Research Article

Effect of Melt Temperature on the Effectiveness of the Grain Refining in Al-Si Castings

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The results inferred from the present work show that Al_3Ti phase has a strong affinity to react with silicon (Si) in the molten alloy leading to formation of $(\text{Al},\text{Si})_3\text{Ti}$ phase instead. This reaction is independent of the grain refiner type. The molten liquid temperature would change its morphology from platelets at 750°C into dendritic structure at 950°C . It has also been observed that $(\text{Al},\text{Si})_3\text{Ti}$ phase platelets precipitate within the α -aluminum dendrites, whereas TiB_2 or AlB_2 particles are released into the surrounding interdendritic regions. Introduction of the grain refiner, regardless its type, would cause change in the α -aluminum dendrite morphology from an elongated to a more rounded form. The results also reveal that addition of 100 ppm B will reduce the initial grain size by $\sim 85\%$ which is more than the effect of addition of 0.2% Ti in the form of Al-10%Ti (about 65%). Elimination of undercooling is important to obtain the maximum grain refining effect.

1. Introduction

Many theories have been proposed to explain the mechanism of grain refining. Two among them are the nucleation and phase diagram theories. The nucleation theory is mainly based on the presence of borides in the added grain refiner master alloy (e.g., TiB_2 , AlB_2 , and $(\text{Al},\text{Ti})\text{B}_2$). The phase diagram theory (Figure 1) is based on the presence of pro-peritectic TiAl_3 phase particles [1–3]. When a master alloy containing Al-Ti-B is added to molten metal such that the amount of Ti is less than 0.15%, often boron particles are found at the centers of the grains, with dendrites enriched in titanium growing outside of the grains. In the case of the use of master alloys, AlB particles have been observed to be released towards the grain boundaries, whereas Al_3Ti particles are located at the centers of the grains [4]. Easton and StJohn [5] have confirmed this observation when the master alloy used does not contain Ti. In addition, release of aluminum borides towards the grain boundaries has no significant effect on the grain refining process.

From the thermodynamics point of view, the solubility of Al_3Ti is independent of the presence of boron (B). The experimental data obtained by Mondolfo et al. [7],

however, show that the presence of B would displace the peritectic reaction towards the Al-rich extremity of the Al-Ti phase diagram, leading to the formation of TiB_2 . Sigworth [8] and Bäckcrud et al. [9] suggested that Al_3Ti particles are more effective in terms of grain nucleation than TiB_2 phase particles. The authors proposed a hypothesis to explain why the presence of borides would slow down the dissolution rate of Al_3Ti when the Al-Ti-B master alloy is added to liquid aluminum. According to [8, 9], borides would form layers around the aluminide particles resulting in slowing their effectiveness.

Davies et al. [10] and Maxwell and Hellawell [11] observed the presence of Al_3Ti particles within the α -Al dendrites. The solidification curves obtained by Arnberg et al. [12] revealed the absence of undercooling indicating that the nucleation of grains took place by the peritectic reaction at temperatures higher than the melting temperature of aluminum. Crossley and Mondolfo [13] suggested that the reported improvement of Al-Ti-B master alloy as a grain refiner may be interpreted in terms of the displacement of the peritectic reaction of 0.15% Ti towards the extremity of the aluminum diagram leading to thermodynamically stable Al_3Ti nucleating sites at low

FIGURE 1: (a) Al-Ti phase diagram [3]. (b) Aluminum-rich corner of the Al-B phase diagram [6]. (c) Temperature-time curve obtained from the A356.2 alloy (untreated).

addition, for example, 0.02%. This proposition, however, is incompatible with the Al-Ti-B phase diagram [14, 15].

Mohanty et al. [16–19] injected synthetic TiB_2 particles (about $5\text{ }\mu\text{m}$ in diameter) into liquid aluminum along with different amounts of Ti. In the absence of excess of Ti, the effectiveness of TiB_2 particles for grain refining was poor, and TiB_2 particles were observed at the grain boundaries. Increasing the concentration of Ti resulted in improving the grain refining effectiveness of the borides, and the boride particles were observed at the center of the solidified grains. At Ti concentration higher than the peritectic concentration, layers of Al_3Ti were formed on the surfaces of the TiB_2 particles where layers of $\alpha\text{-Al}$ were precipitated.

Jones and Pearson [20] have proposed the concept of hypennucleation at the TiB_2 /liquid metal interface. According to the authors, the addition of excess of Ti causes segregation of Ti atoms at the TiB_2 /liquid metal interface leading to the formation of a stable layer on the surface of the TiB_2 particles. These layers were proven to stay stable at temperatures below the fusion temperature of aluminum. The work of Schumacher and Greer [21, 22] and Kearns et al. [23] shows that AlB_2 particles would be considered as good nucleates in the absence of Ti. Master alloys of the type Al-B are largely used in the production of ultrapure aluminum to react with transition elements such as V, Cr, and Zr [24, 25].

Boron is not considered as an effective grain refiner when added to pure aluminum [26]. Once Si is added to Al, grain refining is activated together with a change in the $\alpha\text{-Al}$ dendritic structure [27]. Two types of B compounds exist in the Al-B master alloys: AlB_2 and AlB_{12} [28]. The AlB_2 compound is stable at room temperature and contains 44.5%B [29]. It is inferred from the Al-B binary diagram presented in Figure 1(b) that there is a peritectic reaction at 975°C: $\text{L} + \text{AlB}_{12} \rightarrow \text{AlB}_2$. A eutectic reaction (liquid $\rightarrow \alpha\text{-Al} + \text{AlB}_2$) takes place at 660°C making the maximum solubility of B in Al about 20 ppm, where the $\alpha\text{-Al}$ grains would precipitate on the AlB_2 particles. The melting points of AlB_2 and AlB_{12} are $1665 \pm 50^\circ\text{C}$ and $2163 \pm 50^\circ\text{C}$, respectively, resulting in the formation of solid dispersoid particles in the molten liquid [6]. Fundamentally speaking, the addition of a grain refiner to the molten metal would result in the nucleation of new grains or its reaction with other elements in the molten metal to form nucleation sites.

The present study was undertaken to investigate the effect of the following:

- (1) Type of the applied grain refiner, that is, Al-5%Ti-1% B and Al-4%B in comparison with Al-10%Ti. The latter forms a complex intermetallic with Si, which slows down its effectiveness as a grain refiner.
- (2) Effect of superheating (750°C or 950°C) prior to casting.

2. Experimental Procedure

The composition of the A356 alloy used in this study is shown in Table 1.

Samplings from the different melts prepared were poured into a preheated (600°C) cylindrical graphite mold to achieve near-equilibrium solidification conditions

TABLE 1: Chemical composition (wt.%) of as-received A356.2 ingot.

Ingot type	Si	Mg	Fe	Cu	Mn	Zn	Ti	Pb	Al
A356.2	6.78	0.33	0.11	0.02	0.04	0.04	0.03	0.03	Bal.

FIGURE 2: Optical micrographs of (a) Al-10%Ti, (b, c) Al-5%Ti-1%B, and (d) Al-4%B master alloys used in the present study.

(solidification rate $\sim 0.8^{\circ}\text{C/s}$). The grain refiner was introduced in the form of Al-10%Ti, Al-5%Ti-1%B, or Al-4% B cut rods. Prior to pouring, the molten metal was mechanically stirred to prevent sedimentation of the added grain refiner at the bottom of the crucible. Prior to casting, the melt surface was skimmed to remove oxide films. The temperature-time data were obtained using a K-type (chromel-alumel) thermocouple inserted through a hole at the bottom of the graphite mold along the centerline, its tip reaching up to one-third the height of the mold from the bottom. The cooling curves were recorded using a data acquisition system attached to the thermocouple (Figure 1(c)). Chemical analysis of all melts/castings was determined using a Spectrolab Jr CCD Spark Analyzer (average of three burns per sample).

The solidified castings were sectioned perpendicular to the centerline axis of the cylinder, at the level of the thermocouple tip, and polished for metallographic examination, using standard polishing procedures. The polished samples were examined using an optical microscope and an electron probe microanalyzer (JEOL JXA-8900L operating at 20 kV), equipped with energy dispersive X-ray spectroscopic (EDS) and wavelength-dispersive spectroscopic (WDS) facilities.

For measurements of the grain size, the polished samples were chemically etched using Keller's reagent (66 vol.%

HNO₃, 33 vol.% HCl, and 1 vol.% HF), diluted with water using a plastic bottle with a fine nozzle to slow down the etching process. Once etching was completed, the sample surfaces were rinsed, dried, and then photographed using a setup consisting of four projectors emitting red, blue, green, and yellow light. The grain sizes were measured from the digital photographs using Sigma Scan Pro 4.0 software, employing a method similar to the line intercept method.

3. Results and Discussion

Figure 2 shows the size and distribution of Al₃Ti, TiB₂, and AlB₂ in the master alloys used in the present investigation. The average Al₃Ti particle length varies between 10 and 50 μm, whereas the average length of TiB₂ is less than 1 μm. In order to arrive at a clearer understanding of the grain refining mechanism when Al-10%Ti master alloy is used, different concentrations of Ti, varying between 0.1 and 0.6 wt.%, were added. The molten metal was poured at 750°C or 950°C (depending on the amount of added Ti). In each case, the liquid metal was held for 30, 60, and 90 minutes prior to pouring. During the holding time, the liquid metal was continuously stirred using a graphite impeller. Figure 3 exhibits the variation in the nucleation temperature as a function of the added Ti content and melting conditions.

FIGURE 3: Variation of the nucleation temperature as a function of added Ti and melting conditions. Points above 0.6 wt.% Ti are extrapolation.

FIGURE 4: Variation in the grain size as a function of added Ti and melting conditions.

Based on this figure, the following observations may be made:

- (1) The nucleation temperature is strongly influenced by the Ti concentration regardless the melting conditions. At 750°C, 0.3%Ti (broken line in Figure 3) results in depressing the nucleation temperature regardless the holding time.
- (2) At 950°C, adding 0.1%Ti produces the same effect as that observed for 0.3%Ti at 750°C. In this case, increasing the Ti content results in a continuous decrease in the nucleation temperature.
- (3) Holding time seems to have no significant effect on the nucleation temperature. In contrast, the melting temperature separates the curves into two distinct series.

The variation in the alloy grain size as a function of Ti and melting conditions is illustrated in Figure 4. The initial average grain size of the as-received alloy was about $1854 \pm 20 \mu\text{m}$ when the molten metal was poured at 750°C. Although addition of 0.15–0.2%Ti proved to be sufficient to reduce the grain size to approximately $600 \pm 10 \mu\text{m}$ (~70%), there was a tendency for slight increase in the grain size at the holding time of 90 min. This increase may be interpreted in terms of either particle sedimentation or loss in the effectiveness of grain refining. These results are in good agreement with those reported by other researchers [30–32]. As mentioned previously [1, 2], the Al_3Ti particles have the tendency to react with Si from the surrounding matrix to form a complex compound, mainly $(\text{Al,Si})_3\text{Ti}$ which contains 10%Si, as shown in Figure 5 and Table 2.

FIGURE 5: Element distribution in the (Al,Si)₃Ti platelets.

TABLE 2: Identification of the phase rich in Ti.

Points	Element	at.%	Suggested composition
1	Al	63.895	(Al,Si) ₃ Ti
	Ti	24.224	
	Si	10.096	
2	Al	63.935	(Al,Si) ₃ Ti
	Ti	23.994	
	Si	10.144	
3	Al	64.300	(Al,Si) ₃ Ti
	Ti	24.101	
	Si	10.006	
4	Al	63.969	(Al,Si) ₃ Ti
	Ti	24.391	
	Si	10.085	
5	Al	64.762	(Al,Si) ₃ Ti
	Ti	24.017	
	Si	10.061	
6	Al	64.762	(Al,Si) ₃ Ti
	Ti	24.017	
	Si	10.061

(a)

(b)

(c)

FIGURE 6: (a) Morphology of the new (Al,Si)₃Ti phase particles (arrows) (melting temperature ~950°C); (b) Ti distribution in (a); (c) white arrows in (a) and (c) indicate possible fragmentation of the (Al,Si)₃Ti platelets.

The morphology of Al₃Ti depends on the pouring temperature: platelets (750°C; Figure 5) or dendritic (950°C; Figure 6). In all cases, however, the (Al,Si)₃Ti/TiB₂ phase particles are seen to be localized within the α -Al dendrites (Figure 7) suggesting that these particles are acting as nucleation sites.

Figure 8(a) shows that once the Al-5%Ti-1%B master alloy is added to the liquid metal, it decomposes into TiB₂ and Al₃Ti particles. Due to the high density of the Al₃Ti phase (approximately 3.3 g/cm³) compared to the density of liquid aluminum at 750°C (~2.4 g/cm³), some of the Al₃Ti particles may tend to precipitate towards the bottom of the melting crucible or agglomerate as shown in Figure 8(b). Unlike Al₃Ti particles, the TiB₂ particles are precipitated

(a)

(b)

(c)

(d)

FIGURE 7: Morphology of α -Al as a function of the added grain refiner: (a) no melt treatment, (b) localization of (Al,Si)₃Ti phase particles within the α -Al dendrites in the A356.2 alloy treated with 0.3%Ti and poured at 750°C, and (c) 0.1%Ti, 200 ppm B. Note the rosette morphology of the α -Al dendrites (open arrows). (d) 0.1%B.

FIGURE 8: Decomposition of Al-5%Ti-1%B master alloy poured at 750°C after 60 minutes stirring: (a) 0.1%Ti and (b) 0.4%Ti.

FIGURE 9: Variation in the nucleation temperature as a function of Ti content and melting conditions.

in the interdendritic regions. It is inferred from Figure 9 that, in contrast to Al_3Ti addition, introduction of TiB_2 particles leads to a continuous increase in the alloy nucleation temperature with the increase in the added amount of Ti. Thus, the increase in the concentration of TiB_2 particles would result in the nucleation of new equiaxed grains at rates higher than their growth rates, causing grain refining at a lower level of Ti (0.1%) compared to that obtained from the addition of Al-10%Ti master alloy (Figure 4).

FIGURE 10: Variation of the nucleation temperature as a function of the added B and melting conditions.

FIGURE 11: Undercooling measured in the A356.2 alloy as a function of the added B and pouring temperature.

FIGURE 12: Variation of the grain size as a function of the added B and pouring temperature.

FIGURE 13: (a) Presence of AlB_{12} in ultrapure aluminum (possible decomposition of AlB_{12} to AlB_2) and (b) X-ray image of B distribution in AlB_{12} phase particles in (a) (arrow).

In general, the effectiveness of a nucleating agent is determined by several factors, for example, its chemical stability, density, size, and the amount of constitutional undercooling which is a function of the alloy chemical composition. Kori et al. [33] and Nafisi and Ghomashchi [34] studied the effectiveness of Al-4%B master alloy as a grain refiner of A356 alloy. The results show that a small addition of boron shifts up the cooling curve causing the recalescence to disappear entirely. The dendritic structure transforms from a columnar to equiaxed morphology. For master alloys containing mainly AlB_{12} particles, it is proposed that the dissolved boron, the AlB_2 particles present in the master alloy, and some transformation of AlB_{12} to AlB_2 are responsible for the enhanced refining.

In the present study, B was added to the A356.2 alloy melts in different concentrations, as shown in Figures 10 and 11. As may be observed, the nucleation temperature increases relatively slowly compared to that seen in the case when Al-5%Ti-1%B master alloy was used. This observation is more clearly noted when the molten metal was poured at 950°C. Evidence of reduction in undercooling with the increase in B concentration is observed in Figure 11. From the thermal point of view, an ideal grain refiner would remove the recalescence entirely [34–36].

Figure 12 demonstrates the variation in the alloy grain size as a function of the added B and pouring temperature. It is evident that addition of 200 ppm B to the melt at 750°C is sufficient to produce finer grains ($\sim 250\mu m$) than those obtained from using the Al-10%Ti master alloy ($\sim 850\mu m$) or

TABLE 3: WDS analysis (at.%) of AlB_2 and AlB_{12} phases observed in Figure 13(a).

Al	B
34.15	63.19
35.40	64.47
31.47	66.64
33.62	65.51
7.32	91.56
8.52	90.78

FIGURE 14: Presence of B and Si in Al-7%Si alloy treated with 800 ppm B. Note the geometric shape of the particles in Zone A.

FIGURE 15: Distribution of (a) B and (b) Si in the 800 ppm B-treated Al-7%Si alloy shown in Figure 14.

the as-received alloy ($\sim 1854\mu m$) poured at 750°C, as presented in Figure 4. In this case, Figure 13 reveals the possibility of the coexistence of the two B-based compounds in

FIGURE 16: Evolution of the grain size in A356.2 alloy: (a) no addition, (b) Al-10%Ti (0.2%Ti), (c) Al-5%Ti-1%B (0.1%Ti), and (d) Al-4%B (100 ppm B). Pouring temperature: 750°C; stirring time: 30 minutes.

FIGURE 17: Comparison of the grain size observed in A356.2 alloy as a function of the type of the grain refiner added.

pure aluminum as confirmed by the associated WDS analysis (Table 3), whereas Figure 14 shows the distribution of B and Si phases in Al-7%Si alloy. As can be seen, both elements precipitate away from each other (marked zones A and B) in Figures 14 and 15. This observation is confirmed by

the X-ray elemental distribution for each zone (Figure 16), indicating that there is no affinity for the reaction between these two elements. In contrast, when Ti was added with B (as Al-5%Ti-1%B master alloy) to the 1050 commercial aluminum, a clear interaction between Ti and B took place, leading to the formation of TiB_2 . Thus, it could be concluded that B has no grain refining capacity when added to ultrapure aluminum, which is not the case when the metal contains traces of Ti, leading to the possible formation of different nucleation sites that coexist, such as AlB_{12} , AlB_2 , and TiB_2 in Al-Si alloys. Evolution of the grain size of A356.2 alloy using different grain refiners is exhibited in Figure 16, whereas Figure 17 displays the variation in the grain size of A356.2 alloy as a function of the added type of the grain refiner.

4. Conclusions

Based on the obtained experimental results reported in this study, the following conclusions may be made:

- (1) Addition of grain refiner master alloys in large amounts increases the nucleation temperature of the formation of α -aluminum and eliminates the undercooling.

- (2) The Al-4%B master alloy is more effective as a grain refiner compared to other types of master alloys. The presence of traces of Ti in the base A356.2 alloy would react with B leading to the formation of TiB_2 , which, in turn, would improve the effectiveness of the master alloy used.
- (3) Since B has no affinity to react with Si in the base alloy, AlB_2 particles are more effective as nucleation sites than the Al_3Ti particles.
- (4) Addition of a grain refiner also changes the morphology of the α -Al dendrites from elongated to a rosette or more rounded form.
- (5) Maintaining the liquid metal for a long period prior to pouring may lead to agglomeration of the intermetallic particles which would reduce the refining effectiveness of the master alloy used.
- (6) Addition of 0.2 wt.% Ti is sufficient to obtain good grain refining. Increasing the Ti content beyond that would lead to more precipitation of intermetallics with no further improvement in grain refining.

Conflicts of Interest

The authors declare they have no conflicts of interest.

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