

Effect of Sr addition on microstructure of as-cast Mg-Al-Ca alloy

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Abstract: The microstructure evolution of Mg-Al-Ca alloys modified by the addition of strontium was investigated. It was found that Sr addition leads to the coarsening of α -Mg matrix. However, with the Sr content increasing from 0.1% to 0.5%, the grain size decreases from 83.9 to 65.8 μm . The addition of Sr ranging from 0.1% to 0.3% refines the Al_2Ca phase. It changes the morphology of the Al_2Ca phase from bone-shaped to granular or banding, and increases its volume fraction. The decrease of grain size of the α -Mg matrix is due to the increase of the effective undercooling degree of the melt and the constitutional undercooling in a diffusion layer ahead of the advancing solid/liquid interface in the alloy modified by the Sr additions. The modification mechanism of Al_2Ca is attributed to the adsorption of Sr additions to the Al_2Ca crystal. When the Sr content increases to 0.5%, the alloy is over-modified.

Key words: Mg-Al-Ca alloy; strontium; calcium; microstructure

1 Introduction

Magnesium alloys are widely used for structural components in industrial products due to their specific characteristics of low density, high specific strength and good recycle ability [1]. Industrial demand to this kind of materials is rapidly increasing since they can highly enhance the energy consumption efficiency, particularly in the products of vehicles and airplanes [1–2]. Recent efforts to develop high-performance magnesium alloys resulted in a number of alloys [3–7]. One important research direction is to add Ca into Mg-Al alloy to develop Mg-Al-Ca ternary alloys. Ca is a relatively inexpensive addition element to improve the mechanical properties of magnesium alloys at room temperature and high temperatures [8–10]. The improved creep resistance at high temperature is attributed to the morphology, size and distribution, thermal stability and interface coherency of the Ca-containing compounds with the Mg matrix. However, the cast defects, such as hot-crack defects of the Ca-containing magnesium alloys,

obviously limit their applications [11–12]. It was reported that the addition of Ca above 1% may decrease the elongation due to the formation of brittle eutectic compounds at grain boundaries [8]. LUO [2] reported that increasing Ca content to above 2% could improve the castability by eliminating hot-tearing.

The modification of microstructure is one of the most important, effective and simple methods for improving the mechanical properties of metallic materials. It was reported that the additions of rare earth elements, strontium, bismuth, boron or melt superheating treatment are efficient to modify the morphology of Mg_2Si and eutectic Si in aluminum alloys or magnesium alloys [13–17]. In order to eliminate the negative impacts of Ca addition on the Mg-Al alloy, researchers developed Mg-Al-Ca-Sr alloy [10, 18–19]. The Sr/Al mass ratio is usually high to form new high melting-point phase, such as Al_4Sr . However, fewer work focused on the modification effects of strontium addition on the microstructure and solidification progress of Mg-Al-Ca alloy.

The aim of the present work is to investigate the

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effects of element strontium on the microstructure features of Mg-Al-Ca alloy. Mg-7.7Al-1.3Ca was selected as the base alloy. The influence of Sr on the microstructure development and the correlated temperature of nucleation and growth of primary α -Mg phase and Al_2Ca intermediate compounds was analyzed. Thermal analysis was used to evaluate the formation temperatures of the secondary phases.

2 Experimental

Five alloys were prepared and their designed compositions are listed in Table 1. Calcium and strontium were added with the master alloys of Al-75Ca and Al-10Sr, respectively. Melting was conducted in a crucible electric resistance furnace under protective flux RJ2. The melt was held at homogeneous temperature of 720 °C for approximately 20 min and then poured into stainless steel mould with the preheated temperature of 250 °C.

Table 1 Nominal composition of experimental alloys

Alloy	w(Al)/%	w(Mn)/%	w(Ca)/%	w(Sr)/%	w(Mg)/%
AMC801	7.7	0.3	1.3	–	Bal.
AMC801-0.1Sr	7.7	0.3	1.3	0.1	Bal.
AMC801-0.2Sr	7.7	0.3	1.3	0.2	Bal.
AMC801-0.3Sr	7.7	0.3	1.3	0.3	Bal.
AMC801-0.5Sr	7.7	0.3	1.3	0.5	Bal.

Samples were etched with a solution of 4% (volume fraction) nitric acid + ethyl alcohol for revealing the structures and 1.5 g picric acid + 5 mL acetic acid +25 mL ethyl alcohol for showing the grain boundaries. To reveal grain boundaries, the samples were held at 420 °C for 36 h, and then water-quenched before etching. Microstructure observations were carried out using Leitz-MM-6 type optical microscope (OM) and JEOL/JSM-5600 LV type scanning electron microscope (SEM) equipped with an energy-dispersive X-ray spectrometer (EDS). The average grain size of each sample was measured from the central zone of a longitudinal section of the truncated cone. Linear intercept method according to ASTM standard E112–88 was used to evaluate the grain size. The phases in the experimental alloys were analyzed by D8000–ADVANCE type X-ray diffractometer (XRD) operated at 30 kV and 20 mA. Thermal analysis was performed using a DTA404PC type differential scanning calorimetry (DSC). Samples of around 15 mg were heated in a flowing argon atmosphere from room temperature to 700 °C for 5 min before being cooled down to 100 °C. The cooling curves were recorded at a

cooling speed of 10 °C/min. A Buehler microhardness tester was used to measure the Vickers microhardness with a loading of 1.96 N and holding-time of 20 s to investigate the effects of Sr on solid solubility of Al in matrix of the as-cast alloys.

3 Results and discussion

3.1 Microstructure

Figure 1 shows the optical microstructures of AMC801 alloys modified by different Sr additions. It can be seen that continuous net-worked secondary phases are observed at grain boundaries in AMC801 alloy without modification (Fig. 1(a)). With increasing the Sr content from 0.1% to 0.3%, the $\text{Mg}_{17}\text{Al}_{12}$ phase at the grain boundaries becomes finer and dispersed (Figs. 1(b–d)). With increasing the Sr content from 0.1% to 0.5%, the grain size decreases from 83.9 to 65.8 μm gradually (see Table 2).

Table 2 Grain size of AMC801 alloys modified by different Sr additions

Sr content/%	0	0.1	0.2	0.3	0.5
Grain size/ μm	64.8	83.9	74.2	71.3	65.8

Figure 2 shows the XRD results of AMC801 alloys modified by different Sr additions. It can be seen that the microstructure of AMC801 alloy is mainly composed of Mg, $\text{Mg}_{17}\text{Al}_{12}$ and a small quantity of Al_2Ca which has very weak diffraction intensity (Fig. 2(a)). After adding Sr, no new phase is observed, and the increase of diffraction intensity of Al_2Ca is insignificant compared with those of other phases.

Figure 3 shows SEM images of AMC801 alloys modified by Sr additions. As shown in Fig. 3(a), AMC801 alloy contains principally three regions in different colors. The matrix is grey, the light grey region (A) along the grain boundaries is $\text{Mg}_{17}\text{Al}_{12}$, and the white bone-shaped region (B) is Al_2Ca . As shown in Fig. 3(d), AMC801-0.3Sr still contains three regions in different colors except for the matrix. Blocks (C) are dark grey, the massive or banding phase (D) is grayish-white, and the claviform phase (point E) is white. They are identified as $\text{Mg}_{17}\text{Al}_{12}$, Al_2Ca and Al_4Sr , respectively. With increasing the Sr content from 0.1% to 0.3%, the bone-shaped Al_2Ca phase becomes granular or banding, and is dispersed at the grain boundaries apart from the $\text{Mg}_{17}\text{Al}_{12}$ phase. The volume fraction of $\text{Mg}_{17}\text{Al}_{12}$ decreases with increasing Sr content. But the volume fraction of Al_2Ca varies at the opposite trend. In Fig. 3 there is no obvious diffraction peak of Al-Sr phase.

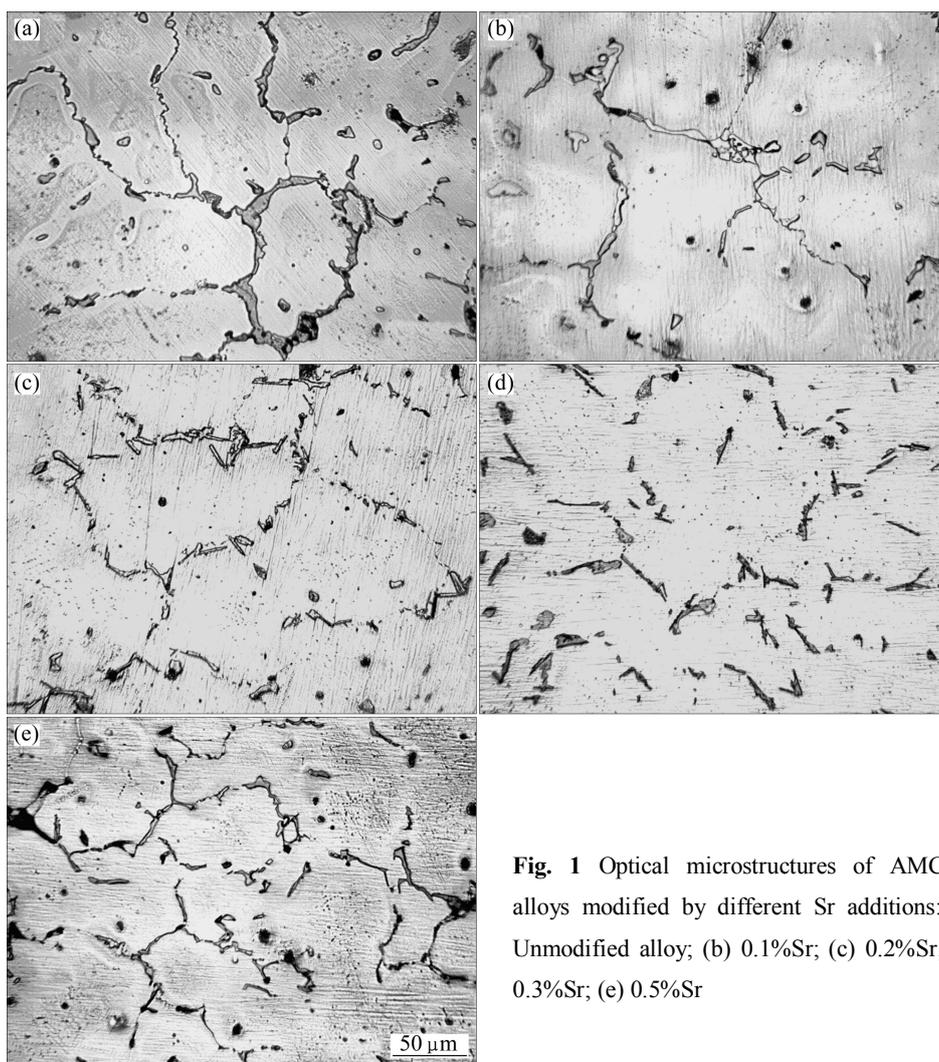


Fig. 1 Optical microstructures of AMC801 alloys modified by different Sr additions: (a) Unmodified alloy; (b) 0.1%Sr; (c) 0.2%Sr; (d) 0.3%Sr; (e) 0.5%Sr

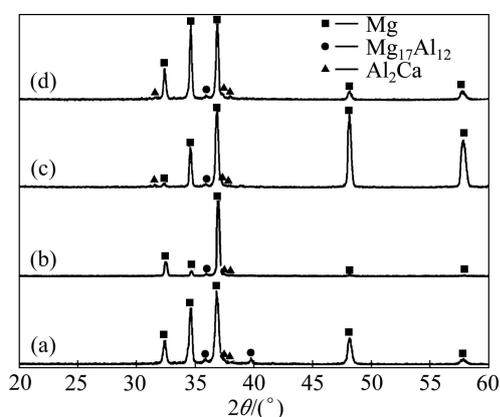


Fig. 2 XRD patterns of AMC801 alloys modified by different Sr additions: (a) Unmodified alloy; (b) 0.1%Sr; (c) 0.2%Sr; (d) 0.5%Sr

However, Al_4Sr could be observed even though its volume fraction is still very low (Figs. 3(c–d)).

3.2 Thermal analyses

Figure 4 shows the differential cooling curves of the

Sr-modified AMC801 alloys. The peak temperatures were taken from the top of each peak. All these characteristic temperatures are summarized in Table 3. The crystallization temperature (t_c) was taken by the extrapolation method from the rising point of the first exothermic peak as marked in the figure. It can be found that after adding 0.1%–0.5% Sr, t_c of AMC801 alloy decreases by approximately 1.7 °C. The effective undercooling degree Δt_c can be expressed as: $\Delta t_c = t_m - t_c$, in which t_m is the melting temperature of alloy. It is

Table 3 Characteristic temperatures of experimental alloys in DSC heating and cooling curves

Alloy	$t_c / ^\circ C$	$t_1 / ^\circ C$	$t_2 / ^\circ C$	$\Delta t_c / ^\circ C$
AMC801	606.3	487.7	441.5	0
AMC801-0.1Sr	604.5	490.9	444.7	1.8
AMC801-0.2Sr	604.7	495.2	445.0	1.6
AMC801-0.3Sr	604.8	507.3	444.0	1.5
AMC801-0.5Sr	604.4	500.8	444.3	1.9

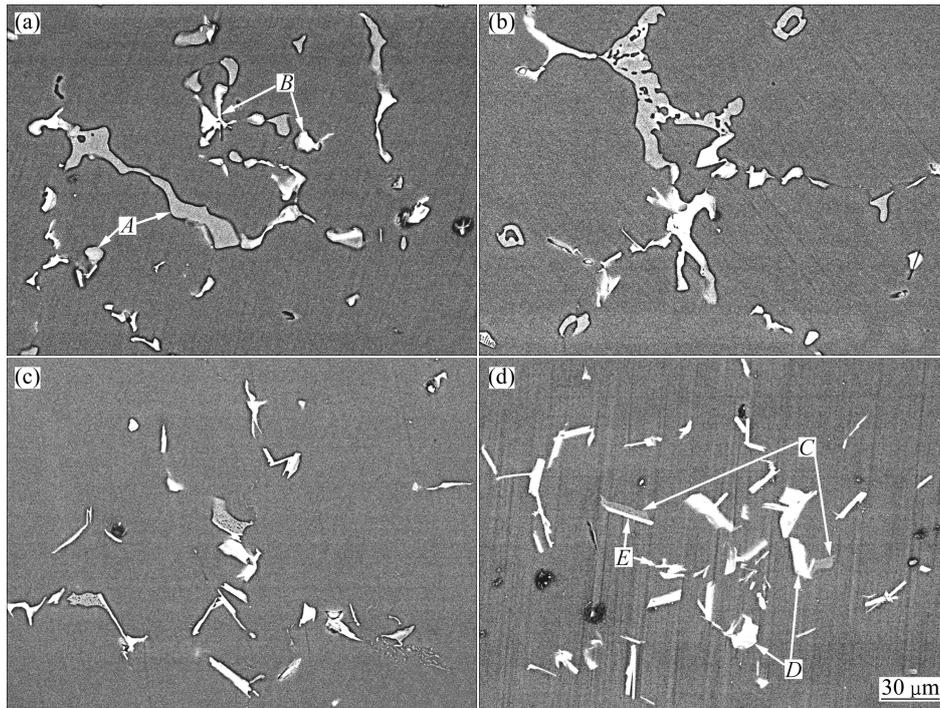


Fig. 3 SEM images of AMC801 alloys modified by different Sr additions: (a) Unmodified alloy; (b) 0.1% Sr; (c) 0.2% Sr; (d) 0.3% Sr

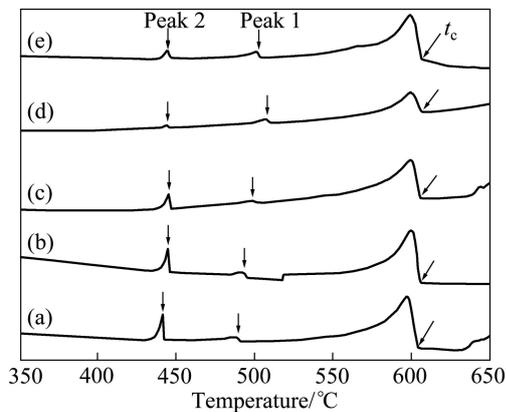


Fig. 4 DSC cooling curves of AMC801 alloys modified by different Sr additions: (a) Unmodified alloy; (b) 0.1% Sr; (c) 0.2% Sr; (d) 0.3% Sr; (e) 0.5% Sr

supposed that t_m is unchanged after adding Sr element. Accordingly, Δt_c of the modified AMC801 alloys increases by approximately 1.7 °C. It can also be found that t_1 , the formation temperature of the Al_2Ca phase, increases from 487.7 to 507.3 °C with increasing Sr content from 0.1% to 0.3%. However, t_1 decreases to 500.8 °C for AMC801-0.5Sr alloy. In addition, t_2 , eutectic reaction temperature of the $Mg_{17}Al_{12}$ phase, increases by approximately 3 °C due to the addition of Sr modifier.

3.3 Vickers-microhardness

Figure 5 shows the Vickers microhardness of the

matrix of the modified AMC801 alloys. The hardness of the α -Mg matrix of AMC801 alloys increases from HV 70 to HV 80 with the Sr content increasing from 0.1% to 0.5% due to the increase of volume fraction of Al_2Ca phase and the refinement of structure. In addition, the addition of Sr increases the solid-solution strength of the α -Mg phase by increasing the Al solute content.

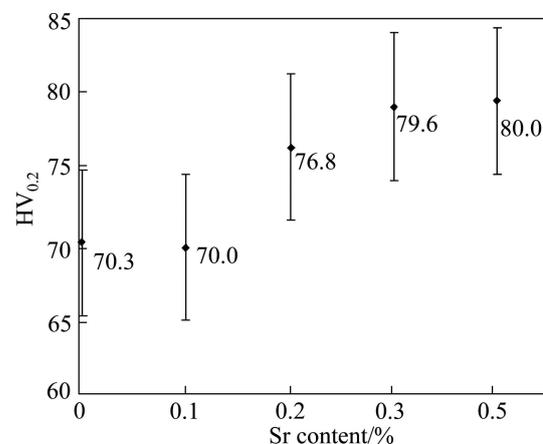


Fig. 5 Vickers-microhardness of matrices of AMC801 alloys modified by different Sr additions

4 Discussion

It is well known that the nucleation and grain growth are the main influencing factors to determine the

final grain size of the alloy. Nucleation ratio relates to the effective undercooling degree of alloy and the undercooling degree of melt. Under the given identical solidification condition (i.e. cooling rate), the nucleation ratio mainly depends on the effective undercooling degree of the alloy, which is the minimum undercooling degree for nucleating of the alloy under certain solidification condition for melt. Generally, the higher the effective undercooling degree of the alloy is, the less the nuclei in the melt are.

Grain growth rate mainly depends on the solute diffusion rate in the melt. Constitutional undercooling in a diffusion layer ahead of the solid/liquid interface affects the growth rate of the nucleus. The higher the constitutional undercooling, the slower the solute diffusion rate, and the slower the growth rate of the nucleus. LI et al [20] mentioned that in the initial growth stage of nucleus during the early stage of solidification, nucleation and growth are competing processes. Therefore, when the nucleus growth is restricted, nucleation in the melt will be promoted. Sr, as the surface activity element, is similar to Ca with strong segregation ability in the melt. It forms the intensive constitutional undercooling in a diffusion layer ahead of the advancing solid/liquid interface which restricts grain growth and promotes nucleation [21].

In this study, the increase of the effective undercooling degree (Δt_c) induces the decrease of the nucleation ratio in the alloys modified by Sr additions under the identical solidification condition. In addition, the constitutional undercooling of the melt increases unobviously after 0.1% Sr addition, and the growth rate of the nucleus is still fast. Accordingly, the grain size of the AMC801-0.1Sr alloy increases by approximately 20 μm , compared with the AMC801 alloy without Sr addition. With increasing Sr content from 0.1% to 0.5%, the constitutional undercooling would also increase, and the restriction on grain growth and the promotion on nucleation become more apparent. The grain sizes of the α -Mg matrix decrease from 83.9 to 65.8 μm , reaching the refinement effects of Ca on the α -Mg matrix (Table 2).

When the α -Mg grows at the steady state, the solute elements, such as Al, Ca, Sr and some unsolved Al_4Sr in the Al-10Sr master alloys, are still abundant in the residual melt. Based on the cooling DSC curves, Al_2Ca starts nucleating and grows in the melt in AMC801 alloys at the temperature of 487.7 $^\circ\text{C}$. After adding 0.1%–0.3% Sr, the formation temperature of Al_2Ca increases from 487.7 $^\circ\text{C}$ to 507.3 $^\circ\text{C}$. According to SHABESTARI's reports [15], the increase of the formation temperature of Al_2Ca can increase the

nucleation rate of Al_2Ca , resulting in refinement of the Al_2Ca phase.

ZHENG et al [22] reported that Sr atoms have the adsorption and poisoning manners to the M_2Si crystal. Figure 6 shows the morphology of Al_2Ca phase. It seems that Sr atoms also have the similar adsorption and poisoning manners to the Al_2Ca crystal. Sr atoms may be adsorbed at the growth front of the Al_2Ca , changing the surface energy during the solidification. With increasing Sr content from 0.1% to 0.3%, this adsorption and poisoning effects become more significant, leading to the bone-shaped Al_2Ca phase change to massive or banding phase (Fig. 3). When Sr addition increases to 0.5%, the modification effect of Sr decreases, due to the formation of some Al_4Sr phases which consume some Sr atoms, resulting in the overmodification of the AMC801 alloy. Thus, the continuous net-worked secondary phase appears again in the AMC801-0.5Sr (Fig. 1).

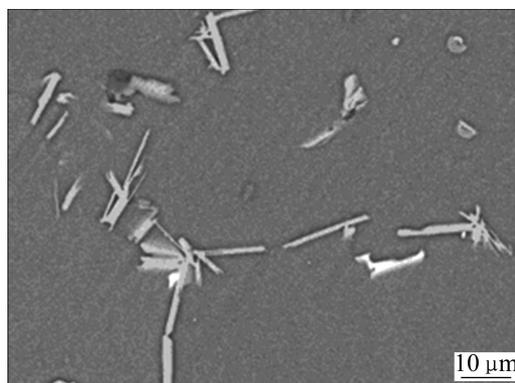


Fig. 6 Al_2Ca phase modified by Sr addition

5 Conclusions

With increasing Sr addition from 0.1% to 0.5%, the grain size of the AMC801 alloys modified by Sr additions decreases from 83.9 to 65.8 μm . The decrease of grain size of the α -Mg matrix is due to the increase of the effective undercooling degree of the melt and the constitutional undercooling in a diffusion layer ahead of the advancing solid/liquid interface. Compared with the unmodified alloy, Sr addition leads to the coarsening of the α -Mg matrix. The Sr modifier also has an effective modification effect on the Al_2Ca in the AMC801 alloys. When Sr addition ranges from 0.1% to 0.3%, it changes the morphologies of Al_2Ca phase from bone-shaped to granular or banding, and increases their volume fraction. When Sr content increases to 0.5%, the overmodification of the AMC801 alloy appears due to the formation of Al_4Sr phase and consumption of Sr atoms.

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Sr 对 Mg-Al-Ca 铸造合金微观组织的影响

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摘要: 研究 Sr 对 Mg-Al-Ca 铸造合金微观组织演变的影响。研究发现, 微量 Sr 会导致镁基体组织轻微粗化。当 Sr 含量从 0.1% 增加至 0.5% 时, 镁基体的晶粒尺寸由 83.9 μm 减小到 65.8 μm 。添加 0.1%–0.3% Sr 对 Al₂Ca 相有显著的变质细化作用, 同时, 使其形貌从条状转化为球状。Al₂Ca 的含量随着 Sr 元素的添加而有所增加。镁基体晶粒细化主要是由于 Sr 的添加增加了熔体的有效过冷度以及合金固/液界面前沿区域形成很强的成分过冷效应引起的。Sr 对 Al₂Ca 的变质作用主要归因于 Sr 在 Al₂Ca 晶体上的吸附。当 Sr 含量增加至 0.5% 时, 合金会出现过变质现象。

关键词: Mg-Al-Ca 合金; 锶; 钙; 显微组织