Note

Modification of Mg₂Si in Mg–4Si Alloys with B

H. Y. WANG, N. ZHENG, W. WANG, Z. H. GU, D. LI and Q. C. JIANG

Key Laboratory of Automobile Materials of Ministry of Education and Department of Materials Science and Engineering, Jilin University, Nanling Campus, No. 5988 Renmin Street, Changchun 130025, P. R. China. E-mail: jiangqc@mail.jlu.edu.cn

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1. Introduction

Under the traditional casting conditions, the microstructures of hypereutectic Mg–Si alloys usually consist of large primary Mg₂Si dendrite and brittle eutectic phases, which greatly deteriorate the mechanical properties of alloys.¹⁾ Grain refinement or modification is an important practice to improve the properties of magnesium alloys.^{2–4)} Some studies were focused on the modification of coarse Mg₂Si phase in magnesium alloys.^{5–9)} It has been reported that addition of Ca or P can modify the morphology of the eutectic Mg₂Si phase from Chinese script type to refined polygonal type in Mg–5Al–1Zn–0.7Si alloys.⁵⁾ However, Yuan *et al.* have claimed that addition of P can produce ignition and result in large quantity of smoke.⁶⁾ Additionally, the modification effect of Sb is much better than that of Ca in Mg–5Al–1Zn–1Si alloy.

Recent studies^{7,8)} indicate that both KBF₄ salt and Y rare earth can modify the primary and eutectic Mg₂Si in hypereutectic Mg–Si alloy by absorption and poisoning mechanism. Furthermore, the modification effect of KBF₄ on the Mg₂Si phase is more effective than that of Y in Mg–5Si alloys.⁹⁾ Unfortunately, the KBF₄ addition is bad for environmental protection and dangerous because of the production of the smoke and sputter. Moreover, the excessive KBF₄ addition can lead to a mass of slag and thus the fluidity of the alloy may become poor. Therefore, it is very necessary to seek the most effective and eco-friendly modifier for Mg–Si alloys.

The Al–B or B containing Si master alloys are widely used as grain refinement agents in the casting of Al–Si alloys due to the powerful grain refining ability.^{10,11)} Wang *et al.*¹²⁾ have concluded that the addition of B can refine eutectic Si since AlB₂ particles can act as nucleation substrates for Si. Nogita *et al.*¹³⁾ have found that B does not cause modification of eutectic Si in Al–10Si alloys, and B-containing samples display eutectic nucleation and growth characteristics similar to that of unmodified alloy. In addition, Wu *et al.*¹⁴⁾ have found that α -Al dendrites and eutectic clusters were significantly refined by the addition of B. Unfortunately, the modification of Mg₂Si in hypereutectic Mg–Si alloys with B has rarely been reported so far.

In this paper, the effect of Mg–B modifier on the primary Mg₂Si in Mg–4Si alloy has been investigated. The purpose

of this study is to develop a new modifier fabricated by a simplified process route for Mg–high Si alloy.

2. Experimental

The powder blenders of Mg (99.6 wt% purity, $\sim 106 \mu\text{m}$) and B (98.0 wt% purity, $\sim 3 \mu\text{m}$) were used to fabricate Mg–30B modifier. The powders were prepared by a ball milling at a rotation speed of 50 rpm for 6 h, and then were cold-isostatically pressed at the pressure of 50 MPa to form cylindrical compact (20 mm in diameter and 10 mm in length). The compacts were then heated at the rate of 20°C/min to the designed temperature (250, 350, 450, 550, 650 and 750°C) and held at that temperature for about 20 min under the protection of high purity argon gas.

Industrially pure Mg ingot (99.85 wt% purity) and Si (99.95 wt% purity) were used as starting materials to prepare Mg–4Si alloy. Detailed preparation of Mg–Si alloy was described in our previous study.⁷⁾ About 300 g of Mg–4Si alloy was remelted at 800°C in a graphite crucible in an electric resistance furnace under the protection of a mixed gas atmosphere of SF₆ (1%, v/v) and CO₂ (Bal.). After holding for 5 min, the Mg–30B compacts sintered at 250°C was added to the melts to get the designed composition of Mg–4Si alloys with different B contents of 0.2 and 1.0 wt%, respectively. The melts were manually stirred for about 3 min using a stainless steel impeller. After that the melts were poured into a steel mold preheated at 150°C to produce rectangular samples of 12×40×95 mm³. The chemical compositions, as measured with an ARL 4460 Metals Analyzer, of the alloys are shown in **Table 1**. Metallographic samples were cut at the same position of the rectangular samples and were prepared in accordance with standard procedures used for metallographic preparation of metal samples. Then the samples were deeply etched with a mixture of 1 vol% HNO₃+2 vol% HCl alcohol solution for about 6 h.

Microstructure and phase analyses were investigated by using scanning electron microscopy (SEM) (Model JSM-5310, Japan) equipped with energy-dispersive spectrometer (EDS) (Model Link-Isis, Britain) and X-ray diffraction (XRD) (Model D/Max 2500PC Rigaku, Japan). Grain size of the primary Mg₂Si was estimated by the line intercept method under low magnification of the microstructures.

3. Results and Discussion

Figure 1 shows the XRD patterns of the unsintered and sintered Mg–30B compacts. The XRD result reveals only Mg phase in the unsintered and sintered Mg–30B compacts at the temperatures of 250, 350 and 450°C, as shown in Figs. 1(a)–1(d). The B phase is not detected by XRD in

Table 1. The Si content of the Mg–Si alloys (wt%).

Designed compositions	Measured compositions	
	Si	Mg
Mg-4Si	4.06	
Mg-4Si-0.2B	4.27	Bal.
Mg-4Si-1.0B	4.22	

these compacts, for B is in an amorphous state. It is suggested from Figs. 1(b)–1(d) that B can not react with Mg in the temperature range between 250 and 450°C. Therefore, the Mg–30B modifier, namely, Mg–30B compact sintered at 250°C, only consists of Mg and B phases. Note that XRD pattern of the Mg–30B compacts sintered at 550, 650 and 750°C (Figs. 1(e)–1(g)) will be discussed later.

Figures 2(a)–2(c) show the SEM micrographs of Mg–4Si alloys with 0, 0.2 and 1.0 wt% B additions, respectively. The XRD result reveals that there are only Mg and Mg₂Si phases in these alloys, as shown in **Fig. 3**. No B-containing phase is detected by XRD due to the low content of B. Without B addition, the primary Mg₂Si exhibits dendritic or polyhedral shape with the average size of ~40 μ m (Fig. 2(a)). When the B content is only 0.2 wt%, there is a significant change in the morphology and size of primary Mg₂Si in Mg–4Si alloys. The primary Mg₂Si transforms into the fine polyhedral shape with the average size of ~11 μ m (Fig. 2(b)). When the B content further increases to 1.0 wt%, the primary Mg₂Si still exhibits modified morphology as fine polyhedral shape (~11 μ m or less), as shown in Fig. 2(c). It is worth noting that 1.0 wt% B addition does not result in the overmodification of the primary Mg₂Si in alloys. From Fig. 2, it is concluded that the modification effect of B on the primary Mg₂Si is very remarkable in Mg–4Si alloys.

To investigate the modification effect of B on the primary Mg₂Si at a relatively low cooling rate, the unmodified and

0.35 wt% B modified Mg–4Si alloys are poured into the sand mold to produce cylindrical samples of Φ 20 mm, respectively. **Figure 4** shows SEM micrographs of the unmodified and modified Mg–4Si alloys. It is interesting to note from Fig. 4(a) that the morphology of the primary Mg₂Si is very coarse dendritic shape (even more than 200 μ m). However, with 0.35 wt% B addition, the primary Mg₂Si exhibits small polyhedral shape (about 50 μ m or less), as shown in Fig. 4(b). This result suggests that the modification effect of B on the primary Mg₂Si is still good at a relatively low cooling rate.

The Mg–4Si alloy with 0.2 wt% B addition is remelted at 800°C and held for 5 min at that temperature in order to study the heredity of B modification, and the result is shown in **Fig. 5**. When the remelting process is 0 time, the average size of the primary Mg₂Si is ~11 μ m. When the remelting process increases from 1 to 4 times, the average size of the primary Mg₂Si varies from ~12 to ~11 μ m. This result suggests that Mg–B modifier possesses good modification heredity during the remelting process.

The XRD patterns of sintered Mg–30B compacts at the temperature of 550, 650 and 750°C are shown in Figs. 1(e)–1(g). When the sintering temperature is 550°C, a small amount of MgO phase forms in the compact due to the poor protection atmosphere (Fig. 1(e)). When the sintering temperature further increases to 650 or 750°C, besides MgO phase, also the MgB₂ phase is identified in the products (Figs. 1(f), 1(g)). It is worth noting that it is difficult for these compacts to dissolve in the melts because of the formation of MgO and/or MgB₂. Thus, the Mg–30B compacts, sintered at the temperature range of 250–450°C, can be developed as a new modifier for Mg–high Si alloy. Based on the sintering experiment (Figs. 1(f), 1(g)), B can

Fig. 1. XRD patterns of (a) unsintered and sintered Mg–30B compacts at the temperatures of (b) 250, (c) 350, (d) 450, (e) 550, (f) 650 and (g) 750°C.

Fig. 3. XRD patterns of Mg–4Si alloys with (a) 0, (b) 0.2, (c) 1.0 wt% B additions.

Fig. 2. SEM micrographs of Mg–4Si alloys with (a) 0, (b) 0.2 and 1.0 wt% B additions.

Fig. 4. SEM micrographs of Mg-4Si alloys with (a) unmodified and (b) modified by 0.35 wt% B (sand mold).

Fig. 5. The effect of remelting process on the size of primary Mg₂Si in Mg-4Si alloy with 0.2 wt% B addition.

be introduced to the melts in the form of Mg-30B modifier at 800°C. According to the previous study,^{7,15)} the mechanism of B modification is attributed to the adsorption and poison manners. Besides, from the fact that the amount of the primary Mg₂Si considerably increases with the addition of Mg-B modifier (Figs. 2 and 4), it can be deduced that the accelerated nucleation of Mg₂Si may occur during solidification. This result is similar to the mechanism of KBF₄ modification on the primary Mg₂Si in Mg-5Si alloy.¹⁵⁾

4. Conclusions

(1) The Mg-30B modifier with the composition of Mg and B phases, sintered in the temperature range between 250 and 450°C, has been developed as a new modifier for Mg-high Si alloy.

(2) Addition of B has a significant effect on the morphology and size of the primary Mg₂Si in Mg-4Si alloys. The primary Mg₂Si transforms from large dendritic shape (~40 μm) in unmodified alloys into the fine polyhedral shape (~11 μm) in alloys modified with 0.2–1.0 wt% B. In

addition, B still has a good modification effect on the primary Mg₂Si at a relatively low cooling rate.

(3) The size of the primary Mg₂Si hardly varies after the remelting process reaches 4 times, suggesting that B modification possesses good heredity.

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