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Re-formation of AlP compound in Al–Si melt

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ABSTRACT

Three morphologies of AlP, i.e. block, flake and dendrite, have been found in Al–Cu–P master alloys fabricated under different conditions. When Al–Cu–P master alloy with flaky AlP is used to refine hypereutectic Al–Si alloy, the morphology of AlP particles located in the center of the primary silicon is significantly different from the flaky ones added through the master alloy; adding blocky AlP into the melt, differences also exist in the morphology of AlP with different fabrication parameters. It is manifested that the AlP substrates re-form from the melt after partial disassociation and dissolution of the previously added AlP particles, which is a necessary part of the refinement process of hypereutectic Al–Si alloys.

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1. Introduction

Al–Si alloys are widely used as typical materials for automobile engines due to their favorable properties, such as high strength and lightweight [1]. Recently, there has been a growing interest in hypereutectic Al–Si alloys as the candidate material for high-quality engines instead of conventional near eutectic Al–Si alloys by virtue of a higher volume fraction of primary silicon which provides excellent mechanical properties [1–3]. The brittleness of Si crystals, however, decreases the properties of hypereutectic Al–Si alloys. Therefore, many efforts have been made to achieve fine primary Si with beneficial morphologies and distributions through different processes, such as melt stirring [4,5], rapid solidification [6], ultrasonic treatment [7], refinement treatment [8–14], etc. It is generally recognized that primary silicon can be effectively nucleated by AlP particles [9,15]. Hence, adding phosphorus is of vital importance in most casting technologies of hypereutectic Al–Si alloys. Al–P series master alloys, such as Al–P and Al–Cu–P master alloys, have gained popularity because they cause little gas pollution and have a stable and lasting effect. They have higher refining efficiency than other master alloys due to the fact that AlP particles which can heterogeneously nucleate primary silicon have formed in advance in the master alloys rather than formed in Al–Si melt through reaction. Although studies have revealed the effectiveness of Al–P series master alloys to refine hypereutectic Al–Si alloys [9,16], little attention has been paid to Al–P master alloys themselves, and the behavior of the pre-existing AlP particles contained in the master alloys in the melts. The current research was therefore designed to explore the behavior of AlP particles in the melts.

2. Experimental procedures

Al–16%Cu–2%P master alloys (all compositions quoted in this work are in wt.% unless otherwise stated) are used as the source of AlP particles added to Al–Si melt, which were fabricated by commercial pure Al (99.7%) and Cu–8%P master alloy in an alumina crucible by a high frequency induction furnace. Al–Cu–P melts were held for 5 min and then poured into a cast iron mold with the same sample size of 100 mm × 40 mm × 30 mm at 1000, 1200 and 1500 °C, respectively, named Sample-1, -2 and -3. Sample-4 was gained by pouring the melt into another cast iron mold with a sample size of 100 mm × 40 mm × 3 mm after being held for 5 min at 1500 °C.

Al–30Si alloy ingots were chosen as the base alloy to perform the refinement experiments, and were prepared from commercial pure aluminum (99.7%) and pure silicon (99.0%) in a 25 kW medium induction furnace. All the experiments were carried out in a graphite crucible in a 5 kW electric resistance furnace and all the specimens were obtained from pouring the melts into a cast iron mold with a size of 100 mm × 40 mm × 30 mm.

Five groups of experiments were carried out on the Al–30Si alloys. The first four groups formed a series, all with the addition of 10% Sample-1. The first group of experiments (denoted as G1: G for group) was performed with a holding time of 20 min after adding Sample-1 to Al–30Si melt at different temperatures (850, 950 and 1100 °C). The second one (G2) was carried out at 850 °C while the melts were held for 2, 20 and 40 min, respectively, after the addition of Sample-1. The third one (G3) was held at 850 °C for 20 min while one half of the melt was poured into the cast iron mold and the other half was poured into a sand mold. Melt thermal history was also studied (G4) and the experiment was carried out as is illustrated in Fig. 1. The alloy was heated to 850 °C and held for 20 min after adding the master alloy. Part of it was poured into the cast iron mold (marked as process 1), while the remained was heated to 1200 °C and then slowly cooled down to 850 °C within 5 min, after which it was poured into the mold (marked as process 2). The last group (G5) applied Sample-3 to Al–30Si melt with the added amount of 4% and a holding time of 20 min at 900 °C.

Specimens were derived from the middle of the samples and then mechanically ground using standard procedure. The microstructures of the alloys were observed

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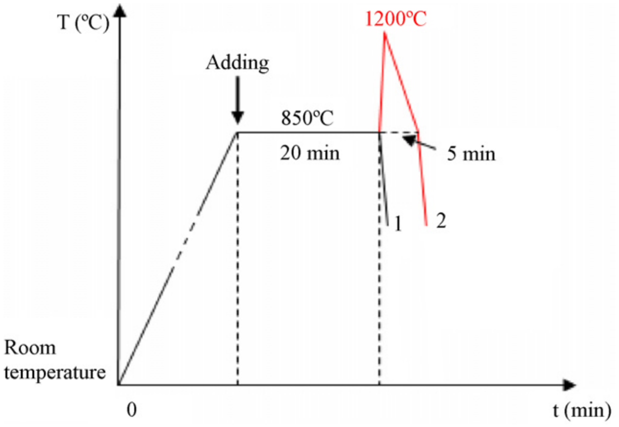

Fig. 1. Illustration of altering the melt thermal history.

by hi-scope-video microscopy and analyzed by electron probe microanalysis (EPMA) JXA-8800R. Since AlP can easily react with water and even air, the polishing process was avoided for all samples.

3. Results and discussion

3.1. AlP morphologies of Al–Cu–P master alloys

Fig. 2 presents the microstructures of fabricated Al–Cu–P master alloys. With EPMA analysis as shown in Fig. 3, it is confirmed that the dark phases are AlP compounds, which are blocky as shown in Fig. 2(a) under 1000 °C, and become completely flaky (stripy in 2D image) shown in Fig. 2(c) at 1500 °C, and turns into a combination of blocky and flaky when the temperature is 1200 °C as shown in Fig. 2(b). Introduction of a higher cooling rate with such a high temperature results in the formation of dendritic AlP. Thus, AlP exhibits three different kinds of morphologies: block, flake and dendrite.

3.2. Effect of experimental parameters on AlP morphologies in Al–30Si melt

Figs. 4–7 show the morphologies of AlP in Al–30Si alloys with the addition of Sample-1, which can be affected by several melting parameters: temperature, holding time, cooling rate and melt thermal history, respectively.

In Fig. 4, with the same holding time (20 min) (G1), AlP shows different morphologies with the increase of temperature. It is blocky at 850 °C, irregular at 950 °C, and flaky at 1100 °C. With the same temperature (850 °C) (G2), AlP also displays various shapes with the variation of holding time as shown in Fig. 5 and flaky AlP becomes more conspicuous when the holding time is 40 min. Fig. 6 shows the microstructure of Al–Si alloys undergoing G3, which reflects the effect of the cooling rate on the morphology of AlP. It is obvious that most of the AlP particles cooling in the cast iron mold are blocky while the flaky ones constitute a very small part. However, the flaky ones are far more numerous than the blocky ones when cooling in the sand mold (Fig. 6 (b)). The morphology of AlP can be greatly changed after an alteration of melt thermal history (G4). It is noticed in Fig. 7 that although the pouring temperatures are the same between processes 1 and 2 (850 °C) (Fig. 1), AlP particles become coarse flakes (Fig. 7(b)), which results in the plate-like primary silicon after the superheating treatment.

Blocky AlP particles contained in Sample-1 were added into the Al–30Si alloy, but AlP in the ultimate alloys hade several shapes: block, flake, or an irregular shape. Thus, the morphology variation of AlP, as shown in Figs. 4–7, after refinement by the same master

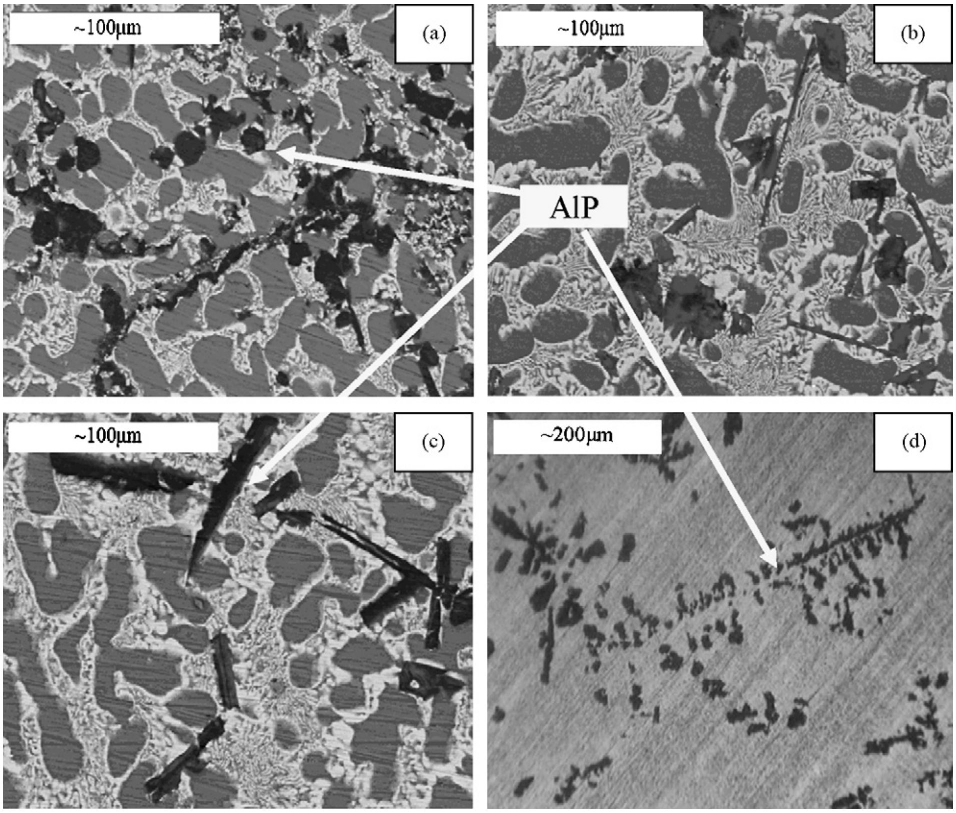

Fig. 2. The structure morphologies of Al–Cu–P master alloys (a) Sample-1 (SEI); (b) Sample-2 (SEI); (c) Sample-3 (SEI); and (d) Sample-4 (optical picture).

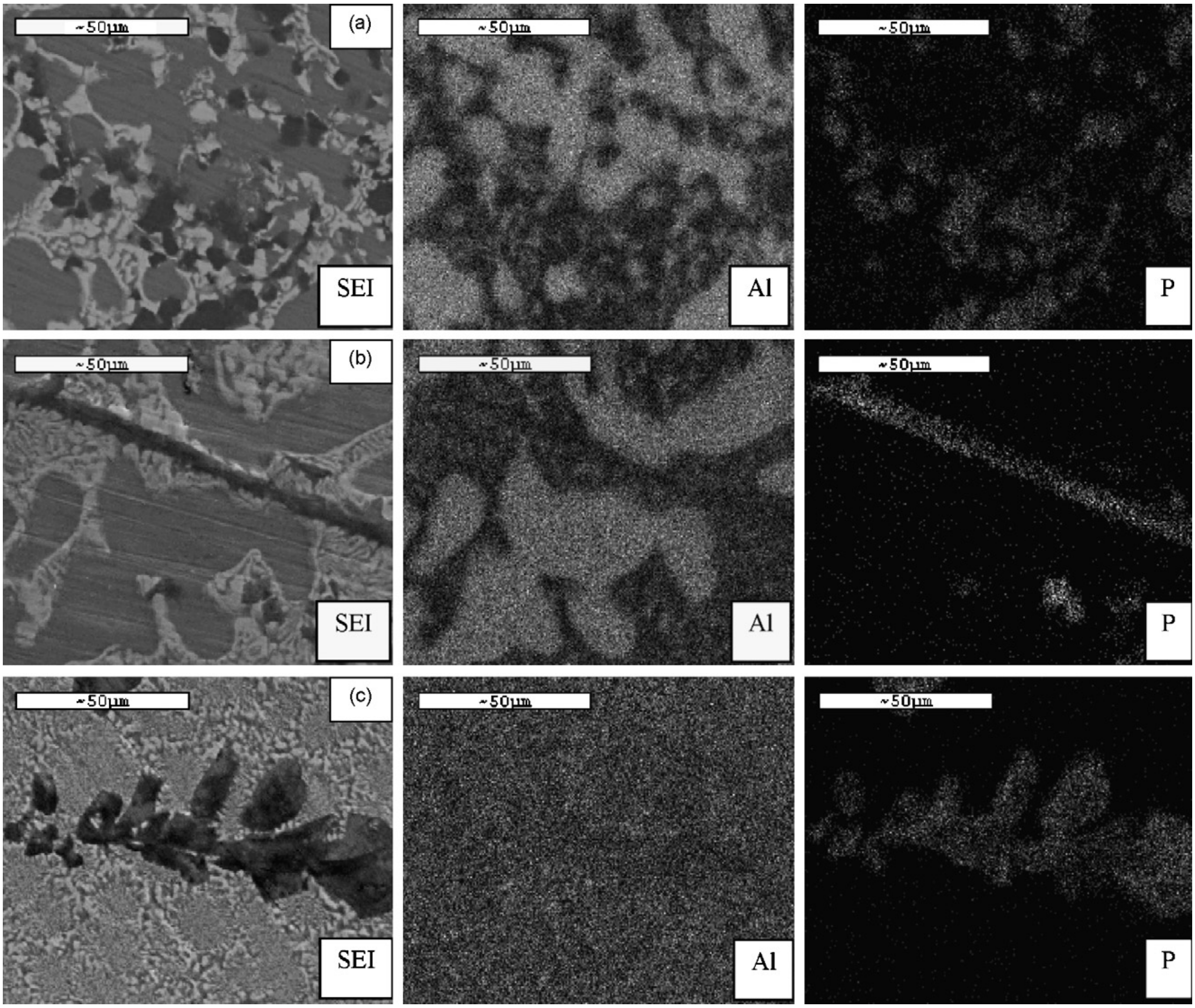

Fig. 3. EPMA analysis of the dark phases in Al–Cu–P master alloys (a) block; (b) flake; and (c) dendrite.

alloy (Sample-1) with different parameters, indirectly indicates that AlP particles are instable after being added into the melt.

3.3. The behavior of AlP in the melt

During the refinement of pure aluminum, the morphology of high melting-point compounds such as TiB_2 and TiC does not change much before or after the treatment. However, in this research, AlP, with a melting point above 1000 °C, has a noticeable variation of morphology. The microstructures of the Al–30Si alloys, before and after refinement by Sample-3 (G5), are shown in Fig. 8. The black particles in the center of the primary silicon are proved to be AlP with EPMA analysis (Fig. 9). It can be seen from Fig. 8 that the coarse primary silicon in the unrefined Al–30Si alloy has transformed into smaller particles, which indicates that Al–Cu–P master alloy containing flaky AlP has already successfully refined Al–30Si. However, the morphologies of the AlP particles located in the center of the primary silicon greatly differ from the coarse flaky

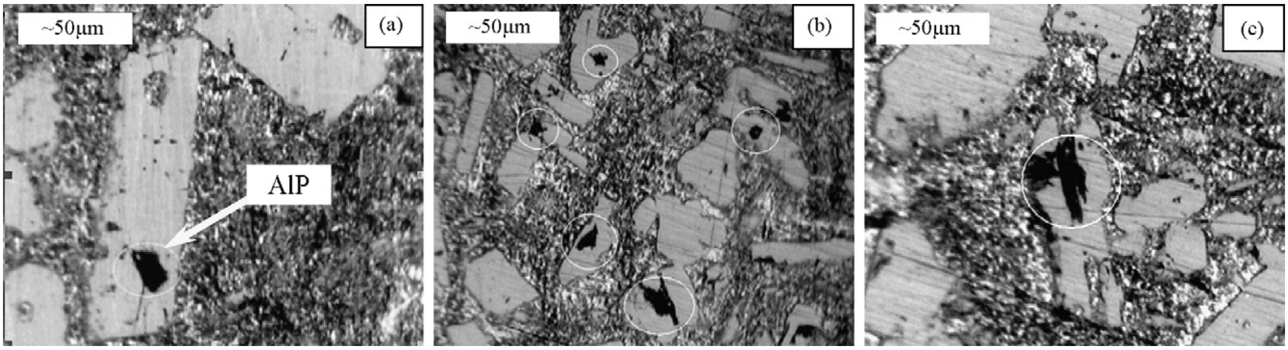

Fig. 4. Effect of the holding temperature on the morphologies of AlP (holding time: 20 min) (a) 850; (b) 950; and (c) 1100 °C.

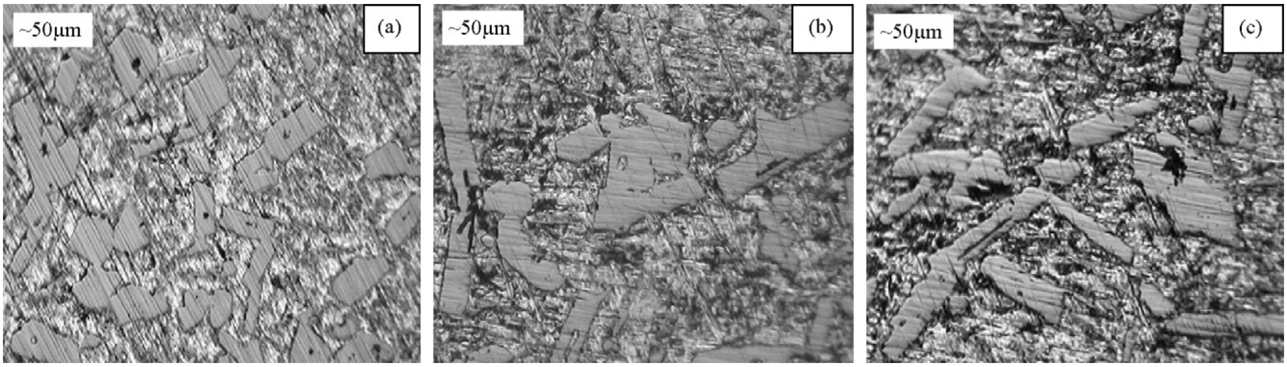

Fig. 5. Effect of the holding time on the morphologies of AlP (temperature: 850 °C) (a) 2; (b) 20; and (c) 40 min.

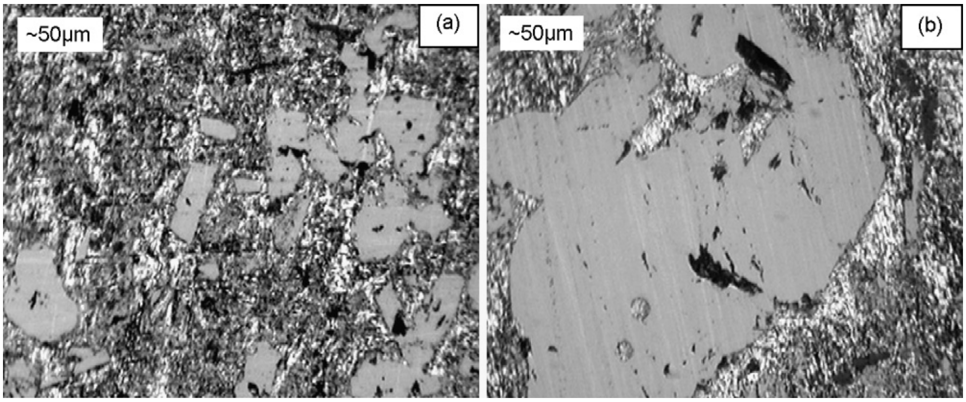

Fig. 6. Effect of cooling rate on the morphologies of AlP (850 °C, 20 min) (a) solidified in cast iron mold; and (b) solidified in sand mold.

ones (Fig. 2(c)) that were previously added into the melt through Al–Cu–P master alloy (Sample-3). The relatively giant flaky AlP particles (about 100 μm) no longer exist in the refined Al–Si alloy and are replaced by numerous fine AlP particles (about 10 μm) distributed throughout, indicating that AlP particles undergo some transformation in the melt.

The difference in chemical potential among various components is the driving force of every physical process. The atoms would transfer from the phase with higher chemical potential to the one with lower chemical potential due to the interaction between homogeneous and heterogeneous atom groups and the injection of entropy of mixing. When AlP is added to the melt, the potential of Al and P in AlP compound is far higher than that in the melt, and, as a result AlP loses stability. Therefore AlP dissociates because of the thermal motion of the melt and then dissolves following the diffusion and transference of the atoms in the melt, thus signifying that a dissolution reaction $\mathrm{AlP} \rightarrow \mathrm{Al} + \mathrm{P}$ takes place. P atoms will keep entering the surrounding melt until it reaches the solubility of P in Al–Si melt, and at this time the AlP will try to maintain the dynamic balance by constant dissolution and re-precipitation which will run through the whole holding time until the melt is cooled.

In the beginning of solidification, the dissolution reaction $\mathrm{AlP} \rightarrow \mathrm{Al} + \mathrm{P}$ is mainly reversed because of the decrease of the equilibrium constant of the reaction and P solubility in the melt, so that P precipitates by attachment to the undissolved solid AlP particles. When Al–30Si melt cools to the liquidus temperature, primary silicon begins to precipitate. As both the crystal structure and lattice parameter of AlP (cubic *F*43*m*; 5.421 Å) are close to that of silicon (cubic *Fd*3*m*, 5.431 Å), and the melting point of AlP is higher than the liquidus temperature, the solid AlP particles heterogeneously

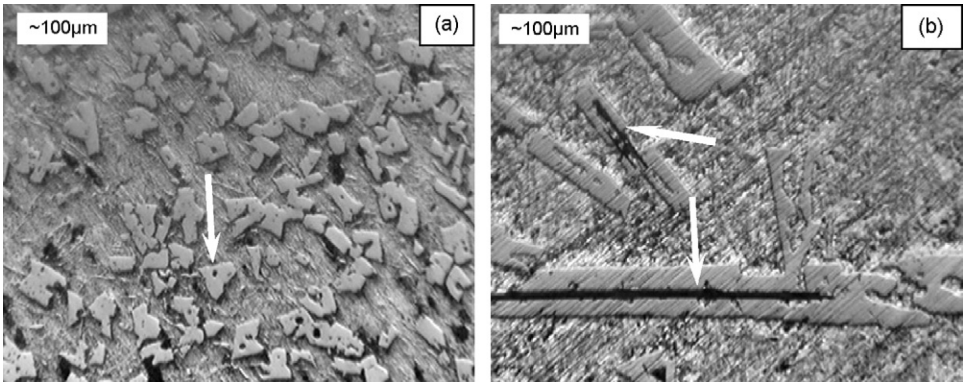

Fig. 7. Effect of melt thermal history on the morphologies of AlP (a) sample poured without superheating (process 1); and (b) sample poured after the superheating (process 2).

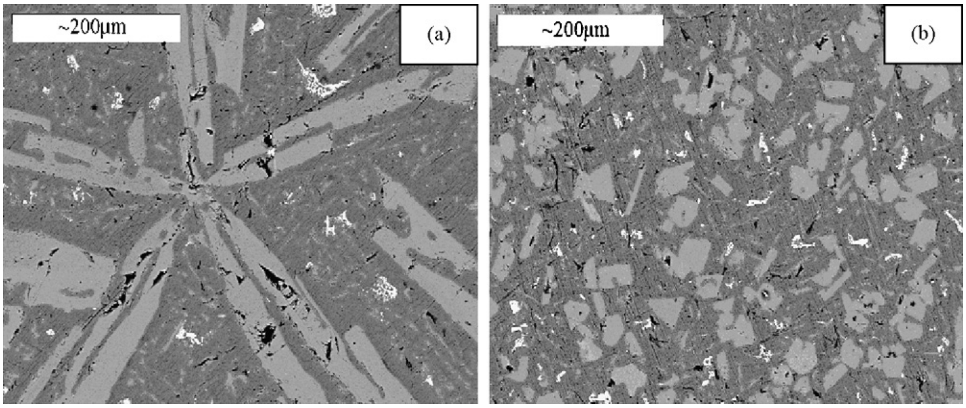

Fig. 8. Microstructures of Al–30Si alloy (a) unrefined and (b) refined by Sample-3 (4% Al–Cu–2P, 900 °C, 20 min).

nucleates primary Si with a cube–cube orientation relationship [9,15]. Furthermore, the newly precipitated AlP is much smaller and can distribute more uniformly in the melt than that which are added externally through Al–Cu–P master alloy, and, the newly arranged surface atoms have little attachment in the melt such as impurity elements or gases, it is therefore easier for Si atoms to attach to the AlP particles. As a result, re-formed AlP particles satisfy the criteria to be favorable nuclei [17], and the re-formation of AlP is of vital importance to keep the high efficiency of refinement.

Flaky AlP substrates in Al–Si alloy are more easily observed with a higher temperature, a longer holding time, or a lower cooling rate. With a higher holding temperature, there is a wider range of temperature for AlP particles to re-precipitate and grow, and AlP particles turn to flakes during the solidification process. Similarly, with a lower cooling rate, a much longer time is requested for them to grow and become flakes. When the holding time is longer, the dissolution reaction can proceed more thoroughly leading to more dissolved AlP which will re-precipitate from the melt later. During the superheating treatment with the temperature rising to 1200 °C, a larger portion of AlP dissolves in the melt; when the temperature cools to 850 °C, the dissolved AlP precipitates from the melt and exists as flakes. Therefore, during the solidification when the temperature drops from 850 °C, primary silicon will precipitate from the melt with the flaky AlP as the nuclei, resulting in the coarse structure of Al–Si alloy. This indicates that AlP tends to grow into flakes with sufficient growth time, and it will stay in block form if the growth time is shorter.

Knowing the behavior of AlP particles after being added to Al–Si melt may help to mature the refinement technology of hypereutectic Al–Si alloys, and could promote the emergence of new technology and develop a heterogeneous nucleation theory.

3.4. The structure of dendritic AlP

The morphologies of AlP observed in experiments always exhibit as block or flake [18]; however, the dendritic AlP is obtained from

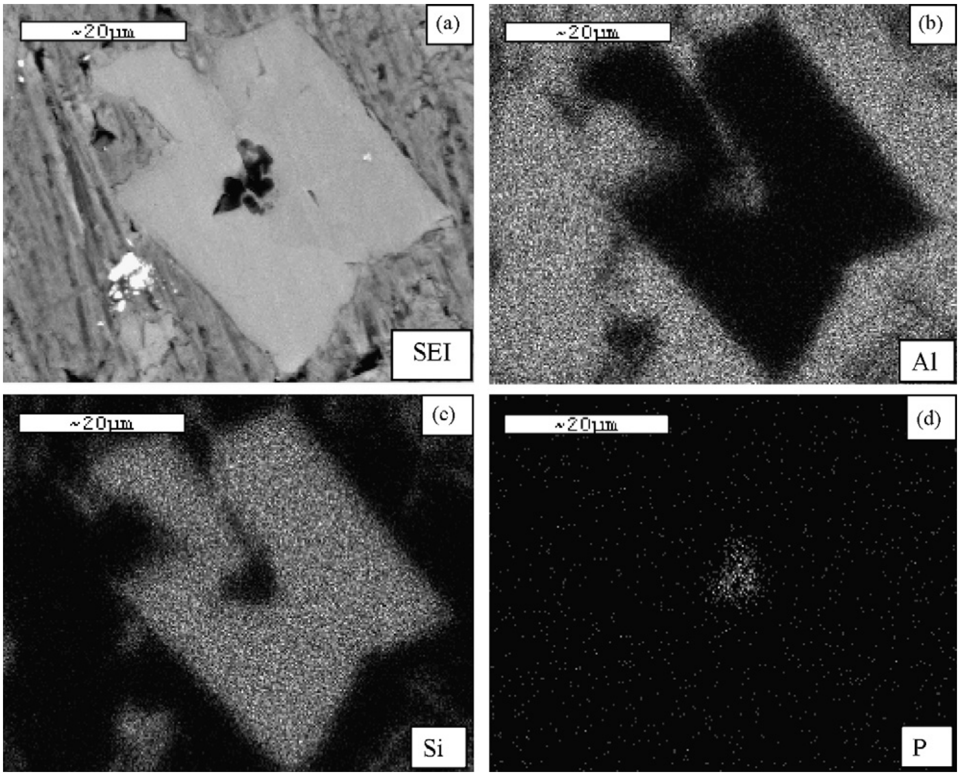

Fig. 9. EPMA analysis of the microstructure of Al–30Si alloy refined by Sample-3 (a) SEI; (b) ~ (d) the X-ray images for respective elements: Al, Si, P.

the increase of the cooling rate at 1500 °C. AlP crystals have a facet or smooth solid–liquid interface when they grow, but the emergence of dendritic morphology signifies that the crystals have a rough interface. Therefore, the growth mechanism of AlP derived from this condition must have undergone a transition. It is assumed that as the undercooling increases, the smooth interface transforms into a rough one, which can be explained by the principle that is called "kinetic roughening transition". According to Temkin [19], there is a multi-atomic layer on the solid–liquid interface containing some disordered atoms, rather than the well-arranged ones, leading to the transformation of rough interfaces of single to multi-atomic layer. With the increase of the undercooling, the layer becomes thicker and the interface becomes rougher, leading to the faceted-nonfaceted transition of the growth mechanism, and resulting in the formation of dendritic AlP. However, the exact mechanism of the formation of the dendritic AlP needs further investigation.

4. Conclusions

The behavior of AlP added into Al–30Si melt through Al–Cu–P master alloys was investigated. It is concluded that AlP substrates in the refined Al–30Si precipitate from the melt after partial dissasociation and dissolution of the AlP particles that were previously added into the melt. The re-formation of AlP is of vital importance to maintain the high efficiency of refinement as the dissociation, dissolution and precipitation of AlP particles will result in a remarkable increase of fresh AlP particles, which is significant for renascent AlP particles to be favorable nucleating substrates of primary silicon during solidification.

During the refinement of Al–Si alloys applying different parameters, it is found that higher temperature, longer holding time and lower cooling rate are favorable for the formation of flaky AlP substrates.

Acknowledgments

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