Refinement of Primary Silicon Crystals by Novel P-doped γ-Al$_2$O$_3$ Particles in Solidification of Hypereutectic Al-Si Alloys

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Abstract

In this study, P-doped γ-Al$_2$O$_3$ was used as a potent substrate to refine and modify primary and eutectic silicon in solidification of hypereutectic Al-Si alloys. Using P-doped γ-Al$_2$O$_3$ could be a clean source of Phosphors without adding impurities. The optical micrographs indicated that the irregular coarse morphologies of primary silicon particles in solidification of Al-18Si alloy are changed to fine regular particles. The addition of P-doped α-Al$_2$O$_3$ and P-doped γ-Al$_2$O$_3$ resulted in the decrease of the average particle size of primary Si from 52 μm to 25 μm and 22 μm respectively. It is clear that, adding P-doped γ-Al$_2$O$_3$ gave good refinement of primary Si of Al-18Si alloy in comparison with the addition of P. Subsequently, using finer P-doped γ-Al$_2$O$_3$ powder gave narrower particle size range compared to that of adding P.

Introduction

For decades, considerable effort has been made towards the development of lightweight engineering materials. Due to their combination of satisfactory mechanical properties and excellent castability, Al-Si alloys are widely used in transportation and other industrial sectors [1-3]. The wear resistance of Al-Si alloys is related to the presence of hard primary silicon crystals formed during solidification, but comes at the expense of poor machine tool life. Therefore, several methods have been used to refine primary silicon in order to increase the industrial applicability of hypereutectic Al-Si alloys. Currently, refinement of Al-Si alloys is achieved by adding phosphorous in the form of Cu-P, Al-Cu-P or Al-Fe-P master alloys. The formation of aluminium phosphide (AlP) particles that act as potent substrates for heterogeneous nucleation of primary silicon is the well accepted explanation of the refining effect of phosphorus. This may be related to the fact that the AlP and silicon have very close crystal structure and lattice parameter with less than 1% mismatch between them [4].

It is well documented that the common inclusions in commercial aluminium and aluminium alloys are oxides, carbides, borides, nitrides, fluorides, and chlorides [5, 6]. Alumina Al_2O_3 is the most common oxides that found in commercial aluminium alloys. The oxide film is initially in the form of γ-Al_2O_3, in aluminium alloys. It is a thin film that prevents further oxidation over continued heating at higher temperatures (~800 °C). This oxide film transforms to α-Al_2O_3, after an incubation period. The occurrence level of γ-Al_2O_3 has been found to be the highest in the α-Al phase and is believed to be a very potent substrate for the nucleation of the matrix phase [5, 7]. Doping γ-alumina with element such as La, Ba, P, or S can shift the phase transformation to higher temperatures [8]. Experimental data that reported in the literature, concluded that some Si particles were nucleated and grown on oxide bifilms during solidification of hypereutectic Al-Si alloys. Studies by Campbell and Cao [9, 10] reported that Si particles formed on long oxide films. They also explained the cracks in eutectic Si was due to nucleation of Si on short bifilms. Microstructures presented by Pennors *et al.* [11] revealed that AlP particles are aligning along oxide bifilms. Furthermore, Zhang *et al.* [12] found that Si particles were formed on oxide particles upon solidification of Al-15Si alloy. They believed that the distribution of oxide films as well dispersed, discrete, nano scale oxide particles can act as potent and efficient heterogeneous substrates for the nucleation of primary Si. Choi *et al*. [13, 14] used nanoparticles of γ-Al_2O_3 for simultaneous refinement and modification of Si in hypereutectic Al-Si-Cu alloy melts. The incorporation of γ-Al_2O_3 nanoparticles in the melt was achieved by using ultrasonic processing approach. Zhang *et al*. [15] indicated that ultrasonic vibrations to be effective process for refinement and modification of the Si phases in solidification of hypereutectic Al-Si alloys. Therefore, the refinement and modification of Si in the work of Choi *et al.* could be due to the incorporating of γ-Al_2O_3 nanoparticles by sonication process rather than the nanoparticles themselves.

Work conducted by our group on solidification of hypereutectic Al-Si alloys revealed that primary Si particles were well associated with invisible or visible oxide bifilm. Therefore, this study is focused on experimental work aimed to improve the suitability of alumina for simultaneous refinement and modification of Si in hypereutectic Al-Si alloy by doping α-Al_2O_3 and γ-Al_2O_3 powder with phosphorous.

Experimental procedures

Al-18Si alloy was prepared in an electric resistance furnace by melting and diluting an Al-50Si master alloy with commercial purity aluminium LM0 at 800 °C in a clay crucible. Table 1 shows the compositions of raw materials used for the preparation of the alloy. The molten alloy was manually stirred for a few seconds and then cast.

Table 1 Aluminium alloys composition wt%

Alloy	Cu	Mg	Si	Fe	Mn	Ni	Zn	Pb	Sn	Ti	Cr	Al
LM0	0.03	0.03	0.30	0.40	0.03	0.03	0.07	0.03	0.03	-	-	Bal.
Al-50Si	0.08	0.28	51.0	0.32	0.02	0.01	0.02	0.02	0.01	0.09	0.03	Bal.

Experiments were conducted to study the effect of adding 0.5wt% of α-Al_2O_3 and γ-Al_2O_3 powder (0.5 µm in size) (un-doped) on the morphology of silicon phases in solidification of hypereutectic Al-18Si alloy at 800 ºC.

In order to improve the refinement of primary silicon by alumina, P-doped Al_2O_3 was prepared by impregnation of (α or γ) Al_2O_3 powder with an aqueous solution of phosphoric acid [16]. 5 g of Al_2O_3 (α or γ) powder (0.5µm in size) was mixed with 50 ml of aqueous solution of H_3PO_4 (11 wt% H_3PO_4) for 72 h. The doping process was followed by filtration, drying at 120 °C for 12 h and finished by calcination at 500 °C for 2 h. The dry powder was ground and wrapped in aluminium foil before use in refinement of Al-18Si alloy. The doping process and casting experiments were repeated by using coarser γ-Al_2O_3 powder, 3µm in size.

For comparison, experiment was conducted to refine primary silicon by phosphorous. The Al-18Si alloy was melted at 800 ºC and then P was added in the form of CuP shot (Supplied by Aura Metals Ltd). Samples for all above experiments were taken by a preheated steel mould (35mm in diameter and 40mm in height) coated by Boron Nitride which was then water cooled at cooling rate ≈ 15 K/s. The resulting samples were sectioned and prepared by the standard technique of grinding and polishing. Microstructure characterization was accomplished using an optical microscope (Carl Zeiss Axioskop 2 MAT) equipped with image analysis software. The average particle size of primary Si particles was counted for more than 500 particles per sample.

Results and discussion

Our previous work [17] showed that primary Si particles were well incorperated with invisible or visible oxide bifilm. Examples of which primary Si nucleated with visible oxide bifilm are presented in Fig. 1.
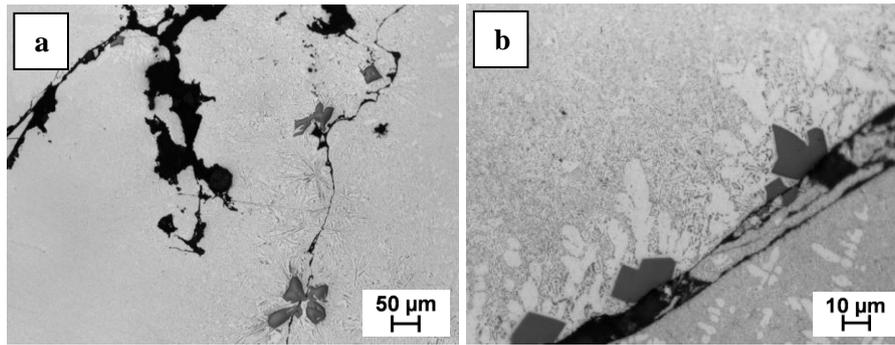
Figure 1 Optical micrographs showing the association of primary Si with oxide bifilms in Al-18Si alloy cast from 800 ℃. (a) low magnification and (b) high magnification.

Optical micrographs of Al-18Si alloy without and with the addition of 0.5 wt% of α-Al_2O_3 and 0.5 wt% of γ-Al_2O_3 particles (0.5 μm in size) illustrated in Fig. 2.
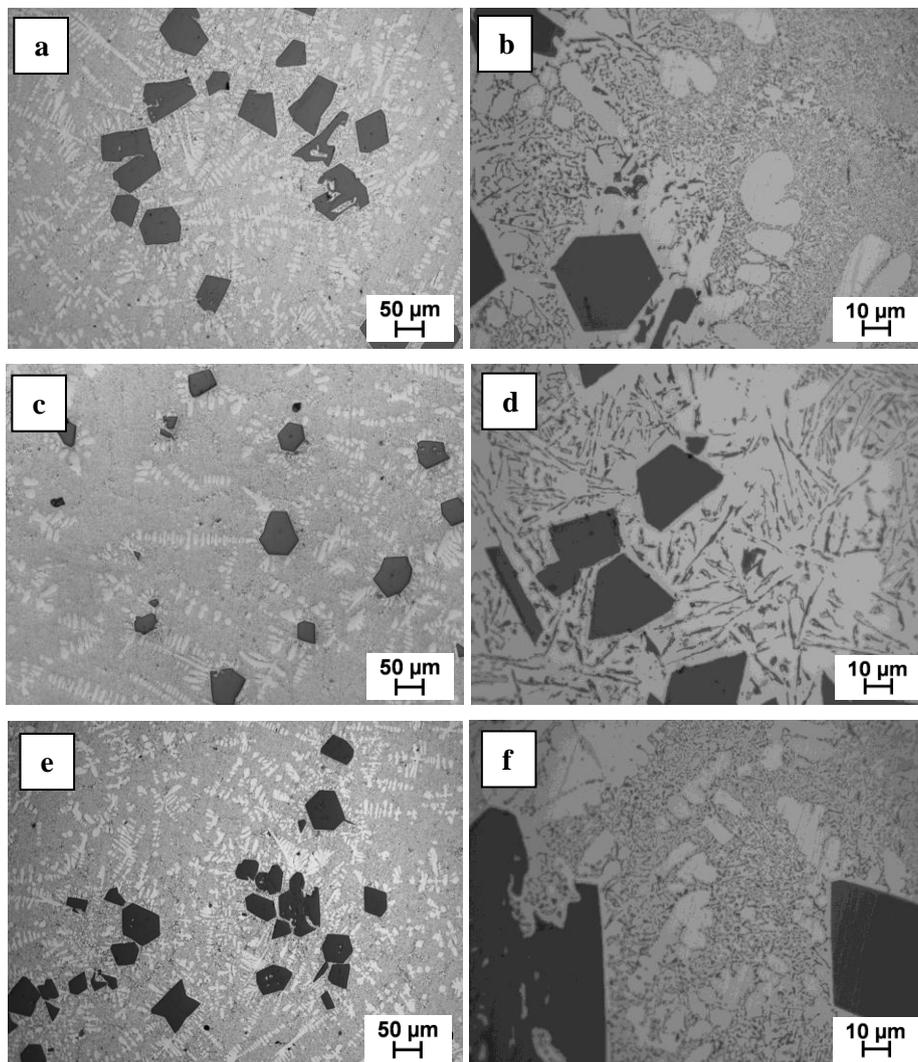
Figure 2 Optical micrographs of as-cast alloys: (a,b) Al-18Si alloy; (c,d) Al-18Si with the addition of 0.5wt% α-Al_2O_3 (0.5 μm); (e,f) Al-18Si with the addition of 0.5wt% γ-Al_2O_3 (0.5 μm). (a,c & e) low magnification to show the size and distribution of primary Si and (b,d & f) high magnification to show the eutectic structure.

The untreated Al-18Si contained irregular coarse primary Si crystals with average particle size of $\approx$ 52 μm (as shown in Fig. 2(a,b)). The eutectic Si had a mostly fibrous morphology this is because of high Ca content in commercial purity alloy (> 200 ppm) [17]. Adding 0.5 wt% of α-Al$_2$O$_3$ showed no change in the size and morphology of primary Si, and the eutectic Si lost its modification (see Fig. 2(c,d)). However, adding 0.5 wt% of γ-Al$_2$O$_3$ resulted in slight reduction in the average particle size of primary Si $\approx$ 48 μm with no change in modification level of eutectic Si as shown in Fig. 2(e,f).

Fig. 3 shows the effect of adding 0.5 wt% of P-doped α-Al$_2$O$_3$ and 0.5wt% of P-doped γ-Al$_2$O$_3$ (0.5 μm in size). The micrographs revealed that in adding P-doped α-Al$_2$O$_3$ and P-doped γ-Al$_2$O$_3$ the average particle size of primary Si decreased from 52 μm to 25 μm and 22 μm respectively. However, the addition of P-doped α-Al$_2$O$_3$ did not retain its modified structure (Fig. 3b). It is clear that P-doped γ-Al$_2$O$_3$ led to good refinement of primary Si with no change in modification level of eutectic Si in solidification of commercial purity Al-18Si alloy, as shown in Fig. 3 (c,d).
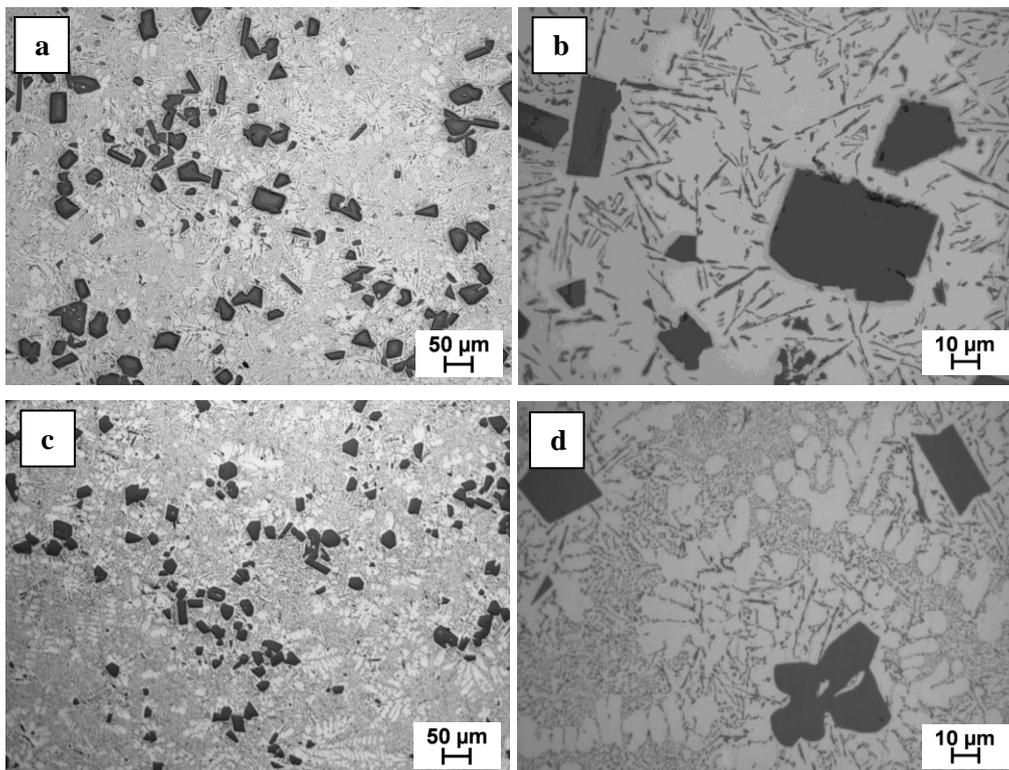
Figure 3 Optical micrographs of as-cast alloys: (a,b) Al-18Si with the addition of 0.5wt%P-doped α-Al$_2$O$_3$ (0.5 μm in size); (c,d) Al-18Si with the addition of 0.5wt% P-doped γ-Al$_2$O$_3$ (0.5 μm in size). (a,c) low magnification to show the size and distribution of primary Si and (b,d) high magnification to show the eutectic structure.

The effect of alumina particle size was tested by adding 0.5 wt% P-doped γ-Al$_2$O$_3$ powder with average particle size of 3 µm, i.e. coarser particles, to the commercial purity Al-18Si alloy. As shown in Fig. 4 (a,b) and Fig. 3(c,d), the addition of 0.5wt % of coarse P-doped γ-Al$_2$O$_3$ powder and 0.5wt% of fine P-doped γ-Al$_2$O$_3$ powder gave average particle size of primary Si $\approx$25 µm and 22 µm respectively compared with average particle size $\approx$ 52 µm for commercial Al-18Si. These results showed similar trend compared with the refinement of primary Si obtained by adding 100 ppm P, as shown in Fig. 4(c,d), where the average particle size of primary Si was 20 µm and the eutectic Si morphology changed from a fibrous to a plate-like structure. The effect of different form and size of alumina powder on the average particles size of primary Si and compared with P addition are summarized in Table 2.
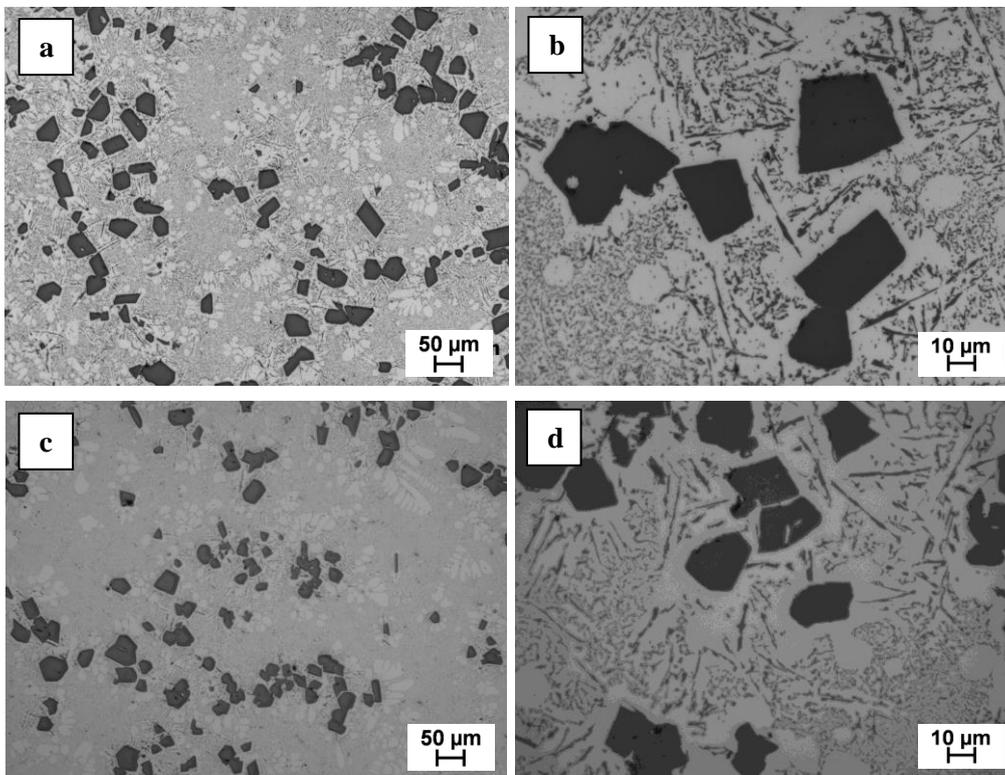
Figure 4 Optical micrographs of as-cast alloys: (a,b) Al-18Si with the addition of 0.5wt% P-doped γ-Al$_2$O$_3$ (3 µm); (c,d) Al-18Si with the addition of 100 ppm P. (a,c) low magnification to show the size and distribution of primary Si and (b,d) high magnification to show the eutectic structure.

Table 2 Effect of different form and size of Al_2O_3 powder without and with P on the average particles size of primary Si (µm) and compared with P addition.

Alloy	Al-18Si	Al-18Si +α-Al_2O_3 (0.5 µm)	Al-18Si +γ-Al_2O_3 (0.5 µm)	Al-18Si +P-doped α-Al_2O_3 (0.5 µm)	Al-18Si +P-doped γ-Al_2O_3 (0.5 µm)	Al-18Si +P-doped γ-Al_2O_3 (3 µm)	Al-18Si +100 ppm P
Size of primary Si (µm)	52	52	48	25	22	25	20

The particle size distributions of primary Si in commercial Al-18Si alloy, Al-18Si with 0.5wt%P-doped γ-Al_2O_3 (0.5 µm in size), Al-18Si with 0.5wt% P-doped γ-Al_2O_3 (3 µm in size), and Al-18Si+100ppm P additions are shown in Fig 5. It is clear that adding finer P-doped γ-Al_2O_3 powder gave narrower particle size range similar to that obtained of adding P.
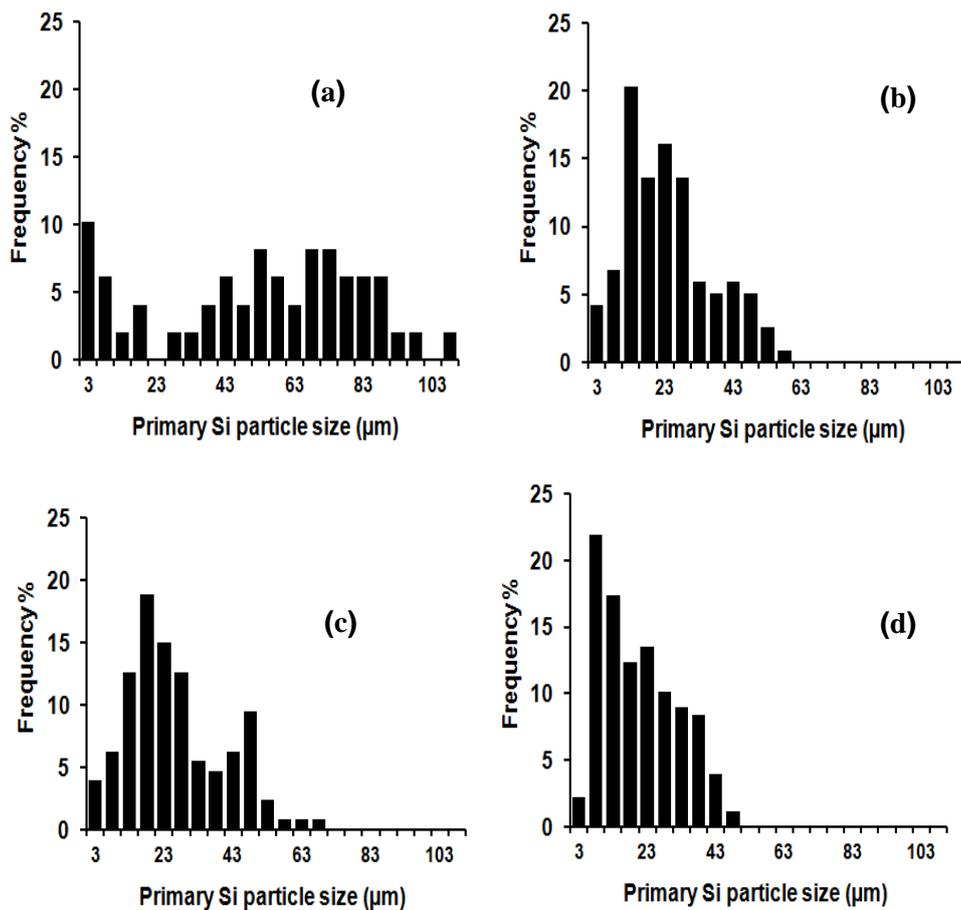
Figure 5 Particle size distribution of primary Si in: (a) Al-18Si alloy; (b) with 0.5wt% P-doped γ-Al_2O_3 (0.5 µm in size); (c) with 0.5wt% P-doped γ-Al_2O_3 (3 µm in size) addition; and (d) with 100ppm P.

It is well known that phosphorus has high tendency to be adsorbed on the surface of γ-Al_2O_3 which form a mono layer of phosphorus during the adsorption process [16]. The adsorption capacity of P on alumina surface ranged between 15 and 30 mg/g of alumina having an average particle size between 1mm and 400nm respectively [18, 19]. The high porosity and large surface area of γ-Al_2O_3 is behind its high adsorption capacity of P and then high efficiency to refine primary silicon in comparison to α-Al_2O_3. This may explain why P-doped γ-Al_2O_3 is more efficient than P-doped α-Al_2O_3. However, further characterisation is required to conclude that.

The adsorbed AlP particles on γ-Al_2O_3 surface may serve as nucleation sites for primary silicon. This hypothesis is in accordance with Pennors *et al.* [11] work, in which they presented clear microstructures exhibiting AlP particles aligning along oxide bifilms and serve as nucleation sites for primary silicon. The micrographs in Fig. 3 show that P-doped γ-Al_2O_3 is more efficient than P-doped α-Al_2O_3 or undoped Al_2O_3 to act as a potent substrate for nucleation of primary Si in solidification of hypereutectic Al-Si alloys.

Summary

The conclusion from this study is that: the P-doped γ-Al_2O_3 is a potent substrate to refiner primary silicon in the solidification of hypereutectic Al-Si alloys. Using P-doped γ-Al_2O_3 could be a clean source of P without additional impurities. However, adding Cu-P, Al-Cu-P or Al-Fe-P master alloys as a source for P, leading to incorporation of impurities. The obtained results are in agreement with the hypothesis, in which nucleation of Si around oxide biofilms may due to the adsorption of the phosphorus on the oxide bifilm in aluminium alloys upon processing cycles.

Acknowledgement

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