Modification of Mg$_2$Si in Mg–4Si Alloys with B

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1. Introduction

Under the traditional casting conditions, the microstructures of hypereutectic Mg–Si alloys usually consist of large primary Mg$_2$Si dendrite and brittle eutectic phases, which greatly deteriorate the mechanical properties of alloys. Grain refinement or modification is an important practice to improve the properties of magnesium alloys. Some studies were focused on the modification of coarse Mg$_2$Si phase in magnesium alloys. It has been reported that addition of Ca or P can modify the morphology of the eutectic Mg$_2$Si phase from Chinese script type to refined polygonal type in Mg–5Al–1Zn–0.7Si alloys. However, Yuan et al. have claimed that addition of P can produce ignition and result in large quantity of smoke. Additionally, the modification effect of Sb is much better than that of Ca in Mg–5Al–1Zn–1Si alloy.

Recent studies indicate that both KBF$_4$ salt and Y rare earth can modify the primary and eutectic Mg$_2$Si in hypereutectic Mg–Si alloy by absorption and poisoning mechanism. Furthermore, the modification effect of KBF$_4$ on the Mg$_2$Si phase is more effective than that of Y in Mg–5Si alloys. Unfortunately, the KBF$_4$ addition is bad for environmental protection and dangerous because of the production of the smoke and sputter. Moreover, the excessive KBF$_4$ 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 master alloys are widely used as grain refinement agents in the casting of Al–Si alloys due to the powerful grain refining ability. Wang et al. have concluded that the addition of B can refine eutectic Si since AlB$_2$ particles can act as nucleation substrates for Si. Nogita et al. 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. have found that α-Al dendrites and eutectic clusters were significantly refined by the addition of B. Unfortunately, the modification of Mg$_2$Si 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 Mg$_2$Si 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, ~106 μm) and B (98.0 wt% purity, ~3 μm) 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. 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 SF$_6$ (1%, v/v) and CO$_2$ (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 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 Mg–4Si alloys with different B contents of 0.2 and 1.0 wt%, respectively.

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 Mg$_2$Si 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

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

Table 1. The Si content of the Mg–Si alloys (wt%).
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 Mg$_2$Si 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 Mg$_2$Si exhibits dendritic or polyhedral shape with the average size of ~40 μm (Fig. 2(a)). When the B content is only 0.2 wt%, there is a significant change in the morphology and size of primary Mg$_2$Si in Mg–4Si alloys. The primary Mg$_2$Si transforms into the fine polyhedral shape with the average size of ~11 μm (Fig. 2(b)). When the B content further increases to 1.0 wt%, the primary Mg$_2$Si still exhibits modified morphology as fine polyhedral shape (~11 μm 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 Mg$_2$Si in alloys. From Fig. 2, it is concluded that the modification effect of B on the primary Mg$_2$Si is very remarkable in Mg–4Si alloys.

To investigate the modification effect of B on the primary Mg$_2$Si 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 φ20 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 Mg$_2$Si is very coarse dendritic (even more than 200 μm). However, with 0.35 wt% B addition, the primary Mg$_2$Si exhibits small polyhedral shape (about 50 μm or less), as shown in Fig. 4(b). This result suggests that the modification effect of B on the primary Mg$_2$Si 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 Mg$_2$Si is ~11 μm. When the remelting process increases from 1 to 4 times, the average size of the primary Mg$_2$Si varies from ~12 to ~11 μm. 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 MgB$_2$ 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 MgB$_2$. 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
be introduced to the melts in the form of Mg–30B modifier at 800°C. According to the previous study, the mechanism of B modification is attributed to the adsorption and poisoning manners. Besides, from the fact that the amount of the primary Mg$_2$Si considerably increases with the addition of Mg–B modifier (Figs. 2 and 4), it can be deduced that the accelerated nucleation of Mg$_2$Si may occur during solidification. This result is similar to the mechanism of KBF$_4$ modification on the primary Mg$_2$Si in Mg–5Si alloy.

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 Mg$_2$Si in Mg–4Si alloys. The primary Mg$_2$Si 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 Mg$_2$Si at a relatively low cooling rate.

(3) The size of the primary Mg$_2$Si hardly varies after the remelting process reaches 4 times, suggesting that B modification possesses good heredity.

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