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Effect of strontium on crystallization of Mg_2Si phase in Al-Si-Mg casting alloys①

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[Abstract] Optical microscope and SEM were used to observe the changes of the microstructure of Al-11.6%Si-0.4%Mg alloys with varying strontium additions and the effect of strontium on the crystallization of Mg_2Si phase was discussed. It is found that Mg_2Si phase nucleates on the surfaces of the eutectic silicon flakes in the unfully modified alloys, growing as meshwork or bamboo-shoot shape, however, very few and fine Mg_2Si particles phase are isolated at the boundaries of the eutectic cells in the fully modified alloys. Strontium has an important influence on the crystallization of Mg_2Si phase in Al-Si-Mg casting alloys and it is thought to be related to the increase of the amount of dendritic α phase and the modifying degree of eutectic silicon phase.

[Key words] Al-Si-Mg alloy; strontium modification; Mg_2Si; crystallization
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1 INTRODUCTION

Development of modern industry requires lighter and more strengthening products. The Al-Si casting alloys with excellent combination properties have an increasingly wide applications[1]. Hypo-eutectic Al-Si casting alloys, such as A356 with excellent strength and ductility, have been widely used in many applications, but the castability is poor compared with that of near-eutectic Al-Si alloys. However, the applications of the near-eutectic Al-Si alloys are limited, because of its lower strength and ductility, especially in some important products undergoing a larger load. Investigation on improving the strength and ductility of the near-eutectic Al-Si alloys is scant at present. So it is believed that the research and development of these alloys with excellent compositive properties will be paid more and more attention by the materials researchers and the castings producers.

The structure refinement is one of the most important methods for improving the strength and ductility of the alloys. For the near-eutectic Al-Si alloys, modifying treatment has been a basic practice. Adding sodium or strontium can cause a transition of the eutectic silicon phase from coarse flakes to fine fibers and consequently improve the mechanical properties, especially the ductility[2~7]. The recovery of sodium in aluminum melts is poor, and it oxidizes quickly and the modification effect fades fast too. It has been reported that sodium has the problem of "over-modification". So controlling the modifying treatment with sodium salt is thought to be difficult[3, 6, 8, 9]. Besides these, this modifying treatment also results in environment problems. Strontium has a good modifying ability, just under sodium, and the modification effect is capable of retaining a long period. The recovery of it in aluminum melts is about 90%[5]. It is commonly thought that the modification with strontium has not got the problem of "over-modification"[3, 6~9]. Apparently, the modifying with strontium can be controlled more easily than that with sodium salt. With increasingly investigating and understanding the modifying behaviors of strontium, the modifying treatment with strontium has been accepted widely. The recent work of the authors indicated that the addition of strontium in near-eutectic Al-Si alloys results in a considerable increase of the amount of dendritic α phase, and a decrease of both the primary dendrite spacing and secondary dendrite arm spacing, promoting the columnar growth of dendrites[1, 10]. The dendritic α phase plays an important role in improving the mechanical properties of near-eutectic Al-Si alloys[11]. For the alloys containing magnesium, the increase of the amount of dendritic α phase consequentially increases the amount of magnesium dissolving in α solution, and decreases the amount of Mg_2Si crystals accordingly. Magnesium is one of the most important alloying elements in Al-Si casting alloys. After the solution-ageing heat treatment, the precipitation of the transitional phase of Mg_2Si crystal can remarkably rise the strength. It has not been reported up till now whether or not adding strontium has an influence on the crystallization of Mg_2Si phase in Al-Si-Mg casting alloys. If strontium affected the crystallization of Mg_2Si phase, it could be foreseen that it might have an influence on the disso-

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lution and precipitation of Mg_2Si phase during heat treatments and hence on the processing regulations of heat treatments. As a part of the studies on improving the strength and ductility of the near-eutectic Al-Si alloys, it is quite necessary to investigate the effect of strontium on Mg_2Si phase.

2 EXPERIMENTAL

The experimental alloys with a nominal composition of Al-11.6%Si-0.4%Mg-0.15%Fe (mass fraction, the same below) were melted in an electrical resistance furnace using a graphite crucible with 2.5 kg melt per heat. An Al-10%Sr master alloy was added to the melt at ~ 730 ℃ with slight stirring. According to the recovery of strontium in the melts measured by ICP Spectrometer, the amounts of strontium in the alloy are obtained as 0, 0.010%, 0.015%, 0.020%, 0.025%, 0.030% and 0.0375%. After holding for 30 min, SW-RJ-1 flux was introduced for degassing. Then, the melt was poured at ~ 720 ℃ into a standard tensile sample (12 mm in diameter, 60 mm in length) mold (grey iron, preheating at 200 ℃). Metallographic samples were cut from the gage parts of the tensile test bars. After etching in a Keller's reagent, microstructures were observed and recorded using Olympus optical microscope. SEM (Jeol-JSM6300 and Hitachi X-650), fitted with X-ray energy dispersive, was adopted for some deeply etched samples. X-ray mapping was used to observe the microcosmic distributions of magnesium, silicon, strontium, iron and/or aluminum.

3 RESULTS AND DISCUSSION

In Al-11.6%Si-0.4%Mg alloys, magnesium has no distinct influence on the modification effect of strontium and the change of the morphology and size of eutectic silicon phase with the amount of strontium is similar with that in Al-11.6%Si alloys[1]. Because of the presence of magnesium, some microstructures, which have not been observed in the alloys without magnesium, have been found.

3.1 Mg_2Si phase in unfully modified alloys

When the amount of strontium is below or equal to 0.015%, the eutctic silicon phase does not fully change into fibrous, so these alloys are named unfully modified alloys (involving the unmodified alloy). When the amount of strontium is above or equal to 0.020%, all the eutectic silicon phase present as fine fibers. These alloys are named fully modified alloys. Fig. 1 shows the optical micrographs of the as-cast microstructures of Al-11.6% Si-0.4% Mg alloys. Some meshwork structures (as arrowed), hoar and

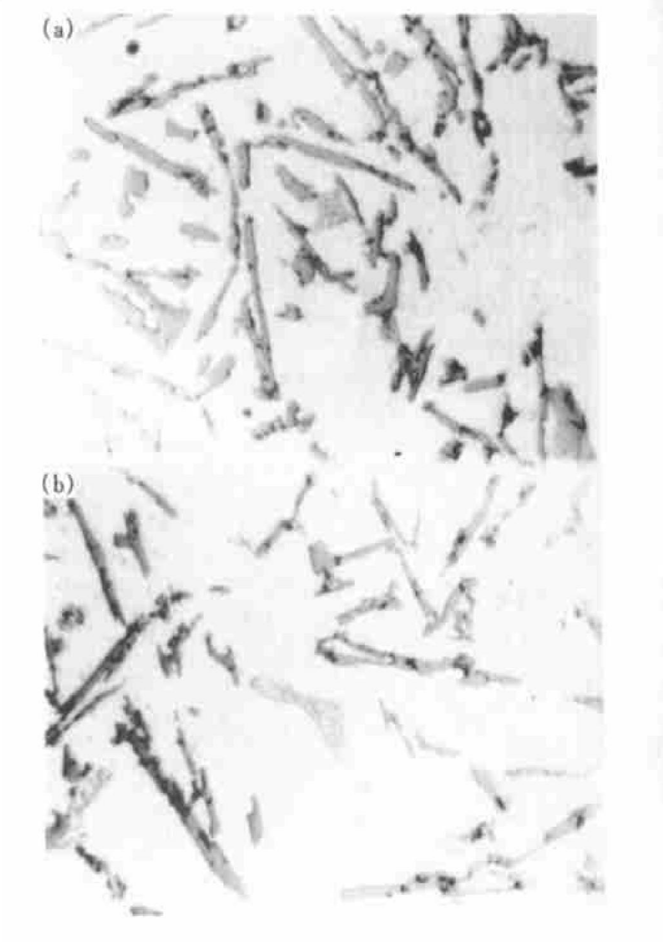

Fig. 1 Optical micrographs of as-cast Al-11.6%Si-0.4%Mg alloys with unfull modification
(a) —Without Sr; (b) —0.010%Sr

blighter than eutectic silicon phase, are observed. These structures have not been found in Al-11.6%Si alloys. Besides an individual meshwork phase is isolated in the α phase (as seen in Fig. 1(b)), most meshworks have one or a few "heads" connecting to the eutectic silicon flake. The SEM micrographs clearly show that these meshworks (as arrowed in Fig. 2) have a close connection with eutectic silicon flakes. EDAX results (as listed in Table 1) indicates that these structures contain Al, Si, Mg and a little Fe and Sr. The mole ratio of Mg to Si is 1∶2, and, however, the one of Mg_2Si compound is 1.73∶1[12]. There are only α(Al), Si and Mg_2Si phases present in Al-Si-Mg ternary phase diagram. Although 0.4%

Table 1 Energy dispersive X-ray tracing of meshwork structure in Fig. 2(b)

Element line	w / %	x / %
Mg $K_α$	11.47	13.60
Al $K_α$	60.72	56.28
Si $K_α$	22.85	28.58
Fe $K_α$	0.82	0.34
Sr $L_α$	4.14	1.20
Total	100%	100%

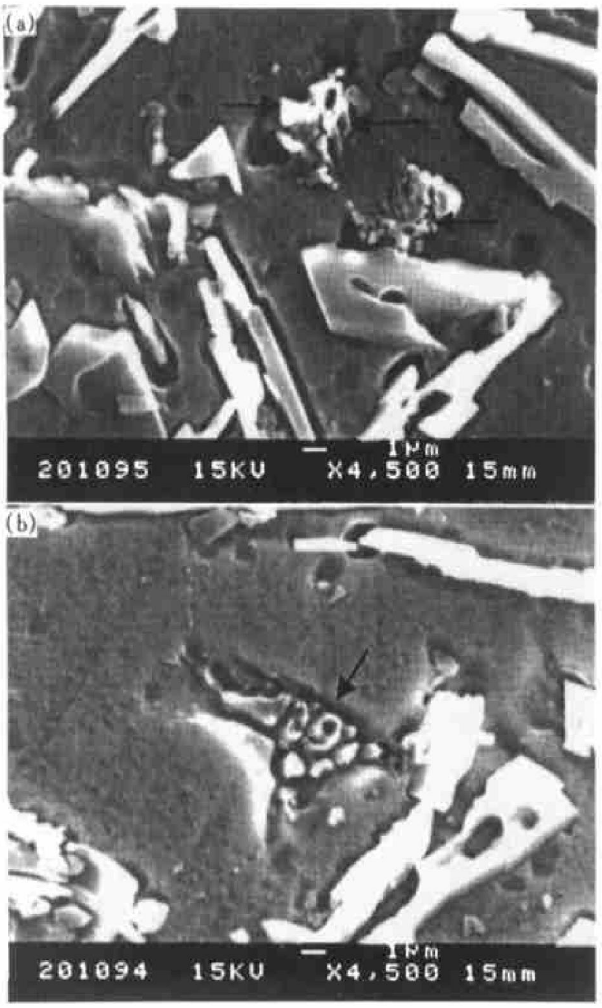

Fig. 2 SEM micrographs of as-cast Al-11.6% Si-0.4% Mg alloys with unfull modification
(a) —Without Sr; (b) —0.015% Sr

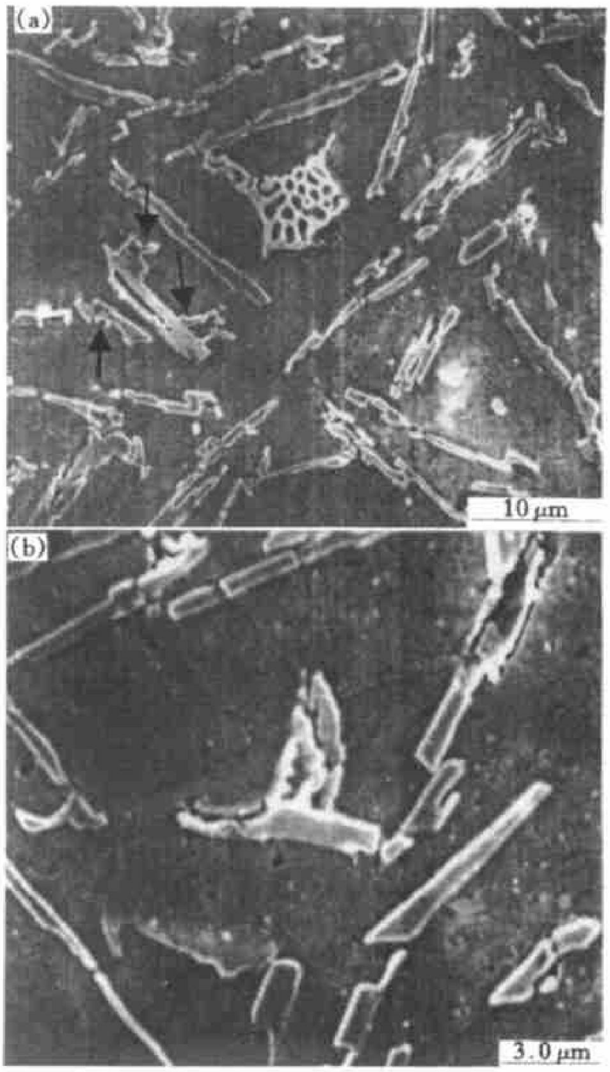

Fig. 3 SEM micrographs of Al-11.6% Si-0.4% Mg with 0.010% Sr modification
(a) —Meshwork structure;
(b) —Bamboo-shoot shape structure

Mg in the alloys is below the solubility of magnesium in Al-Si alloys (about 0.5% ~ 0.6%), ternary eutectic reaction, $L \rightarrow \alpha(Al) + Si + Mg_2Si$, may occur under non-equilibrium solidification. So it can be conclude that these meshworks are α + Si + Mg_2Si ternary eutectic. Fig. 3(a) clearly shows a meshwork and it is worth noting that many tubers (as arrowed) are present on the surfaces of eutectic silicon flakes. The high magnification SEM micrograph (as seen in Fig. 3(b)) shows a bamboo-shoot shape structure, epitaxially growing on the eutectic silicon flake. The morphology is rather different from the eutectic silicon flake, without the facet growth characteristic of silicon crystal. EDAX suggests that it is Mg_2Si phase too[1].

Although the space groups of the Mg_2Si and Si phase are $Fm3m$ and $Fd3m$ respectively, their crystal lattices are same, FCC[12]. The surfaces of Si flakes are {111}, the low energy face. So it is possible for Mg_2Si to nucleate and grow epitaxially at the surface of eutectic silicon flakes, which has been well demonstrated by the above microstructure observations. From the results above, it can be obtained that in the unfully modified Al-11.6% Si-0.4% Mg alloys, Mg_2Si crystals may present as meshwork or bambooshoot shape structure, epitaxially growing on theeutectic silicon flake.

3.2 Mg_2Si phase in fully modified alloys

When the alloy is fully modified, namely, all the eutectic silicon crystals are fine fibers, eutectic cells can be observed clearly[1]. The meshwork structure or bamboo-shoot shape structure, present in the unfully modified alloys, disappears now, but some blight particles are found at the boundaries of the eutectic cells, whose size is larger apparently than that of the fibers in the eutectic cells, as shown in Fig. 4(a). These particles were not found in Al-11.6% Si alloys yet, so the authors suspected it might be another shape of Mg_2Si phase. Fig. 4(b) shows the high magnification microstructure of the eutectic cell boundary zone. The result of X-ray mapping in the eutectic zone is shown in Fig. 5 and indicates there is no definite proof for the presence of Mg_2Si. EDAX result of the large particles at the eutectic cell boundaries suggests it is still silicon crystals. But a very small particle is found at the boundary of eutectic cells too, as arrowed in Fig. 4(b). The energy dispersive X-ray tracing of it, as listed in Table 2, suggests it is Mg_2Si crystal. Apparently, this fine Mg_2Si particle phase has not the epitaxial growth relation to the silicon phase. Its morphology is also completely different, the size is only about 1 μm, and the amount is rather low. From the results above, it is suggested that the nucleation of Mg_2Si phase is suppressed in the fully modified alloys.

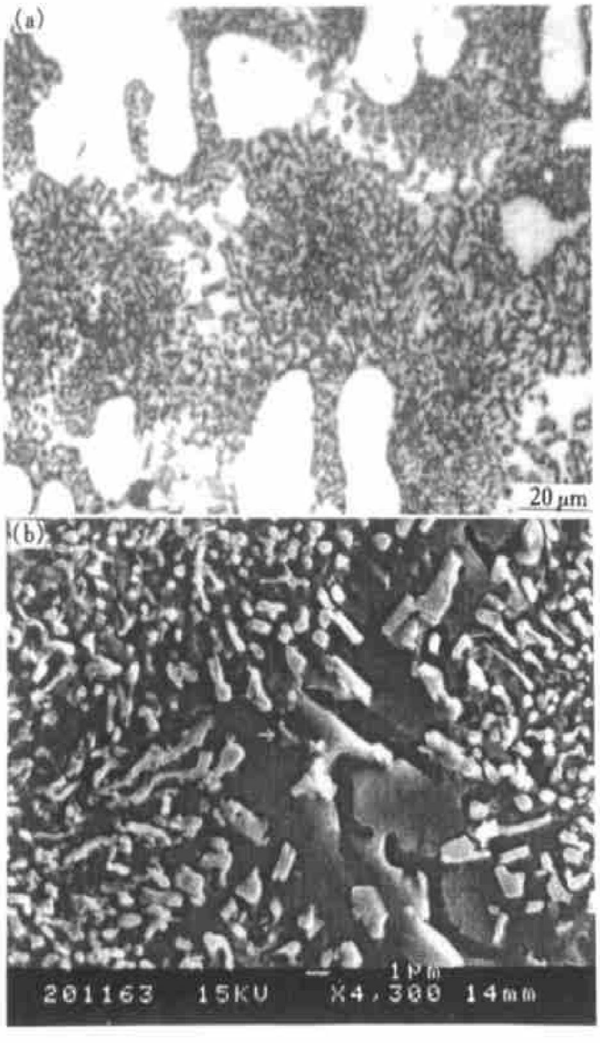

Fig. 4 SEM micrographs of eutectic cell boundary zone in Al-11.6%Si-0.4%Mg alloys with 0.0375%Sr modification

3.3 Discussion

The crystallization of Mg_2Si phase in unfully modified alloys is completely different from that in the fully modified alloys, in terms of the morphology, size and amount. It demonstrates that strontium presents in Al-Si-Mg casting alloys has an important influence on the crystallization of Mg_2Si phase. During the solidification of Al-Si-Mg alloys, the binary eutectic reaction $L \rightarrow \alpha + Si$, which is the main

Table 2 Energy dispersive X-ray tracing of fine particle in Fig. 4(b) (as arrowed)

Element line	w / %	x / %
Mg K_α	13.76	15.17
Al K_α	65.35	64.90
Si K_α	20.89	19.93
Total	100%	100%

eutectic reaction, has taken place before the ternary eutectic reaction ($L \rightarrow \alpha + Si + Mg_2Si$) occurs. Because both the Mg_2Si and Si phase belong to the FCC crystal lattice, it is rational to consider that the {111} faces of the eutectic silicon flakes, crystallizing prior to the Mg_2Si phase, may have the potency of affording the nucleation sites for Mg_2Si phase. So the nucleation of Mg_2Si crystal is easy, and Mg_2Si phase can grow on to the *s* eutectic silicon flakes, presenting as meshwork structure or bamboo-shoot shape structure. But in the fully modified alloys, the amount of Mg_2Si crystals is too small to be observed easily. Why do these remarkable changes occur? The first reason is thought to be related to the increase of the amount of dendritic α phase with the addition of strontium[1, 10]. When the strontium content in Al-11.6%Si-0.4%Mg alloy increases from 0.015% (unfull modification) to 0.020% (full modification), the amount of dendritic α phase increases from 21.06% to 41.24% by 95.8%[1, 11]. The increase of the amount of dendritic α phase consequentially results in the increase of the amount of magnesium dissolving in the α solution, so the amount of magnesium consumed in the crystallization of Mg_2Si phase decreases sharply. The second reason is related to the modifying degree of strontium on the eutectic silicon phase. In the unfully modified alloys, a gradual change of the morphology and size of the eutectic silicon phase with increasing the addition of strontium has been observed[1], but the facet characteristic of silicon flakes has not completely changed. The surface of the silicon flakes as the nucleation sites for Mg_2Si phase is abundant, so Mg_2Si crystals can nucleate and grow at the surfaces of the silicon flakes, forming the meshwork structure or bamboo-shoot shape structure. In the fully modified alloys, the eutectic silicon phase presents as fibrous and the surface of the silicon crystals is not single {111} face. High density twins and stacking faults have been demonstrated to present at the surface of the eutectic silicon fibers[3, 4, 13~15]. So the surface of the silicon phase has no longer the potency as the nucleating sites of Mg_2Si phase. In addition, the accumulation of strontium atoms in the liquid in front of the growth front of silicon crystal forces atoms of strontium into the lattice of silicon crystal[4] and hence the lattice constant may be changed. Likewise, it makes the nucleation of Mg_2Si crystal so

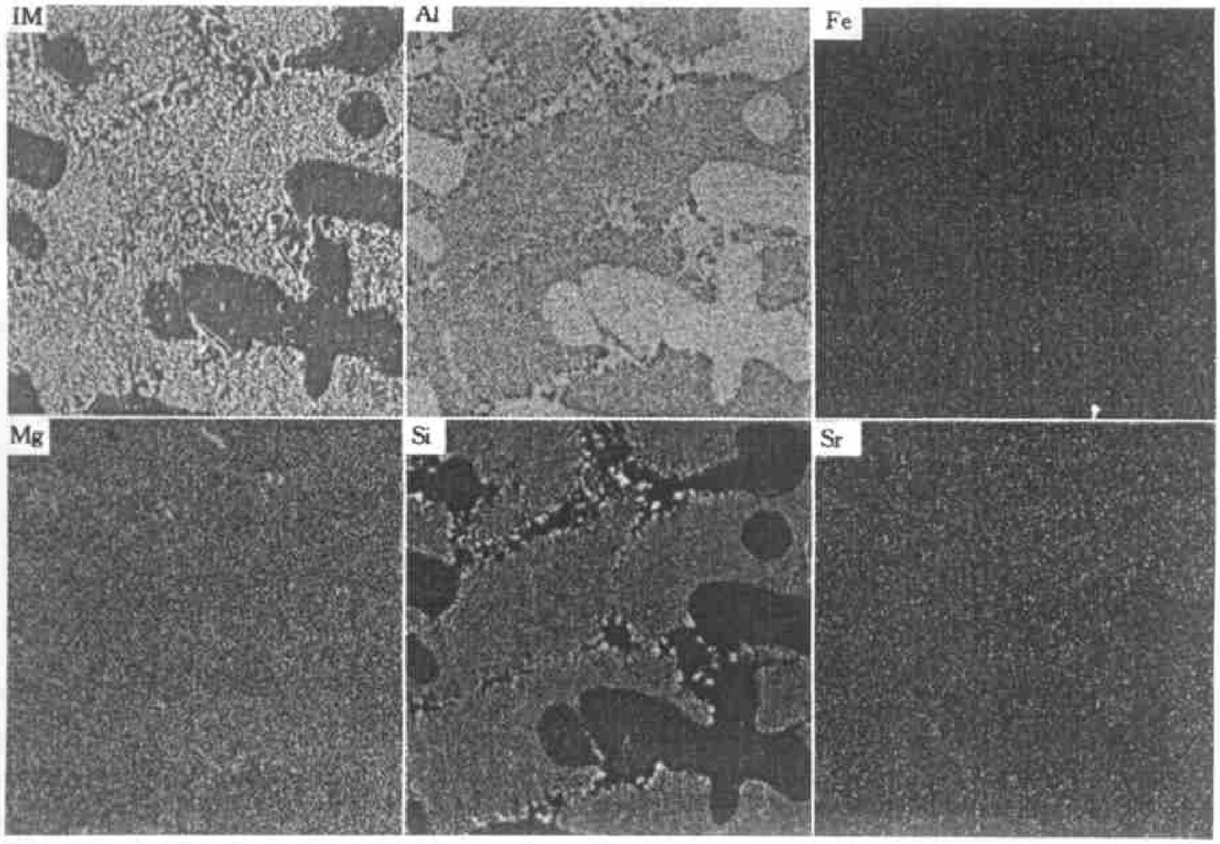

Fig. 5 X-ray mapping of eutectic zone in Al-11.6%Si-0.4%Mg alloy modified with 0.0375%Sr

difficult that magnesium is forced to retain in the α solution during non-equilibrium solidification. It is anticipated that the highlight on the effect of strontium on the crystallization of Mg_2Si crystal will afford some instructions for the casting practice of the Al-Si-Mg casting alloys.

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