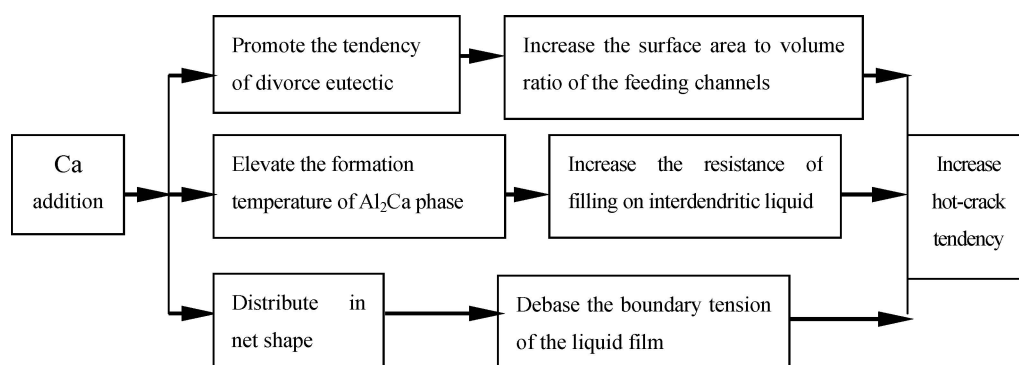


Figure 8 The sketch of mechanism on hot-crack property of AZ91D alloy with Ca addition.

elevate the tendency of the divorce eutectic and the formation temperature of the Al₂Ca phase. Ca addition into AZ91D alloy also aggravates the resistance of feeding, resulting in the worst filling capacity. At the same time, the Ca-contained phase distributes as a net-shape on the grain boundary. It has the lower boundary tension of the liquid film, something, which also deteriorates the hot-crack property of magnesium alloys. It could be supposed that through some other element addition, that element could suppress the above influence during solidification. Therefore, the disadvantageous influences of the Ca addition on magnesium alloy would decrease and even disappear, which would assist in further developing the elevated temperature of magnesium alloy contained Ca. Considering the advantageous microstructure and strength by grain-refinement with Ca addition into AZ91D alloy, we must add the composite elements in magnesium alloy in order to improve the synergistic properties of magnesium alloys, such as the toughness and hot-crack properties. For these studies, we are now investigating the addition of Ca/Sr composite into AZ91D alloy, these results will be reported later.

5. Conclusions

This article mainly focused on the investigation on the effect and mechanism of Ca addition into AZ91D alloy on the hot-crack and microstructure. The conclusions from the experiments are as follows: By increasing the amount of added Ca, the hot-crack property of AZ91D alloy decreases but the grain-refinement of AZ91D alloy is improved. The hot-crack mechanism of Ca addition into AZ91D alloy is conjectured to be that Ca addition elevates the tendency of the divorce eutectic and the formation temperature of the Al₂Ca phase. The Ca-contained phase is distributed as a net-shape on the grain boundary and debases the boundary tension of the liquid film, deteriorating the filling capacity and lowering the hot-crack property of magnesium alloy.

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