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Nucleating role of an effective in situ Mg_3P_2 on Mg_2Si in Mg–Al–Si alloys

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ABSTRACT

Refinement and modification effects of the Al–3.5P master alloy on Mg_2Si phases in Mg–4Al–2Si alloys were studied in this work. Mg_2Si phases in Mg–4Al–2Si alloys can be modified well at 740 °C with the addition of 1.5% Al–3.5P master alloy. The mean size of primary Mg_2Si decreases from about 70 μm to less than 15 μm, and the morphology changes from coarse dendritic or equiaxed to polygonal shape. In addition, the amount of eutectic Mg_2Si obviously decreases and the morphology changes from coarse Chinese script to fine fiber shape. XRD and EPMA results show that a reaction between AlP and Mg occurs in the melt forming a new Mg_3P_2 phase which serves as the heterogeneous nucleation substrates of Mg_2Si.

1. Introduction

With the rapid development of the automotive industry, demands for the light weight, low fuel consumption and exhaust emission are becoming increasingly urgent these years. Magnesium alloys and their composites, as the lightest structural alloys, have great potential for applications in the automobile and aerospace industries [1,2]. Meanwhile, improving the elevated temperature properties of magnesium alloys has become a critical issue for the further application. Many previous investigations show that the Mg–Al–Si alloy is a kind of potential elevated temperature magnesium alloy. It is known that the intermetallic compound Mg_2Si exhibits a high melting temperature of 1085 °C, low density of $1.99 \times 10^3\ \mathrm{kg\,m^{-3}}$, high hardness of $4.5 \times 10^9\ \mathrm{Nm^{-2}}$, a low thermal expansion coefficient of $7.5 \times 10^{-6}\ \mathrm{K^{-1}}$ and a reasonably high elastic modulus of 120 GPa [3,4]. Whereas, undesirable coarse dendritic primary Mg_2Si and brittle Chinese script eutectic phases are prone to forming in Mg–high Si alloys under a low solidification rate. As a result, it will lead to a detrimental effect on the mechanical properties of the alloys since long cracks can easily form along the interface between Mg_2Si and α-Mg matrix.

Various researches are aimed at improving the mechanical properties of Mg_2Si reinforced Mg- and Al-based alloys through processes, such as hot extrusion [5], rapid solidification [6] and mechanical alloying [4,7]. However, compared with the above-mentioned techniques, modification treatment is a more cost-effective processing technique and available for generally commercial application. Much work has been focused on the modification effects of rare earth [8], KBF_4 [9,10], Sr [11], Sb [12,13], Bi [14], Ba [15], Ca and P [16] on the primary and eutectic Mg_2Si in magnesium alloys. However, it was reported that certain internal defects exist. For example, although KBF_4 has a good effect on the modification of Mg_2Si phase in Mg–5Si alloys, a large quantity of smoke and sputter [9,10] is produced, which is harmful to the surrounding environment. Besides, Bi [14] and Ba [15] can modify and refine the primary Mg_2Si, but the Mg_2Si phase becomes coarse again when the adding amount exceeds a limit.

In the present study, the modification effects of the environment-friendly Al–P master alloy on the size and morphology of Mg_2Si phases in Mg–4Al–2Si alloys were investigated. And the modification mechanism of P-containing modifier on Mg_2Si phase was also discussed.

2. Experimental procedures

Commercial pure Mg (99.8%, all compositions quoted in this work are in wt.% unless otherwise stated) and Al–33.3Si ingots were used as raw materials to prepare the designed Mg–4Al–2Si alloys. Mg ingots were melted and heated up to 740 °C in a preheated stainless steel crucible in a 5 kW electric resistance-heating furnace under the protection of flux (mixture of $MgCl_2$, KCl, $BaCl_2$, CaF_2 and NaCl + $CaCl_2$). After 30 min, the Al–33.3Si master alloys were submerged deeply into the Mg melts and held for 1 h, and then the starting materials were got. The Al–33.3Si master alloys used in the experiment were produced by a 25 kW medium frequency induction furnace using commercial pure Al (99.7%) and commercial pure crystalline Si (99.9%). The Al–3.5P master alloy was supplied by Shandong Shanda Al&Mg Melt Technology Co. Ltd.

In order to identify the modification effect of the Al–3.5P master alloy on Mg_2Si phases, various parameters of the modification process were considered. The Mg–4Al–2Si alloys were remelted before the refinement and modification experiments. After the addition of Al–3.5P master alloy, the melt was stirred for 30 s for homogenization and held for a certain minutes. Then, the slag was cleaned and the melt was poured into a cylindrical steel mold to produce the castings with

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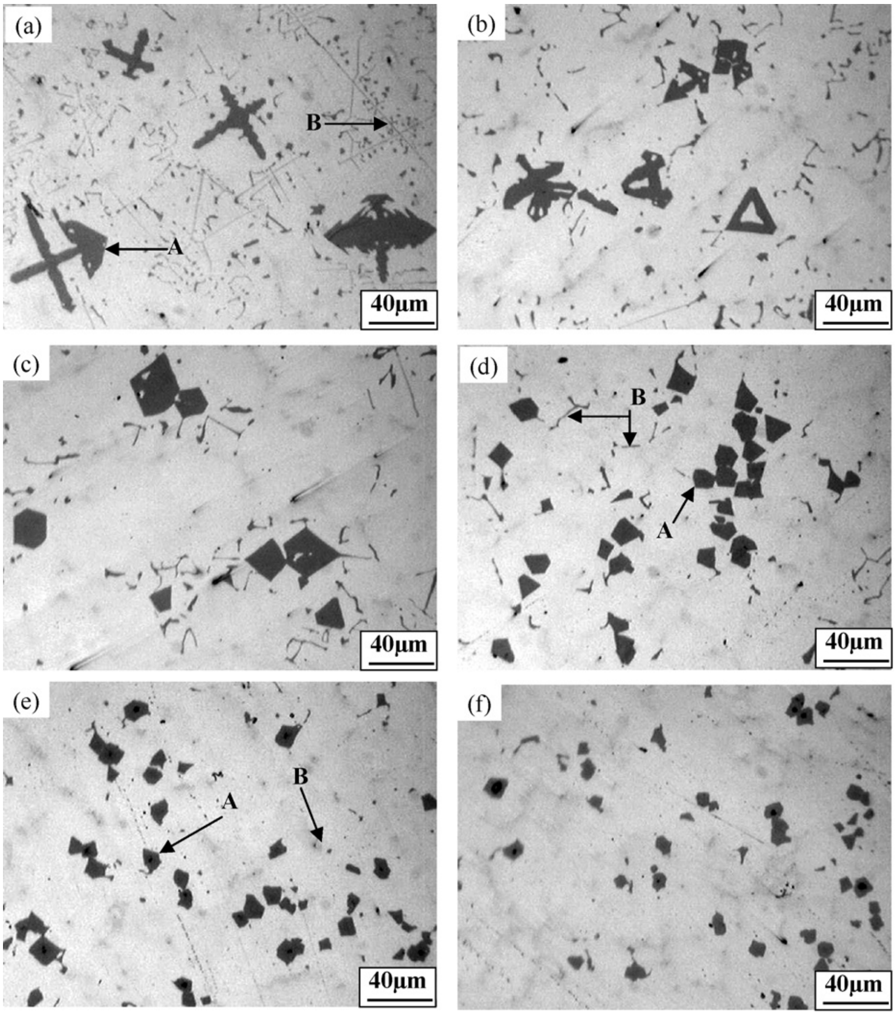


Fig. 1. Microstructures of Mg–4Al–2Si alloy by adding different amounts of Al–3.5P master alloys at 740 °C (a) without addition; (b) with addition of 0.5% Al–3.5P; (c) with addition of 1.0% Al–3.5P; (d) with addition of 1.5% Al–3.5P; (e) with addition of 2.5% Al–3.5P; and (f) with addition of 4.5% Al–3.5P.

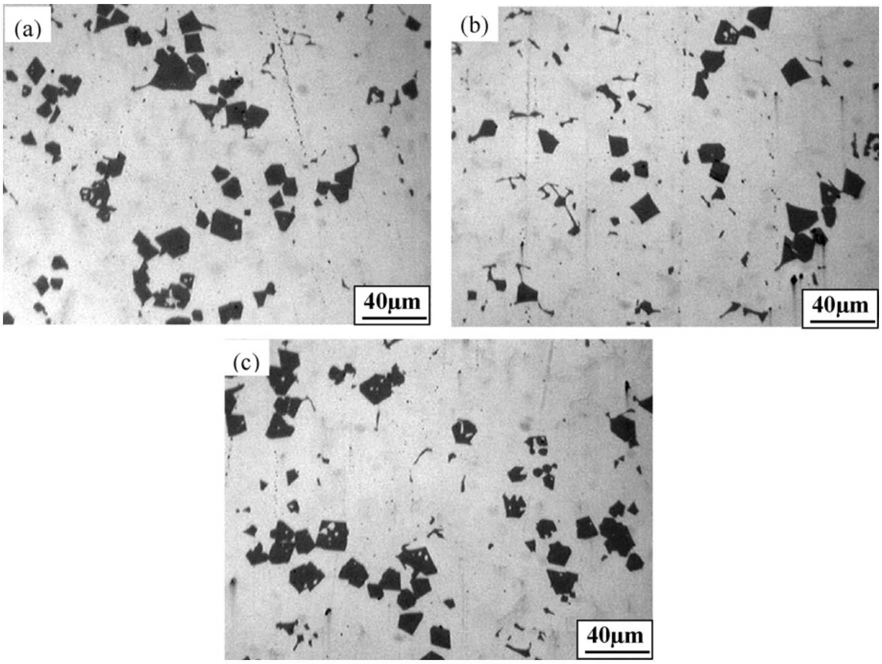


Fig. 2. Microstructures of Mg–4Al–2Si alloys modified by adding 1.5% Al–3.5P master alloy and holding for 30 min at different temperatures: (a) at 690 °C; (b) at 740 °C; and (c) at 790 °C.

25 mm in diameter and 80 mm in length. The experiments of first group are to treat Mg–4Al–2Si alloys with different amounts of Al–3.5P master alloys (0, 0.5, 1.0, 1.5, 2.5 and 4.5%) at 740 °C for 30 min. The second group of experiments is to refine the Mg–4Al–2Si alloys with 1.5% Al–3.5P master alloy at different temperatures (690, 740 and 790 °C) and hold the melts for 30 min. The third group of experiments is to hold the alloys at 740 °C for 10, 30, 60 and 120 min after the addition of 1.5% Al–3.5P master alloy, respectively. The melts were poured into the same type of steel mold preheated to about 100 °C to produce the samples.

To define the phase which serves as the heterogeneous nucleation substrates of Mg_2Si, a verification test was designed by adding 8% Mg and 2% crystalline Si into the melted Al–3.5P master alloy at about 800 °C in the high frequency furnace for a few minutes. Phase identifications were studied by X-ray diffraction (XRD, Rigaku D/max-rB, Japan).

All metallographic specimens were cut at the same position of cylindrical samples, and then mechanically ground and polished. The microstructure analysis was conducted using a high scope video microscope (HSVM) (KH-2200MD2, Japan), a field emission scanning electron microscope (FESEM) (SU-70, Japan) and electron probe micro-analyzer (EPMA) (JXA-8840, Japan). The tensile test bars were machined to 'dog-bone' type specimens and the tensile strengths at room temperature were tested by a universal testing machine (model CMT700, China).

3. Results and discussion

3.1. The melt treating technological parameters of Al–P master alloy

3.1.1. Effect of addition level of Al–3.5P master alloy on the microstructure of Mg–4Al–2Si alloy

The optical microstructures of Mg–4Al–2Si alloy before and after adding different amounts of Al–3.5P master alloys at 740 °C are presented in Fig. 1. It can be observed clearly from Fig. 1(a) that the typical microstructure of coarse dendritic primary Mg_2Si crystals (marked as A) and Chinese script eutectic Mg_2Si structures (marked as B) exist in the unmodified Mg–4Al–2Si alloy. Furthermore, their distribution is inhomogeneous, the primary Mg_2Si aggregates in a small area and eutectic Mg_2Si is widely distributed in the matrix, which would seriously dissever the matrix and leads to poor properties. Fig. 1(b)–(d) shows that a favorable modification effect is obtained with the amount of Al–3.5P master alloy increases from 0 to 1.5%. The average size of primary Mg_2Si in the alloy decreases from about 70 μm to less than 15 μm and the morphology changes to regular polygonal shape (marked as A). Meanwhile, the coarse Chinese script eutectic Mg_2Si changes to fine fiber shape (marked as B) and the amount decreases evidently, which is beneficial to mechanical properties of the alloy. As shown in Fig. 1(e) and (f), Al–3.5P master alloys exhibit no over-modified effect on primary Mg_2Si, the mean size of Mg_2Si keeps decreasing even when the content of Al–3.5P master alloy further increases to 4.5%, and the morphology remains unchanged. This phenomenon is very different from many other modifiers, such as Y, Bi and Ba in Mg_2Si/Mg alloys [8,14,15].

3.1.2. Effect of modification temperature on the microstructure of Mg–4Al–2Si alloy

Fig. 2 shows the microstructures of Mg–4Al–2Si alloys at different temperatures by adding 1.5% Al–3.5P master alloy and holding for 30 min. In Fig. 2(a), the size of primary Mg_2Si decreases evidently when alloys are modified at 690 °C, while most of Mg_2Si phases exhibit aggregation in the matrix. When the melting treating temperature increases to 740 °C, a satisfactory effect is obtained and the average size of primary Mg_2Si decreases to 15 μm or less, as seen in Fig. 2(b). While, an opposite effect appears when temperature increases to 790 °C, the primary Mg_2Si becomes coarse again as shown in Fig. 2(c).

It proves that melt treating temperature is an important factor for phosphorus modification process. The modifier will exist as coagulation which cannot dissolve completely and diffuse uniformly in the melt at a low temperature, thus it cannot obtain a favorable refinement and modification effect. If the modification temperature is too high, it will lead to the oxidation of melting alloy and increase suction gas which is adverse for the modification process.

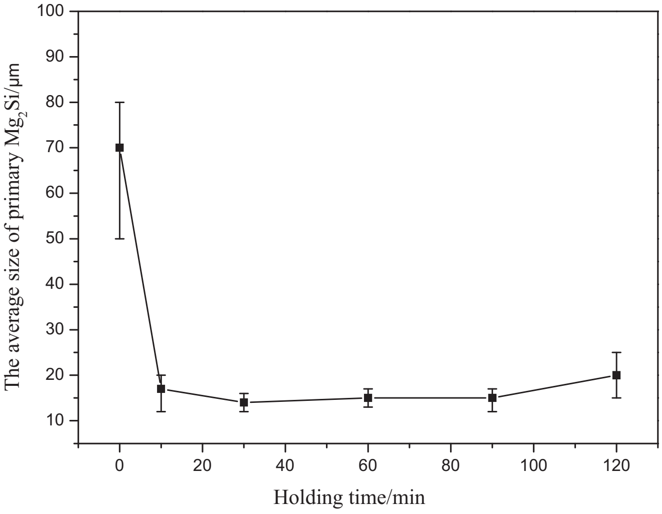


Fig. 3. Relation between the average size of primary Mg_2Si in modified Mg–4Al–2Si alloys and holding time.

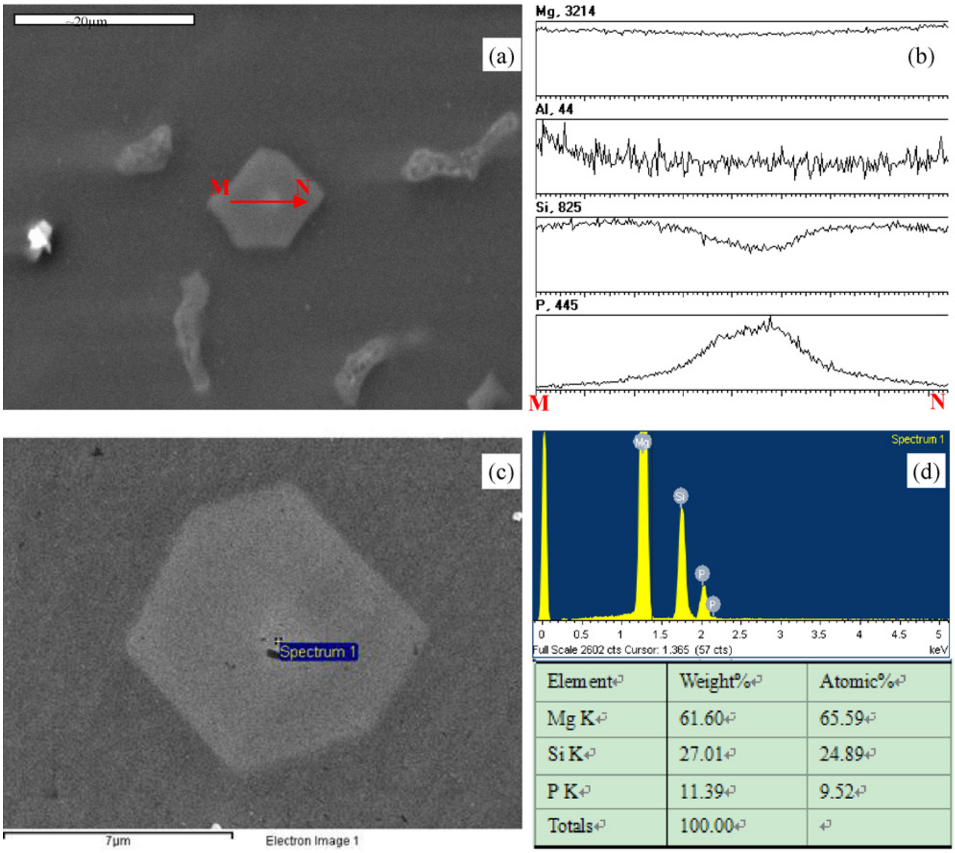
3.1.3. Effect of holding time on the modification performance of Al–3.5P master alloy

Fig. 3 presents the variations of the average size of primary Mg_2Si in Mg–4Al–2Si alloys after different holding time with 1.5% Al–3.5P master alloy at 740 °C. It is pleased to show that even when the alloy is held for only 10 min, the size of primary Mg_2Si decreases obviously to less than 15 μm. A satisfactory effect is obtained when being held for 30 min under the same condition as others. A good refinement and modification effect is still maintained with increasing holding time to 60 min. In fact, the modification effect of Al–3.5P master alloy is very stable, which means that the modification effect exhibits less fading with a long holding time to 1.5 h or even after remelting.

3.2. The modification mechanism of Al–3.5P master alloy in the melt-treating process

The modification of P on primary Si [17,18] in Al–Si melt has been studied a lot and it is well known that AlP has the similar lattice parameter and low disregistry with Si, so it was suggested to be the active ingredient in the refinement of primary Si particles. Besides, AlP has a good lattice matching coherence relationship with Mg_2Si, and it can act as the nuclei achieving the refinement of the primary Mg_2Si in Al–Mg_2Si alloys [19]. However, little research has been carried out on the effect in the Mg-based alloys. What is more, the behavior of P added into Mg alloys is still unclear.

Detailed FESEM and EPMA analyses of possible nucleation sites in the modified Mg–4Al–2Si alloy are shown in Fig. 4. It is obvious that a white tiny particle locates in the center of the polygonal primary Mg_2Si which acts as the nucleus of the primary Mg_2Si. The complete element distribution along the line from M to N across the primary Mg_2Si is illustrated in Fig. 4(b). The result shows that there is a peak of P accompanied by the decrease of Si, whereas the content of Mg basically has no significant decrease in Mg_2Si. In order to confirm the exact composition of the nucleus, EDS test is shown in Fig. 4(d), which reveals that this particle probably consists of Mg, Si and P elements. It is quite possible that the Mg and Si peaks are inevitably from the matrix of Mg_2Si. Therefore, after excluding the portion of Mg in Mg_2Si, the atomic ratio of the Mg/P is close to 3:2. According to the spectrum analysis, it is preliminary deduced



Element	Weight%	Atomic%
Mg K	61.60	65.59
Si K	27.01	24.89
P K	11.39	9.52
Totals	100.00	

Fig. 4. EPMA and FESEM analyses of nucleation sites in modified Mg–4Al–2Si alloys: (a) EPMA back-scattered electron (BSE) micrograph of a nucleation site; (b) chemical composition distribution along M–N; (c) FESM secondary electron (SE) micrograph of another nucleation site; and (d) EDS spectra of the white tiny particle in center.

that the Mg_3P_2 compounds act as nucleating sites of Mg_2Si during solidification.

Based on the above analyses, a chemical reaction must have happened after the addition of the Al–3.5P master alloy during the modification process. The products of the verification test by adding Mg and Si into the melted Al–3.5P master alloy are detected by XRD, as shown in Fig. 5. It shows in Fig. 5(a) that Al and AlP existed in the Al–3.5P master alloy. After the additions of Mg and Si in the master alloy, it proves that besides the production of Mg_2Si, AlP is replaced by a new formed Mg_3P_2 phase which can exist steadily in the alloy, as shown in Fig. 5(b). It can be seen that the analysis result coincides with that shown in Fig. 4(d).

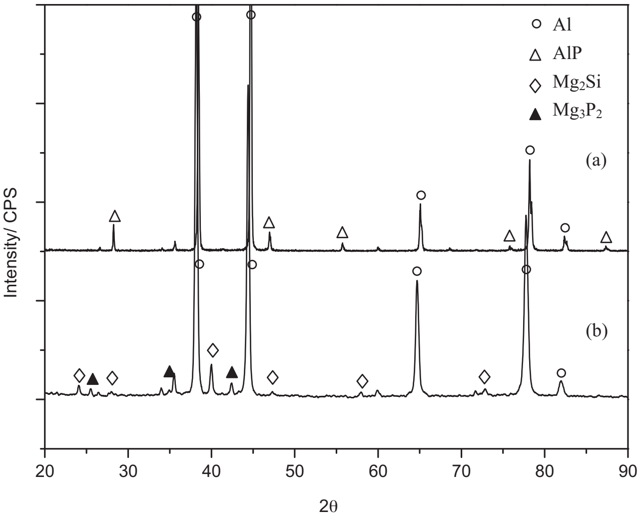


Fig. 5. XRD patterns of (a) Al–3.5P; (b) Al–3.5P with 8% Mg and 2% Si.

Qin et al. [20] and Zhang et al. [21] believed that when AlP is added into the melt, the chemical potential of Al and P atoms in AlP becomes higher than that in the melt, which lead to the instability of AlP. A large driving force would actuate the Al and P atoms to diffuse into the melts. Due to the thermal motion of the melt, AlP resolves and then dissolves following the diffusion and transference of the atoms in the melt, thus the dissolution reaction of AlP takes place, as shown in reaction (1). Since the standard free energy of formation of Mg_3P_2 is lower than AlP [22,23], it is deduced that Mg_3P_2 is easier to be formed and more stable than AlP. So after P atoms entering the melt, another reaction happens and produces the Mg_3P_2 phases, as shown in reaction (2):

$$AlP(s) \rightarrow [Al] + [P] \tag{1}$$

$$3[Mg] + 2[P] \rightarrow Mg_3P_2(s) \tag{2}$$

In other words, when P atoms dissolve into the Mg melts, they will capture the surrounding Mg atoms to form Mg_3P_2, and push Al atoms into Mg melts. On the other hand, Al has a large solubility in Mg melts, which creates a more favorable condition for reaction (1). Then the dynamical equilibrium tends to move to the right because of the decrease of P and Al atoms around the AlP particles. Meanwhile, due to the lower solubility of phosphorus and the density difference, Mg_3P_2 precipitation reaction i.e. reaction (2) carries out very fast. In this way, it is reasonable that the Mg_3P_2 particles can contribute to the refinement of Mg_2Si well in a short time of 10 min.

Therefore, it is concluded that the formation of Mg_3P_2 particles will undergo the following process: dispersion of AlP crystals → dissolution of AlP → reaction → Mg_3P_2 clusters → small particles of Mg_3P_2. It is deduced that the addition of Al–3.5P master alloy in the Mg–4Al–2Si alloy conduces the formation of Mg_3P_2 particles which induce the precipitation of dendritic primary Mg_2Si and achieves the refinement of the dendrite.

When the temperature cools to the liquidus temperature, the primary Mg_2Si begins to precipitate by attaching to the generated particles of Mg_3P_2. When it cools to the eutectic temperature, it is easier for the eutectic Mg_2Si to nucleate and grow on the surface of the first precipitated Mg_2Si. So there is no Chinese script eutectic Mg_2Si existed basically. Furthermore, because the in situ formation of Mg_3P_2 is very small and evenly distributed in the melt, the crystal of Mg_2Si can also uniformly distributed in the matrix. Given a proper inducement temperature and holding time, a satisfactory effect can be achieved, not only the size and morphology but also the distribution of Mg_2Si phases in the matrix.

Compared with the unmodified Mg–4Al–2Si alloys which reveal a low ultimate tensile strength (UTS) is about 115.65 MPa, the UTS of sub-modified Mg–4Al–2Si alloys (with 0.5% Al–3.5P master alloy) increases to 128.94 MPa. Meanwhile, the UTS of Mg–4Al–2Si alloys (with 1.5% Al–3.5P master alloy) which show fully modified microstructures increases to 138.65 MPa with mean size of the primary Mg_2Si decreasing from about 70 μm to less than 15 μm.

It can be concluded that the modification mechanism is attribute to the formation of Mg_3P_2 particles in the melt which serves as the effective nucleating substrates of Mg_2Si. However, the exact modification mechanism of eutectic Mg_2Si phase needs further study. Such information of chemical transformation from AlP to Mg_3P_2 after the addition of the Al–3.5P master alloy in Mg melt may help to enrich the refinement technology of Mg–Si alloys and broaden application range of P-containing modifier in industry production process.

4. Conclusions

(1) Al–3.5P master alloy has a significant modification effect on the Mg_2Si in the Mg–4Al–2Si alloys. The chemical reaction between AlP and Mg in Mg melt produces the more stable in situ Mg_3P_2 compounds which can serve as the heterogeneous nucleation sites of Mg_2Si and contribute to the refinement of primary Mg_2Si.

(2) The addition level of Al–P master alloy and inducement temperature play very important roles for the modification of Mg_2Si phases in the melt-treating process. A favorable modification effect occurs with the increasing addition level of Al–3.5P master alloy at about 740 °C. When the content of Al–3.5P increases from 0 to 1.5%, the morphology of primary Mg_2Si change from coarse dendritic or equiaxed to polygonal shape and the size decreases from about 70 μm to less than 15 μm. Meanwhile the amount of eutectic Mg_2Si phase obviously decreases and the morphology changes from coarse Chinese script to fine fiber shape. Further increasing the addition of Al–3.5P master alloy to 4.5%, the mean size of Mg_2Si continues to decrease.

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