

Morphology modification of Mg₂Si by Sr addition in Mg-4%Si alloy

TANG Shou-qiu¹, ZHOU Ji-xue^{1,2}, TIAN Chang-wen¹, YANG Yuan-sheng^{1,2}

1. New Materials Research Institute, Shandong Academy of Sciences, Ji'nan 250014, China;

2. Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, China

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Abstract: A modification of Mg₂Si in the hypereutectic Mg-4%Si alloy (mass fraction) with Sr was investigated. Two types of Mg₂Si in the alloys were found: polygonal primary Mg₂Si and Chinese script type eutectic Mg₂Si. Adding Al-10% Sr master alloy to the Mg-4%Si alloy clearly reduced the average size of primary Mg₂Si and changed the morphology of eutectic Mg₂Si from Chinese script type to polyhedral or fine fibre shape. The refinement of primary Mg₂Si is mainly attributed to the heterogeneous nucleation mechanism induced by the Sr-rich particles. The modification of eutectic Mg₂Si results from the dissolved Sr, which alters the preferred growth manner of the eutectic.

Key words: Mg-Si alloy; Al-Sr alloy; Mg₂Si; modification; refinement

1 Introduction

Growing demands from the automobile and aerospace industries for lightweight components that reduce energy consumption and air pollution lead to an increasing interest in magnesium alloys and their composites because of their low density, high strength-to-mass ratio and good machinability [1–3].

Among magnesium alloys, the Si-containing Mg alloys offer significant potential as structural materials that can be subjected to comparatively high temperature [4–7]. This is because they are reinforced with Mg₂Si, which exhibit a high melting temperature of 1 085 °C, a low density of 1.99 g/cm³, a high hardness of 4.5×10⁹ N/m², a low thermal expansion coefficient of 7.5×10⁻⁶ K⁻¹, and a reasonably high elastic modulus of 120 GPa [8–9].

On the other hand, Si-containing Mg alloys exhibit a low strength and very low ductility due to the large Mg₂Si particles and the brittle eutectic Mg₂Si [10–11]. For this reason, refinement and modification of Mg₂Si will be needed to improve the mechanical properties. It was reported that the additions of KBF₄, Ca, P, Y or RE produced positive effects on the morphology of Mg₂Si in magnesium alloys containing Si [10–13]. As a beneficial element to the grain refinement of Mg-Al alloys [14–15], Sr was also proven effective in modifying Mg₂Si in

Mg-Al-Si alloys by changing their shape from network shape to fine fibrous shape [16–20]. YANG et al [17–18] reported that Sr could refine Mg₂Si in AZ61-0.7Si alloy because Al₄Sr can theoretically act as the heterogeneous nucleus for Mg₂Si according to the calculation of the disregistry by the two-dimensional lattice misfit mathematical model, and Sr may lower the onset crystallizing temperature and increase the undercooling level. SRINIVASAN et al [19] found that Sr may be incorporated in the Mg₂Si precipitates during solidification of AZ91-Si alloy.

To date, less work has been carried out with regard to the modification effect of Sr on morphology of primary Mg₂Si in hypereutectic Mg-Si alloys. The further research is needed to understand the mechanism for the refinement in structure. The present paper studies the modification effect of Sr on Mg₂Si (both eutectic and primary Mg₂Si crystals) by adding the Al-10%Sr (mass fraction) alloy to Mg-4%Si (mass fraction) alloy. The modification effect of Al on the Mg₂Si phases is also investigated to clarify the modification mechanism of Sr in Al-10%Sr master alloys.

2 Experimental

Commercial pure Mg ingots (99.9% purity) and Si (99.9% purity) were used as raw materials to prepare Mg-4%Si alloy. The Mg-4%Si alloy was melted at

750 °C in an electrical resistance furnace under a protective atmosphere (0.5% SF₆+99.5%CO₂, volume fraction), and 2.7% Al or 3% Al-10%Sr master alloy was then added to the Mg-Si alloy melt. The melt was stirred for 5 min, held at 750 °C for 30 min, and poured into a steel mold preheated at 200 °C to cast bar samples of ϕ 40 mm×100 mm. The microstructure was investigated by optical microscopy. Characteristic and qualitative analysis of the microstructure were conducted using SEM equipped with an energy-dispersive spectrometer (EDS). The size of the primary Mg₂Si particles was measured and calculated with SISCIA8.0 software.

Table 1 lists the actual chemical compositions of the experimental alloys, which were analyzed by inductively coupled plasma spectroscopy.

Table 1 Chemical compositions of experimental alloys

Alloy	w(Si)/%	w(Al)/%	w(Sr)/%	w(Mg)/%
Mg-4Si	3.88	0.00	0.00	Bal.
Mg-4Si-2.7Al	3.69	2.73	0.00	Bal.
Mg-4Si-2.7Al-0.3Sr	3.51	2.81	0.32	Bal.

3 Results and discussion

3.1 Microstructure of Mg-4%Si alloy

The microstructure and EDS analysis of Mg-4%Si alloy are shown in Fig. 1 and Table 2. According to the Mg-Si binary phase diagram, Mg-4%Si alloy is a hypereutectic alloy with a solidified microstructure of

Mg₂Si primary and Mg₂Si-Mg eutectic. The dark area (A) is primary Mg₂Si, the gray area (B) is Mg, and the area C is a rod-like shaped eutectic Mg₂Si. The primary Mg₂Si phases are surrounded by Mg halos, around which the Mg-Mg₂Si eutectic is formed, which is similar to the microstructure of the Mg-5%Si alloy [12]. Due to the relatively high cooling rate, its solidification deviates from the equilibrium route. During solidification, the Mg₂Si precipitates primarily, resulting in an enrichment of magnesium around the primary Mg₂Si, which is attributed to the rejection of magnesium solute. Mg is thus able to nucleate and grow surrounding the primary Mg₂Si. As the temperature decreases to the eutectic point, the eutectic structures of Mg₂Si-Mg form around the Mg halos.

Table 2 Chemical compositions of zones A, B and C analyzed by EDS in Fig. 1(a)

Area	w(Mg)/%	w(Si)/%
A	64.86	35.14
B	100.00	0.00
C	82.31	17.69

3.2 Effects of Sr addition on Mg₂Si

The microstructures of Mg-4%Si alloys unmodified and modified by 2.7%Al or 3% Al-10%Sr are compared in Fig. 2. The magnified microstructures of Mg-4%Si alloys modified by 3% Al-10%Sr master alloy is shown in Fig. 3. By addition of 3% Al-10%Sr to Mg-4%Si alloy,

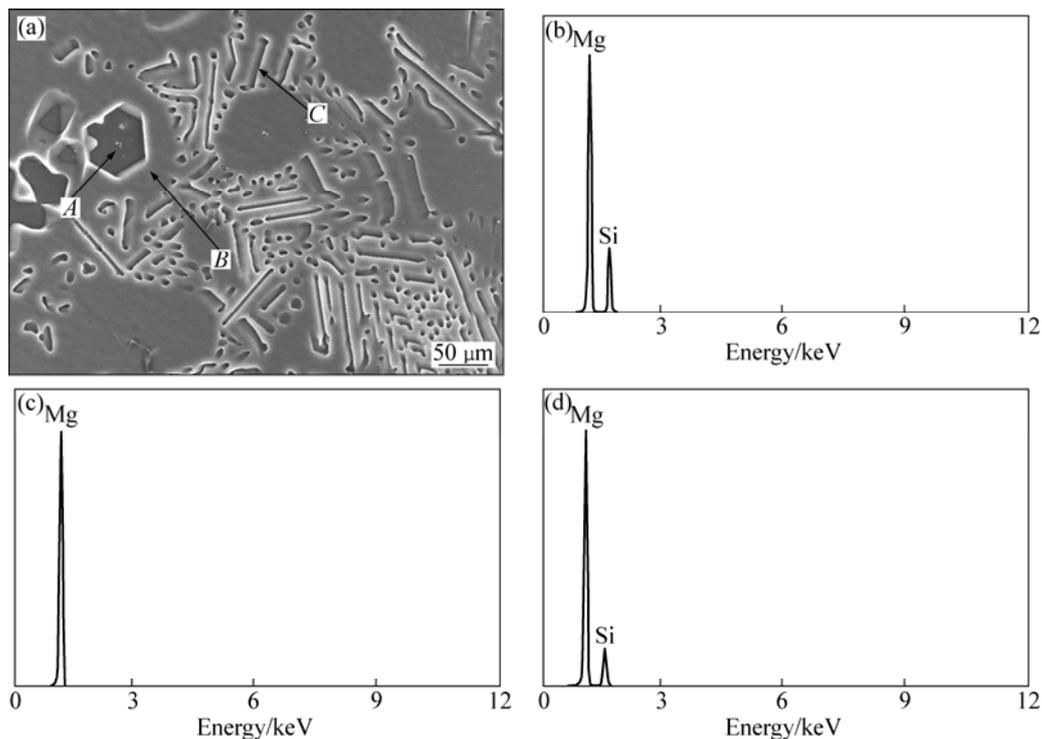


Fig. 1 SEM image of Mg-4%Si alloy (a) and EDS spectra for primary Mg₂Si marked with 'A' (b), Mg marked with 'B' (c) and eutectic Mg₂Si marked with 'C' (d)

the shape of the primary Mg_2Si does not change obviously while the morphology of eutectic Mg_2Si phase changes from Chinese script type to a polyhedral or fine fibers shape, as shown in Figs. 2(a), 2(b) and Fig. 3. Furthermore, the average size of primary Mg_2Si decreases from about $46\ \mu m$ to $16\ \mu m$. In contrast, when only 2.7% is added to the alloy, the morphology of primary Mg_2Si or eutectic Mg_2Si does not change obviously and the average size of primary Mg_2Si slightly reduces from about $46\ \mu m$ to $36\ \mu m$ while the amount of eutectic Mg_2Si decreases, as shown in Fig. 2(c).

SEM image of the primary Mg_2Si phase, and the concentration profiles of elements Mg, Al, Si and Sr in $Mg-4\%Si$ alloy with 3% Al-10%Sr, are shown in Fig. 4. Small particles are found to exist inside the primary Mg_2Si phases, which presumably act as nucleation sites for the primary Mg_2Si . The concentration profiles of elements show that the primary Mg_2Si , especially the core particle inside, is enriched in Sr element. As shown

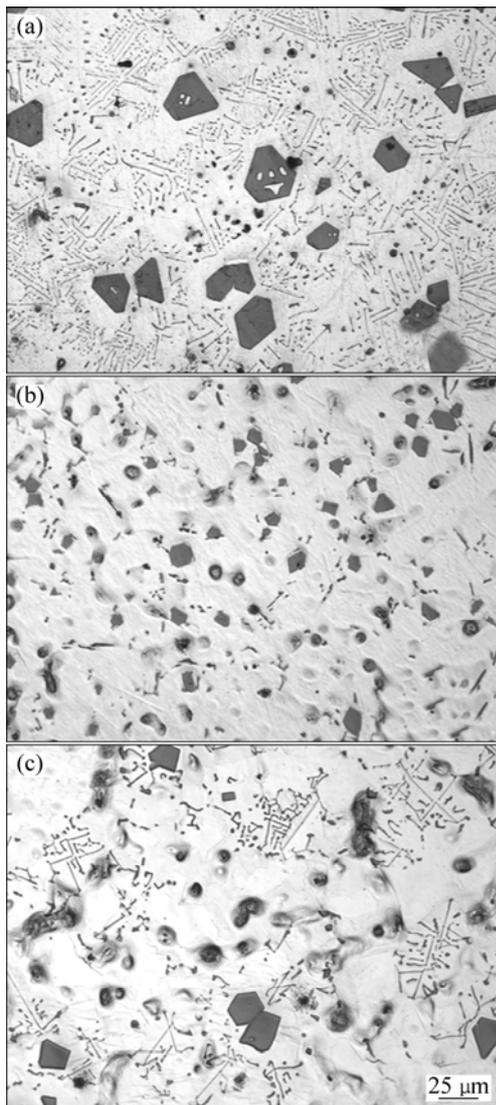


Fig. 2 Microstructures of $Mg-4\%Si$ alloys unmodified (a) and modified by 3% Al-10%Sr master alloy (b) and 2.7% Al (c)

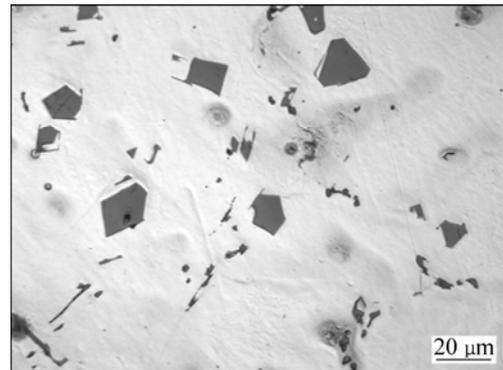


Fig. 3 Magnified microstructure of $Mg-4\%Si$ alloy modified by 3% Al-10%Sr master alloy

in Fig. 4, the separate Al addition could not induce an obvious refinement of primary Mg_2Si , nor is there a core particle introduced inside the primary Mg_2Si in $Mg-4\%Si$ alloy by the addition of 2.7% Al. It is thus presumed that the refinement of primary Mg_2Si mainly depends on the mechanism of heterogeneous nucleation by the core particles that are rich in Sr. According to YANG et al [17–18], Al_4Sr can theoretically act as the heterogeneous nucleus for the Mg_2Si particles according to the calculation of the disregistry by the two-dimensional lattice misfit mathematical model. In addition, the Sr dissolved within primary Mg_2Si is able to modify the primary Mg_2Si crystals.

A SEM image of eutectic Mg_2Si in $Mg-4\%Si$ alloy

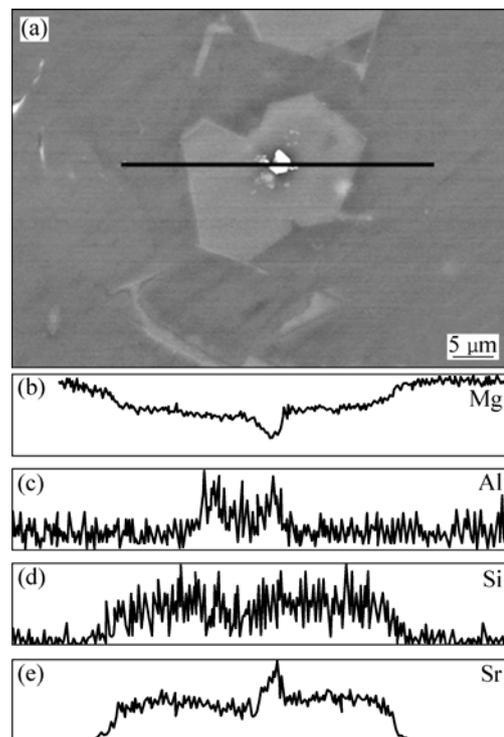


Fig. 4 SEM image (a) and line scanning maps of element Mg (b), Al (c), Si (d) and Sr (e) of primary phase Mg_2Si in $Mg-4\%Si$ alloy modified by 3% Al-10%Sr master alloy

with 3% Al-10%Sr alloy is shown in Fig. 5. The average contents of Mg, Al, Si, Sr within areas A and B in Fig. 5, measured by EDS analysis, are listed in Table 3. As shown in Fig. 5, there is eutectic Mg₂Si in area A but none in area B. It is also noted that the average Sr content in area A is much higher than that in area B, as shown in Table 3, indicating that the eutectic Mg₂Si is enriched in Sr either inside the eutectic Mg₂Si or at the interfaces of eutectic Mg₂Si and Mg. However, no nucleation core was observed in the eutectic Mg₂Si. It is concluded that the dissolved Sr is responsible for the modification of eutectic Mg₂Si.

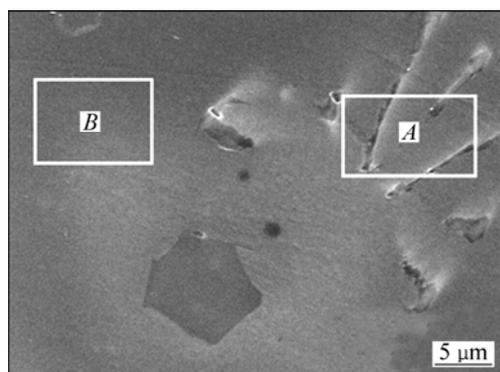


Fig. 5 SEM image of Mg-4%Si alloy modified by 3%Al-10%Sr master alloy

Table 3 Chemical compositions of zones A and B analyzed by EDS in Fig. 5

Area	w(Mg)/%	w(Al)/%	w(Si)/%	w(Sr)/%
A	94.95	1.42	3.15	0.48
B	98.61	1.39	0.00	0.00

In the unmodified alloys, the coarse eutectic Mg₂Si crystals are formed by the preferred growth that occurs at the tips of the branches [18]. When the alloy is modified with 3% Al-10%Sr during the solidification, in addition to the segregation of Sr at the liquid-solid interface, some of the alloys may be adsorbed on the Mg₂Si crystal plane boundaries [19], causing changes of the surface energy of the Mg₂Si crystals from lattice distortion. The preferred growth manner of the eutectic Mg₂Si is depressed, and another type of growth, the isotropic growth manner, is present during the solidification of the modified alloys. Thus, the eutectic Mg₂Si crystals are modified from Chinese script shape to polyhedral or fine fibers shape.

4 Conclusions

1) The solidified microstructure of Mg-4%Si alloy with 3% Al-10%Sr master alloy consists of Mg₂Si primary and Mg₂Si-Mg eutectic. The primary Mg₂Si crystals are surrounded by a layer of divorced eutectic

Mg halos, which are surrounded by the eutectic Mg₂Si-Mg structures.

2) The addition of 3% Al-10%Sr master alloy to Mg-4%Si alloys modifies the eutectic Mg₂Si from Chinese script shape to polyhedral or fine fibers shape, and clearly decreases the average size of primary Mg₂Si phase.

3) The modification of primary Mg₂Si phase depends on the heterogeneous nucleation mechanism induced by Sr-rich particles. The modification of eutectic Mg₂Si phase mainly depends on the dissolved Sr, in which the preferred growth manner of the Mg₂Si phase is depressed, while the isotropic growth is enhanced in the modified alloys.

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Sr 对 Mg-4%Si 合金中 Mg_2Si 的变质作用

唐守秋¹, 周吉学^{1,2}, 田长文¹, 杨院生^{1,2}

1. 山东省科学院 新材料研究所, 济南 250014;

2. 中国科学院 金属研究所, 沈阳 110016

摘要: 研究 Sr 对过共晶 Mg-4%Si(质量分数)合金中 Mg_2Si 相的变质作用与机理。Mg-4%Si 合金中存在多面体形初生 Mg_2Si 相与汉字状共晶 Mg_2Si 相。添加 Al-10%Sr 可以明显细化初生 Mg_2Si 相, 同时可以将共晶 Mg_2Si 相由汉字状变质为多面体状或者纤维状。对初生 Mg_2Si 相的细化作用主要是由凝固过程中含 Sr 颗粒的异质形核作用引起的, 而对共晶 Mg_2Si 相的变质作用是由在凝固过程中熔体中的 Sr 原子在 Mg_2Si 晶体生长表面富集, 从而改变了其生长优势所致的。

关键词: Mg-Si 合金; Al-Sr 合金; Mg_2Si ; 变质; 细化

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