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The investigation of continuous nucleation and refinement of primary Si in Al–30Si mushy zone

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ABSTRACT

In this paper, the refinement performance of Al–P master alloy on mushy Al–30Si alloys was investigated and a new refining method was proposed. The results show that primary Si can be refined partially when the Al–P master alloy is added into mushy Al–30Si alloys, proving that the heterogeneous nucleation of primary Si is a continuous process even in liquid–solid state, which is also confirmed by EPMA results. On basis of these results, a new refining method named as continuous refining method has been proposed, i.e. continuously adding refiners at different temperatures during the cooling and solidifying stage of Al–30Si. Compared with the conventional refinement method by which the alloys are refined at high temperature, better refinement effect can be obtained in the new refinement method: the average size of primary Si is decreased to 30 μm, and the tensile strength increases by 19.6%. Moreover, the mechanism of the continuous refining method was also discussed.

1. Introduction

Aluminum alloy is one category of casting materials which is the second most widely applied after ferrous castings in tonnage terms, and among all aluminum alloys the hypereutectic Al–Si alloys are catching more and more attention as the appropriate material for pistons of gas engines due to their high wear resistance, low density, low coefficient of thermal expansion, high thermal stability, corrosion resistant and thermal conductivity, etc. [1–5]. These properties can be effectively improved by further increasing the silicon content of the alloys. However, the main limitation of hypereutectic Al–Si alloys is attributed to the presence of coarse, irregular and brittle primary Si that easily cracks exposing the soft aluminum matrix to extreme working conditions. So it is deservedly essential for primary Si to improve the morphology, decrease the size and uniformize the distribution. Recently the microstructure of hypereutectic Al–Si alloys can be refined by refiner addition [6–11], melt vibration [12–15], pulse treatment [16], etc., among which phosphorus-containing refiner addition is widely applied in practice. Among all phosphorus-containing refiners, the Al–P master alloy developed these years is able to overcome the shortcomings of other phosphorus-containing refiners (Cu–P master alloy or phosphate salt) such as environmental pollution and instable refinement efficiency, etc., and now has obtained a good application [11].

It is known that the refinement effect of Al–P master alloy is influenced by several melting parameters, such as temperature, holding time etc. Recently the conventional technique that adding refiner at high temperatures (100 °C above liquidus temperature) is widely applied [10]. By using this technique it is possible to achieve significant refinement effect. However, high temperature can increase suction gas and oxidation of the melted alloys [6], which are wasteful of raw-materials and energies. In this article, it is aimed to explore a new method to refine hypereutectic Al–Si alloys in the mushy zone particularly below the liquidus temperature to avoid the aforementioned problems, and the refinement mechanism is discussed. In addition, the continuous refining method, which means that the refiners are continuously added at different temperatures during the cooling and solidifying stage of Al–30Si alloys, is also proposed.

2. Experimental procedures

The Al–30Si alloy used in the experiments was prepared with commercial pure Al (99.7%, all compositions quoted in this article are in wt.% unless otherwise stated) and commercial pure crystalline Si (99.9%) in 25 kW medium-frequency induction furnace, and the Al–3.5P binary master alloy rod (the composition is given in Table 1.) was supplied by Shandong Al&Mg Melt Technology Co. Ltd. Different refinement experiments were all conducted in 5 kW electric resistant-heating furnace. The melt temperatures were controlled by the thermocouple in the resistant-heating furnace, and assisted by the K-model handset thermocouple, making sure that the error is controlled below ±5 °C. All the samples were poured into the same type of cast iron chill mold preheated at about 150 °C before pouring.

The Al–30Si alloys were re-melted in a clay-bonded graphite crucible using the electric resistant-heating furnace and held at 845 °C. The experimental parameters

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Table 1
The composition of Al–3.5P binary master alloy rod.[a].

	P	Other total	Al
Al–P master alloy rod	3.2–3.7	≤0.5	Bal.

[a] Supplied by Shandong Al&Mg Melt Technology Co. Ltd.

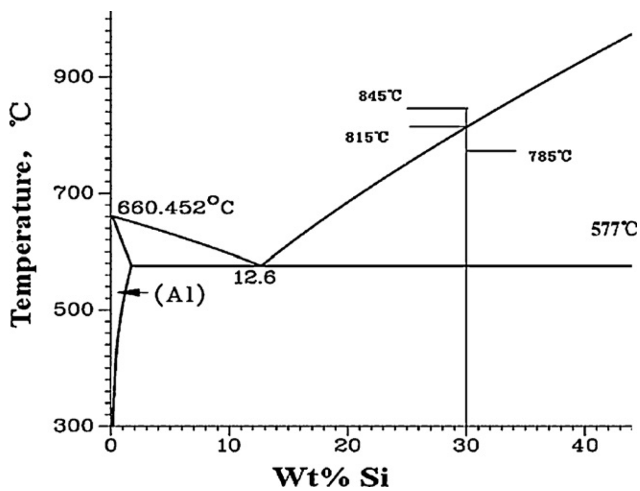

Fig. 1. Refinement temperatures based on Al–Si binary phase diagram.

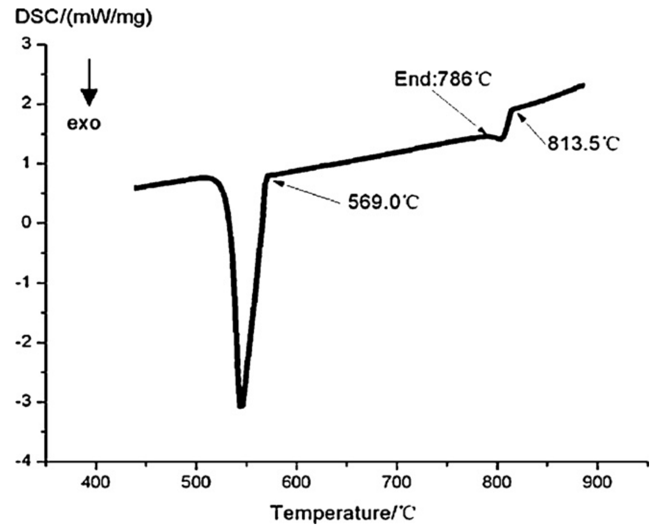

Fig. 2. DSC results for Al–30Si alloys.

were listed in Table 2. Part of the melt was poured into the iron chill mold and Sample-1 was obtained without any additions. Then, Sample-2 was obtained as follows: 1% the Al–P master alloy was added into the melt at the temperature of 845 °C, and after stirred by graphite rod, the melt was poured into the mold. Sample-3 was obtained in the same way as Sample-2 but at 785 °C based on Al–Si binary phase diagram in Fig. 1 and the DSC curve of Al–30Si in Fig. 2.

The processing parameters for the comparison between conventional and continuous methods were given in Table 3. The Al–30Si alloys were re-melted in the electric resistance-heating furnace at 845 °C. Sample-4 was obtained 20 min after the addition of 1% Al–P master alloy into the melt. However, Sample-5 was obtained after adding 0.4%, 0.3% and 0.3% of the Al–P master alloys at 845 °C, 815 °C, and 785 °C, respectively, without holding time. (The three temperature points were obtained through cooling in the air, and the cooling rate was about 2 °C/s.)

Metallographic specimens were all cut from the same position of the casting samples, then mechanically ground and polished using standard routines. The microstructures of primary Si in the investigated Al–30Si alloys were characterized using field emission scanning electron microscope (FESEM) (model SU-70, Japan) and analyzed using electron probe micro-analyzer (EPMA) (model JXA-8840, Japan).

3. Results

3.1. Refining performance of Al–P master alloy on mushy Al–30Si alloys

Fig. 3 shows that the microstructures of Al–30Si alloys under different refining conditions: as seen in Fig. 3(a), primary Si in unrefined Al–30Si alloys exhibits plate-like appearance and the size could reach 400 μm even more; the Sample-2 was obtained under the conventional refining condition (refined at 845 °C with 1% Al–P master alloy). An overwhelming number of primary Si is refined to approximately 50 μm and the morphology evolves from plate-like to blocky shape as shown in Fig. 3(b). Fig. 3(c) presents the microstructure of Al–30Si alloy refined at 785 °C. It is found that when 1% Al–P is added into the melt at 785 °C, part of primary Si phases are refined to approximately 30 μm, while most of primary Si are still in a large size and irregular morphology whose average grain size is about 180 μm, indicating that primary Si is not sufficiently refined under this condition. Fig. 4 shows the difference between the refining effects at the temperature 785 °C and 845 °C which are revealed by the average primary Si grain sizes and its volume fractions.

Table 2
The processing parameters in different refinement experiments.

Alloys designation	Processing parameters				
	845 °C	815 °C	785 °C	Holding time	Pouring temperature
Al–30Si					
Sample-1	–	–	–	–	845 °C
Sample-2	1% Al–P	–	–	–	845 °C
Sample-3	–	–	1% Al–P	–	785 °C

Table 3
The comparison of processing parameters between conventional and continuous methods.

Alloys designation	Processing parameters				
	845 °C	815 °C	785 °C	Holding time	Pouring temperature
Al–30Si					
Sample-4	1% Al–P	–	–	20 min	845 °C
Sample-5[a]	0.4% Al–P	0.3% Al–P	0.3% Al–P	–	785 °C

[a] The three melt temperature points in Sample-5 were obtained through cooling in the air.

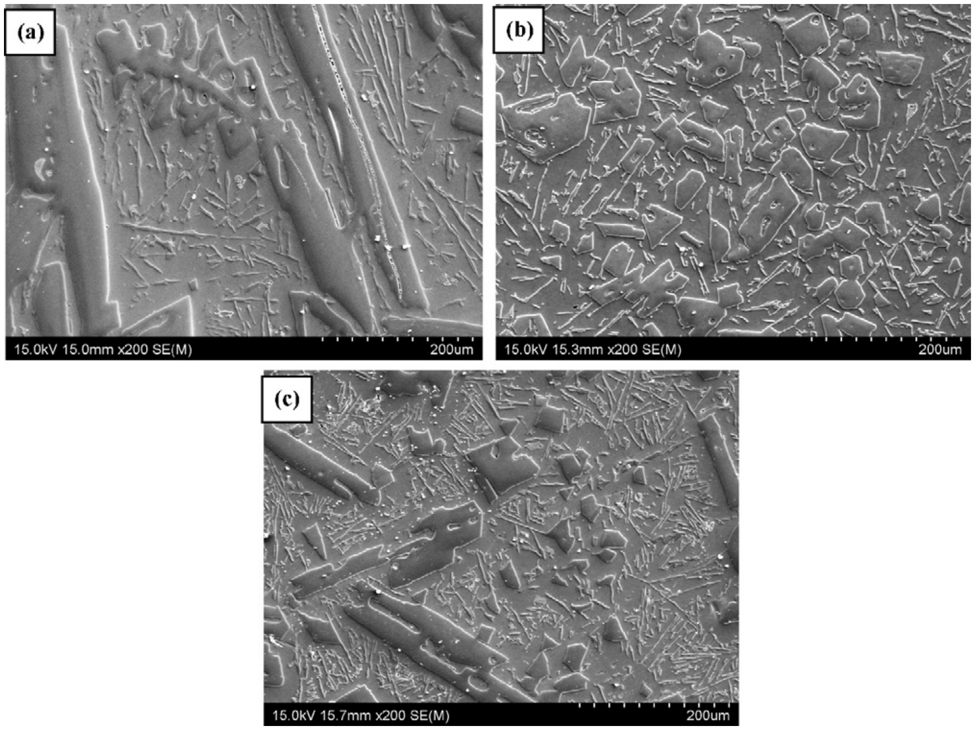

Fig. 3. Microstructures of the Al–30Si alloys under different refining conditions: (a) Sample-1; (b) Sample-2; (c) Sample-3.

Fig. 5 presents the EPMA analysis of a primary Si nucleus in Fig. 3(c). It is noted that the nucleus of primary Si contains Al and P elements which can be clearly recognized from the X-ray images. It proves that the AlP particles added at 785 °C for Al–30Si alloys are still able to play the roles of the heterogeneous nucleating substrate for primary Si.

As related to the DSC curve of Al–30Si alloys without any additions (Fig. 2), below the liquidus temperature the nucleation of primary Si has carried out. But in Fig. 5 it is manifested that when the AlP particles were added into the mushy Al–30Si, the heterogeneous nucleation are still going on, which demonstrates the existence of continuous heterogeneous nucleation.

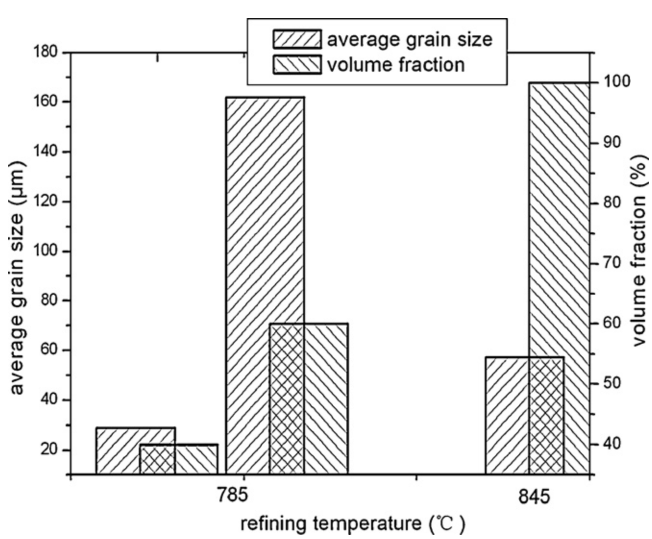

Fig. 4. The difference between the refining effects at the temperature 785 °C and 845 °C.

3.2. *The continuous refining method*

Fig. 6 shows the comparison of microstructures of Al–30Si alloys by different refining methods: when the Al–30Si alloys are treated by the conventional method, under which the alloys are refined at high temperature, the morphologies of primary Si change from plate-like shape (Fig. 3(a)) to fine blocky shape, and the size of primary Si ranges approximately from 40 μm to 60 μm as shown in Fig. 6(a). In comparison with Sample-4, Sample-5 was obtained by the continuous refining method. Statistical analysis shows that the average size of primary Si in Sample-5 is approximately 30 μm, which is smaller than that of Sample-4. Fig. 7 presents the effects of different refining methods on primary Si grain sizes and tensile strengths: the tensile strengths of refined Al–30Si alloys become much higher than that of the unrefined one, which is merely 48 MPa; compared with the conventional refining method, the tensile strength of Al–30Si alloy refined by continuous method increases from 107.41 MPa to 128.48 MPa with the primary Si grain size decreasing from 50 μm to 30 μm. Therefore it can be concluded that better refinement effect can be obtained by the continuous refining method than conventional method.

4. Discussion

4.1. *The continuous nucleation mechanism in mushy zone*

The major phase transformation in Al–30Si alloys is observed in the mushy state, where primary Si nucleates and grows. With temperature decreasing the primary Si starts to nucleate on foreign substrates. Once critical nuclei are formed the growth of primary Si then follows through absorbing dissolved silicon from the melt [17,18] to its surface. Thus in the mushy zone especially at 785 °C, there are lots of primary Si with small sizes formed in the Al–Si melt. If the Al–P master alloy rod is added into the melt at this time, there are two dominant kinds of particles in the melt: the AlP particles and firstly-formed primary Si.

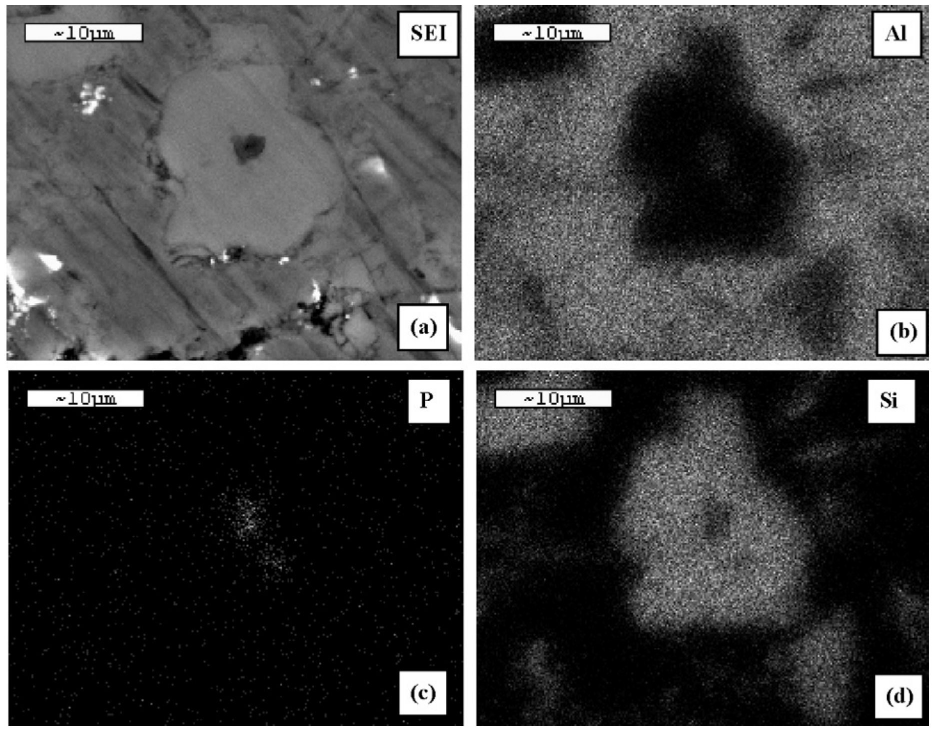

Fig. 5. EPMA of primary Si: (a) SEI of the primary Si; (b)–(d) the X-ray images of different elements: Al, P and Si, respectively.

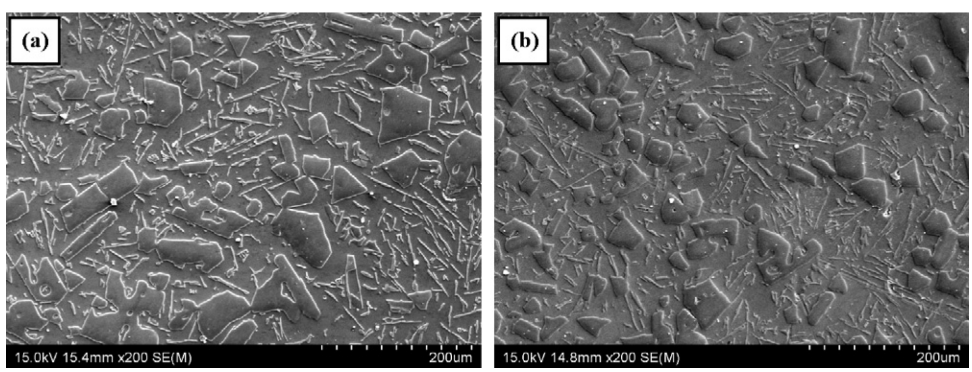

Fig. 6. Comparison of refinement effects between conventional and continuous methods: (a) Sample-4; (b) Sample-5.

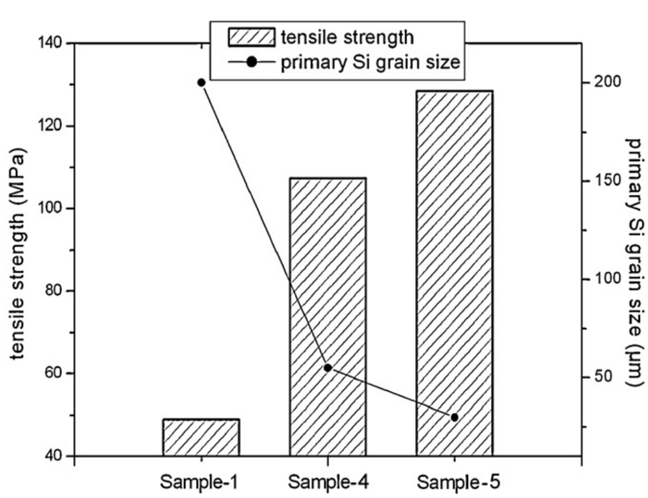

Fig. 7. Effects of different refining methods on primary Si grain sizes and tensile strengths of as-cast Al–30Si alloy.

It is known to all that AlP possesses the similar lattice parameters [19,20] with Si: AlP has a zinc-blende structure with lattice parameter: $a = 5.45$ Å, which is very close to that of Si ($a = 5.42$ Å), as shown in Fig. 8. According to the literature [21], dissolved silicon atoms are able to aggregate on the surfaces of AlP substrates to nucleate with the cube–cube orientation relationship for the sake of the similar lattice parameters. In addition, silicon crystal tends to grow by the aggregating of silicon atoms on the pre-formed primary Si crystals' surfaces in accordance with the Twinning Plane Re-entrant Edge (TPRE) [22] mechanism during the growth stage. Compared with the smooth surfaces of firstly-formed primary Si [23,24] the AlP particles possess much more twinning planes due to that they maintain the intrinsic surface morphologies from disassociation of large AlP added in the mushy zone [25]. In the K. Fujiwara's growth model [26] the attachment events of silicon atoms easily occur at the triangular corners, and simultaneously lead to the formation of more triangular corners which could permit the growth of the crystal. Thus the dissolved silicon atoms are more inclined to aggregate on the surface of AlP added in the mushy zone rather than firstly-formed primary Si. On the basis of these results, it seems reasonable to conclude that the heterogeneous nucleation

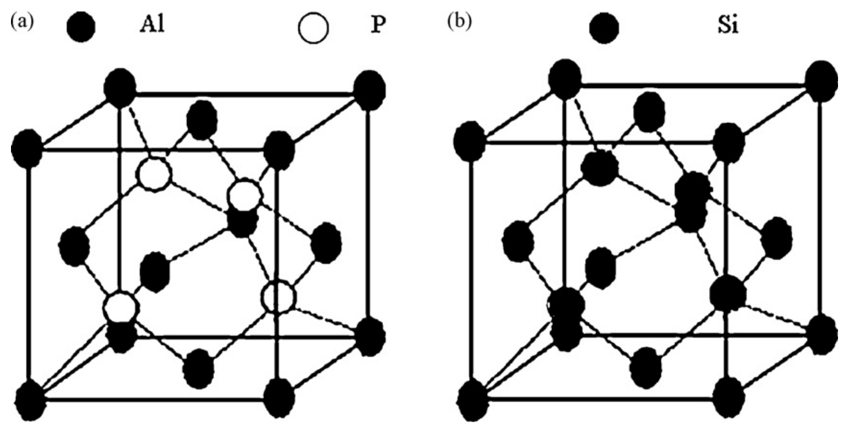

Fig. 8. The crystal structures of (a) AlP; (b) Si.

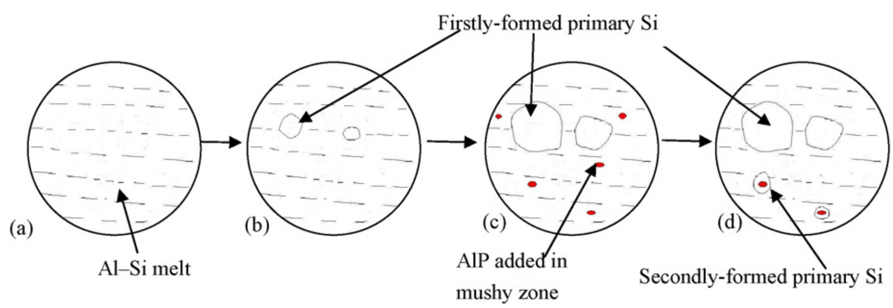

Fig. 9. Schematic illustration of primary Si continuous nucleation process: (a) The Al–Si melts; (b) the precipitation of primary Si at the liquidus temperature; (c) AlP added in the mushy zone and the firstly-formed primary Si; (d) the continuous nucleation of primary Si during growth stage.

during the growth of primary Si has occurred. It is a possible phenomenon which is called the continuous nucleation, and the whole continuous nucleation process of primary Si can be schematically illustrated in Fig. 9.

In the solidification of Al–30Si alloys, the continuous action of nucleation makes it effective to supply more substrates for dissolved silicon atoms in the mushy zone. These substrates could attract dissolved silicon atoms to nucleate, hampering their aggregation towards the firstly-formed primary Si, and eventually restraining the growth of firstly-formed primary Si. As a result, the size of firstly-formed primary Si increase finitely, and the secondly-formed primary Si also has a small size due to the absence of dissolved silicon atoms, just as shown in Fig. 9(d).

4.2. The feasibility of continuous refining method in mushy zone

In case of the addition of Al–P master alloy into Al–30Si alloy melt at high temperature, AlP are extremely likely to act as the heterogeneous nucleating substrates due to the cube-cube orientation relationship [21] during the solidification process. After all enwrapped by silicon to form a silicon atoms layer during nucleation process, these AlP particles could not play the role of heterogeneous nucleation sites any longer. The remaining dissolved silicon atoms can only aggregate on the surfaces of pre-formed primary Si resulting in the growth of the pre-formed primary Si. And with extending holding time these crystals could agglomerate, leaving the primary Si phases of large size in castings.

However, when Al–P master alloys were continuously added into the melt, there would be a quantitative increase of effective AlP substrates for attracting more silicon atoms. According to the continuous nucleation mechanism mentioned above, these AlP particles added below the liquidus temperature have not been enwrapped by silicon atoms, so they can still nucleate primary Si acting as the heterogeneous nucleating sites and hamper the growth of firstly-formed primary Si simultaneously. Therefore, by means of the continuous refining method the continuous heterogeneous nucleation effect of AlP particles in a wide temperature range could be achieved and the size of primary Si is smaller than that in the conventional method. As a result, the continuous refinement method could improve the refinement effect of Al–P master alloy.

5. Conclusions

(1) During primary Si growth in mushy Al–30Si melt, AlP crystals can still nucleate primary Si when AlP particles are supplied continuously during the mushy zone; it proves the existence of the continuous nucleation mechanism for primary Si in a wider temperature range.
(2) An excellent refinement effect of Al–P master alloy can come forth from the continuous refining method. In comparison with conventional method, AlP added in mushy zone can still act as heterogeneous nucleating sites in precipitation of primary Si, so a larger total-amount of AlP playing the actual role can be obtained in continuous refining method, and accordingly the better refinement effect can be easily achieved.

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