Influence of Mg on Grain Refinement of Near Eutectic Al-Si Alloys

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Although the grain-refinement practice is well established for wrought Al alloys, in the case of foundry alloys such as near eutectic Al-Si alloys, the underlying mechanisms and the use of grain refiners need better understanding. Conventional grain refiners such as Al-5Ti-1B are not effective in grain refining the Al-Si alloys due to the poisoning effect of Si. In this work, we report the results of a newly developed grain refiner, which can effectively grain refine as well as modify eutectic and primary Si in near eutectic Al-Si alloys. Among the material choices, the grain refining response with Al-1Ti-3B master alloy is found to be superior compared to the conventional Al-5Ti-1B master alloy. It was also found that magnesium additions of 0.2 wt pct along with the Al-1Ti-3B master alloy further enhance the near eutectic Al-Si alloy's grain refining efficiency, thus leading to improved bulk mechanical properties. We have found that magnesium essentially scavenges the oxygen present on the surface of nucleant particles, improves wettability, and reduces the agglomeration tendency of boride particles, thereby enhancing grain refining efficiency. It allows the nucleant particles to act as potent and active nucleation sites even at levels as low as 0.2 pct in the Al-1Ti-3B master alloy.

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I. INTRODUCTION

GRAIN refinement has been an important technique for improving the soundness and properties of aluminum products for most of this century. The addition of grain refiners, usually master alloys containing potent nucleant particles, promotes the formation of fine equiaxed grains by suppressing the growth of columnar and twin columnar grains. Castings with columnar or large grains have poor castability and mechanical properties compared to fine equiaxed grain castings.[1,2] The finer grain size also reduces the size of defects such as micropores and second-phase particles, thereby contributing to improved mechanical properties. The grain-refinement practice is well established for wrought alloys, but, in the case of foundry alloys, the practice of adding grain refiners and the impact on castability is not fully understood, leading to greatly varying practice from foundry to foundry.[3] Grain refinement of eutectic alloys containing higher concentration of Si is not a common practice. Some attempts have been made in the past to grain refine the α-Al dendrites in these alloys. In general, these alloys are modified by Sr to obtain fine eutectic Si in the microstructure.[4–6] However, this process often results in increased porosity, which leads to poor mechanical properties and overrides the favorable effects of finer silicon microstructure that results from modification.

Grain refinement of Al-Si alloys shows certain interesting trends. Kori *et al.*[7,8] found that Al-0.2Si grain refined using 0.2 pct of Al-5Ti-1B master alloy showed better grain refinement than commercially pure Al, suggesting that Si additions in small quantities improve the grain refinement response of Al. This could be attributed to a possible decrease in the surface tension of the liquid Al (γ_{sl}) in the presence of Si.[8,9] However, Al-Si alloys containing ≥2 pct Si respond poorly to the grain refinement by conventional Al-5Ti-1B master alloy. The presence of large amounts of Si adversely affects the grain refining efficiency of Ti, as reported in several studies.[1,7,9–18] Sigworth and Guzowaski[13] suggested that in the case of grain refinement of Al-Si alloys by conventional Al-5Ti-1B master alloy, titanium silicide coats the surface of Al_3Ti and poisons the effectiveness of the nuclei present in Al-Ti master alloy. Recent work of Schumacher and Mckay[18–21] shows that Si poisoning in commercial casting appears to be consistent with the gradual occupation of Al nucleation sites by $TiSi_2$. They also proved the formation of $TiSi_2$ particles on the basal plane of TiB_2 particles. It is has been suggested[22,23] that the TiB_2 interface is an energetically favorable site for Si. The surface chemistry and, hence, the surface energy factors are thought to adversely affect the TiB_2 as a nucleation site.[8] In a detailed grain refinement study on a number of Al-Si alloys (0.2 to 10 pct of Si), Kori *et al.*[8,9] found that a higher addition level of Al-5Ti-1B master alloy can

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overcome the poisoning effect resulting in finer grain size under different holding times. The improvement in the grain refining response at higher addition levels is usually attributed to the presence of some aluminide and boride particles, which are unaffected by the poisoning elements.

Lu *et al.*[24] demonstrated that AlB_2 is a powerful grain refiner in Al-5Si and Al-7Si alloys, and subsequently, Sigworth[25] has reported the development of an Al-3Ti-3B master alloy, which is better than the conventional Al-5Ti-1B master alloys for grain refinement in Al-7Si alloys. Kori *et al.*[9,26,27] made grain refiners with higher boron content than the conventional master alloys (Al-5Ti-1B), which are found to be efficient grain refiners for Al-Si alloys. These results suggest that binary Al-3B and ternary Al-1Ti-3B master alloys are the most efficient grain refiners for Al-7Si alloy among the various master alloys studied.[9,18,26,27] Birch[28] studied the grain refinement of 99.85 pct Al using the 0.2 pct Al-3Ti-1B master alloy. They also studied the effect of Mg addition on the grain refining efficiency of Al-3Ti-1B master alloy by varying the Mg concentration up to 5 pct in a 99.85 pct cast Al. In this study, a beneficial effect of Mg was observed as the grain size was found to decrease continuously with an increase in the Mg content. Kori *et al.*[8,9] also found that Mg helps in overcoming the poisoning effect of Si in a wide range of Al-Si alloys (7 to 15 pct Si) when grain refined with a Al-5Ti-1B master alloy. However, the mechanism of grain refinement of Al and Al-Si alloy in the presence of Mg has not yet been clearly understood. Moreover, to our knowledge, no work has been reported so far on the influence of Mg addition in Al-Si alloys when grain refined with Al-1Ti-3B master alloy. An attempt has been made in the present work to understand the influence of Mg on the grain refining performance of Al-1Ti-3B and Al-5Ti-1B master alloys in near eutectic Al-Si alloys.

II. EXPERIMENTAL DETAILS

The as-received near eutectic Al-Si alloy was labeled as alloy 1. The near eutectic Al-Si alloy with 0.32 pct Mg was prepared by adding Al-10 pct Mg master alloy to alloy 1, and it was labeled as alloy 2. The chemical compositions of both these alloys are given in Table I. Both these alloys were remelted in a pit-type resistance furnace under a cover flux (45 pct NaCl + 45 pct KCl + 10 pct NaF), and the melt was held at 993 K (720 °C). After degassing with hexachloroethane, the master alloy chips were added to the melt for grain refinement. Melts were poured after holding for a period of 10 minutes into a split-type cylindrical cast iron mold (12.5-mm diameter and 125-mm length). The experiments carried out to study the grain refinement response of alloys 1 and 2 are summarized in Table II.

The microstructures of samples (with and without grain refinements) were characterized by using a Leica optical microscope (Leica, DM LM, Glattbrugg, Switzerland) attached with an image analyzer system. Since the microstructures of both as-cast and grain-refined samples are dendritic in nature, the grain size was represented in terms of the square root of the product of dendrite length and width.[8,9,26,27] Measurements of the length and width for calculation of the grain size are carried out in a manner shown in Figure 1. Grain size analysis was carried out by the linear

Table II. Details of Grain Refinement Used in the Present Study

Alloy	Grain Refiner	Addition Level (Wt Pct)	Elemental Addition Level, Wt Pct	
			Ti	B
Alloy 1	Al-5Ti-1B	0.2	0.010	0.002
		0.5	0.025	0.005
		1.0	0.050	0.010
		2.0	0.10	0.020
Alloy 1	Al-1Ti-3B	0.2	0.002	0.006
		0.5	0.005	0.015
		1.0	0.010	0.030
		2.0	0.020	0.060
Alloy 2	Al-5Ti-1B	0.2	0.010	0.002
		0.5	0.025	0.005
		1.0	0.050	0.010
		2.0	0.10	0.020
Alloy 2	Al-1Ti-3B	0.2	0.002	0.006
		0.5	0.005	0.015
		1.0	0.010	0.030
		2.0	0.020	0.060

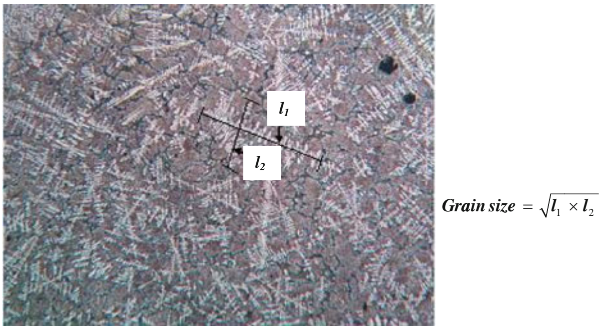

Fig. 1—Illustration of grain size measurement in dendritic Al-Si alloy.

Table I. Chemical Composition of Alloys Used in the Present Work

Alloy Code	Si	Cu	Ni	Fe	Mg	Mn	Zn	Al
Alloy 1	13.20	0.90	0.95	0.45	0.14	0.20	0.14	balance
Alloy 2	13.15	0.85	0.90	0.45	0.32	0.17	0.15	balance

intercept method after etching the polished surface with Keller's reagent (2.5 pct HNO_3, 1.5 pct HCl, 1 pct HF, and 95 pct H_2O). For each sample, a minimum of 120 readings were taken to determine the average grain size of the sample. The Vickers hardness of the untreated and grain-refined samples was determined using a load of 3 kg. Tensile tests of selected untreated and grain-refined samples were carried out using a Shimadzu AG-IS 250 kN (Shimadzu, Singapore) unit. The chosen crosshead speed during the tensile tests was 1 mm/min.

To understand the role of Mg in dispersing the boride agglomeration in AlTiB grain refiner, an attempt was made to prepare Al-10Mg-1Ti-3B master alloy in two different ways: (1) by reacting the KBF_4 and K_2TiF_6 salt fluxes with Al-10Mg alloy, and (2) by reacting the KBF_4 and K_2TiF_6 with pure aluminum along with 10 wt pct additions of Mg to the Al-1Ti-3B master alloy. The microstructures of Al-1Ti-3B and Al-10Mg-1Ti-3B master alloys were studied using an FEI QUANTA* 200 scanning electron microscope (SEM). The SEM samples were electropolished using an electrolytic bath comprising 80 pct methanol and 20 pct HNO_3 by volume. Eutectic and primary Si sizes, with and without grain refiner additions (alloys 1 and 2), were also analyzed using an SEM. For each sample, a minimum of 100 readings were taken to find out the average eutectic and primary Si sizes.

III. RESULTS

Figure 2 shows the microstructure of alloy 1 in the untreated condition. It is clear from the figure that the microstructure consists of primarily eutectic mixture (α-Al + Si) with a considerable amount of dendritic α-Al and a few primary Si particles. Normally the hypereutectic Al-13.2Si alloy should consist of eutectic mixture and primary Si particles when it is solidified under equilibrium cooling conditions. Depending on the amount and type, the presence of alloying elements may shift the eutectic composition of Al-Si alloys. The alloy used in the present study contains appreciable amounts of Cu, Ni, and Fe. Hence, there is a strong possibility that this multicomponent alloy has a eutectic temperature and composition, which is shifted from the normal Al-Si eutectic values. According to Belov *et al.*,[29] under equilibrium cooling conditions, addition of 1.4 wt pct Cu to Al-13Si alloy decreases its eutectic temperature by about 5 °C, whereas the effect of 1.1 wt pct Ni additions does not significantly change the eutectic temperature. Similarly, Liu *et al.*[30] predicted a decrease of 6 °C in eutectic temperature of Al-7Si-0.3Mg alloy with 1 wt pct addition of Cu using Scheil's model. Shankar *et al.*[31] thermodynamically calculated the decrease in eutectic temperature by 275 K (2 °C), when 0.45 wt pct of Fe was added to Al-7Si alloy. The overall decrease of about 6 to 7 °C in eutectic temperature of Al-Si alloy may shift the eutectic composition from 11.8 to about 12.8 wt pct Si. Even in such a condition, the microstructure of alloy used in the present work should consist of essentially eutectic mixture and very few primary Si particles, if it solidified under equilibrium cooling conditions.

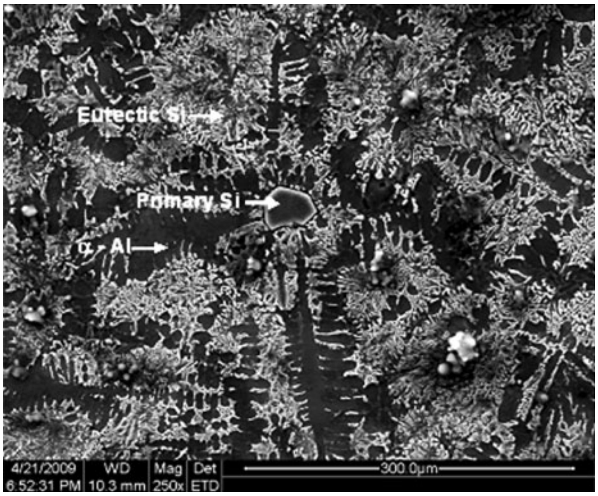

Fig. 2—Microstructure of near eutectic Al-Si alloy without grain refinement.

The presence of both α-Al and primary Si particles in this alloy indicates that the cooling rate was much faster than the equilibrium conditions and the resulting microstructure can be explained using the concept of skewed couple zone theory.[32] The solidification of Al-Si eutectic alloys may begin with the nucleation of either α-Al or Si. The presence of both α-Al and primary Si particles indicates that conditions were favorable for nucleation of both. This situation is possible only if solidification occurred in localized or isolated liquid pockets. In other words, the composition of the melt essentially varied from one region to the next. If α-Al nucleates at the eutectic temperature in a particular region, further supersaturation of melt is necessary before Si can nucleate. The increased supersaturation may be achieved by the growth of α-Al dendrite as primary crystals, thereby forcing the composition of the adjacent liquid toward hypereutectic compositions. The primary Si crystals precipitate from this supersaturated liquid, and the composition of the remaining liquid returns to within the coupled zone where both the phases grow cooperatively. We can also expect certain regions where the undercooled eutectic could become supersaturated, resulting in the formation of highly faceted primary Si phase. Thereafter, the two phases grow cooperatively from the melt at different velocities with a composition that falls outside the coupled zone. Thus, the microstructure consists of eutectic mixture, α-Al, and primary Si in this near-eutectic Al-Si alloy.

Figures 3(a) through (e) show the microstructure of alloy 1 treated with varying amounts of Al-5Ti-1B master alloy. The addition of 0.2 pct of Al-5Ti-1B (0.01 pct Ti) master alloy has resulted in marginal grain refinement of alloy 1 (Figure 3(b)). However, the α-Al grain structure remained predominantly coarse and of a columnar type. Increasing the amount of grain refiner

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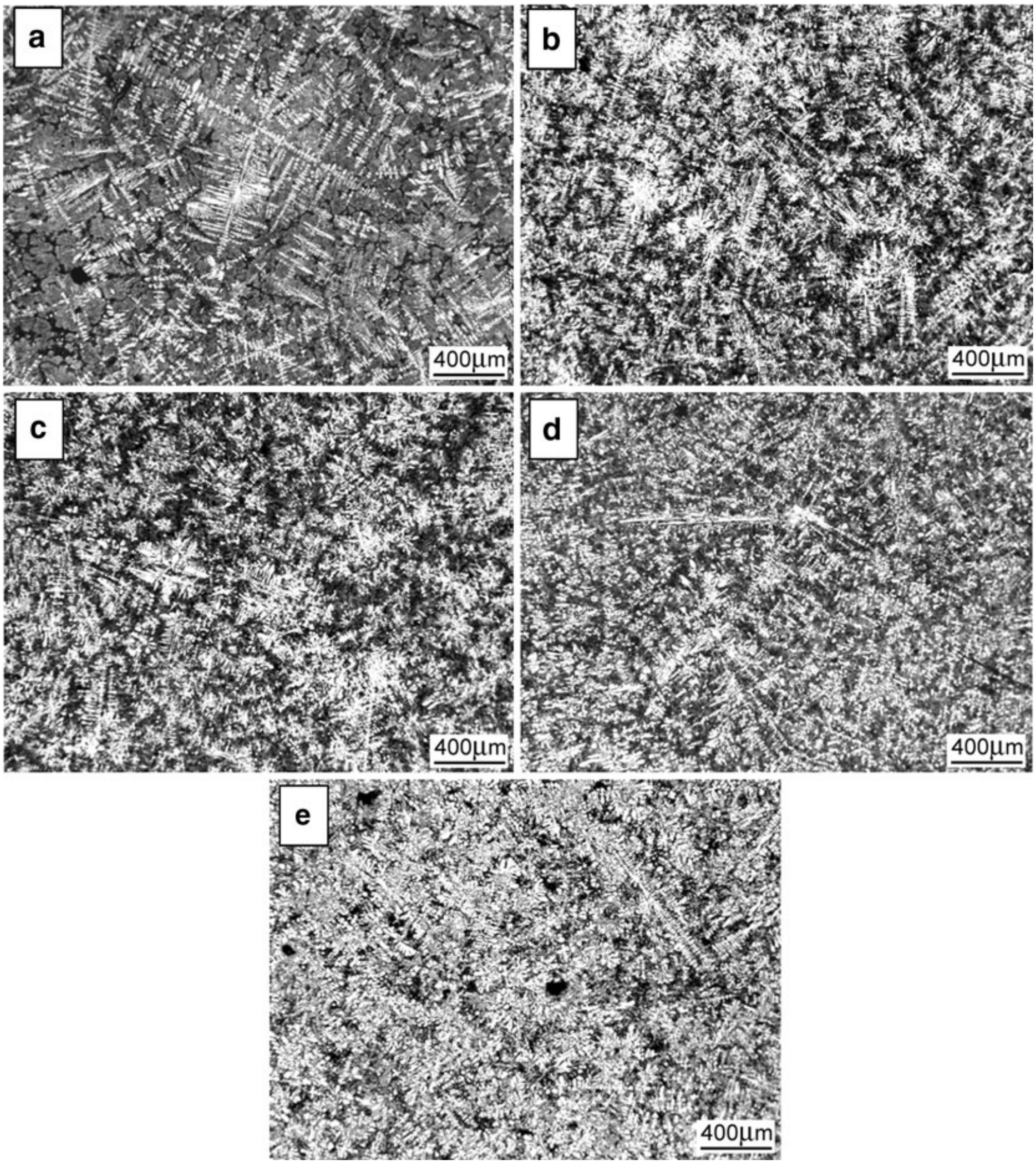

Fig. 3—Microstructure of alloy 1 grain refined with (*a*) 0, (*b*) 0.2, (*c*) 0.5, (*d*) 1.0, and (*e*) 2.0 wt pct of Al-5Ti-1B master alloy.

from 0.5, 1.0, and 2.0 pct (Figures 3(c) through (e)) does not result in any appreciable refinement for this alloy. A comparison of Figure 3(b) with Figure 4(a) shows that the size of α-Al dendrites is marginally reduced with 0.2 pct of Al-1Ti-3B master alloy addition to alloy 1. With increased addition levels of this grain refiner, the grain structure of alloy 1 does get refined with fine columnar α-Al grain structure obtained at about 1 pct additions of Al-1Ti-3B master alloy (Figures 4(b) and (c)). Further increases in the grain refiner levels (Figure 4(d)) does not bring about any significant changes in the grain structure.

Figure 5 shows the effect of different amounts of Al-5Ti-1B master alloy additions to alloy 2. It is very clear from the microstructure that the combined additions of 0.2 pct Mg along with 0.2 pct Al-5Ti-1B result in (1) better grain refinement when compared to the addition of the grain refiner alone, and (2) similar levels of Mg additions along with 1 pct of Al-5Ti-1B master alloy, results in enhanced grain refinement. This observation is consistent with Kori *et al.*,[8,27] who also observed significant improvement in grain refining efficiency of Al-5Ti-1B master alloy in the presence of Mg in a wide range of Al-Si alloys. In a similar manner, combined additions of 0.2 pct Mg along with 0.2 pct of Al-1Ti-3B results in better grain refinement when compared to the additions of just the grain refiner alone (Figure 6(a)). Significant refinement in grain size of alloy 2 was observed with 0.5 pct of Al-1Ti-3B master alloy addition (Figure 6(b)) beyond which the effect of further grain refiner additions is found to be marginal (Figures 6(c) and (d)).

Primary α-Al grain size analysis (Figure 7) of alloys 1 and 2 treated with varying amounts and types of grain

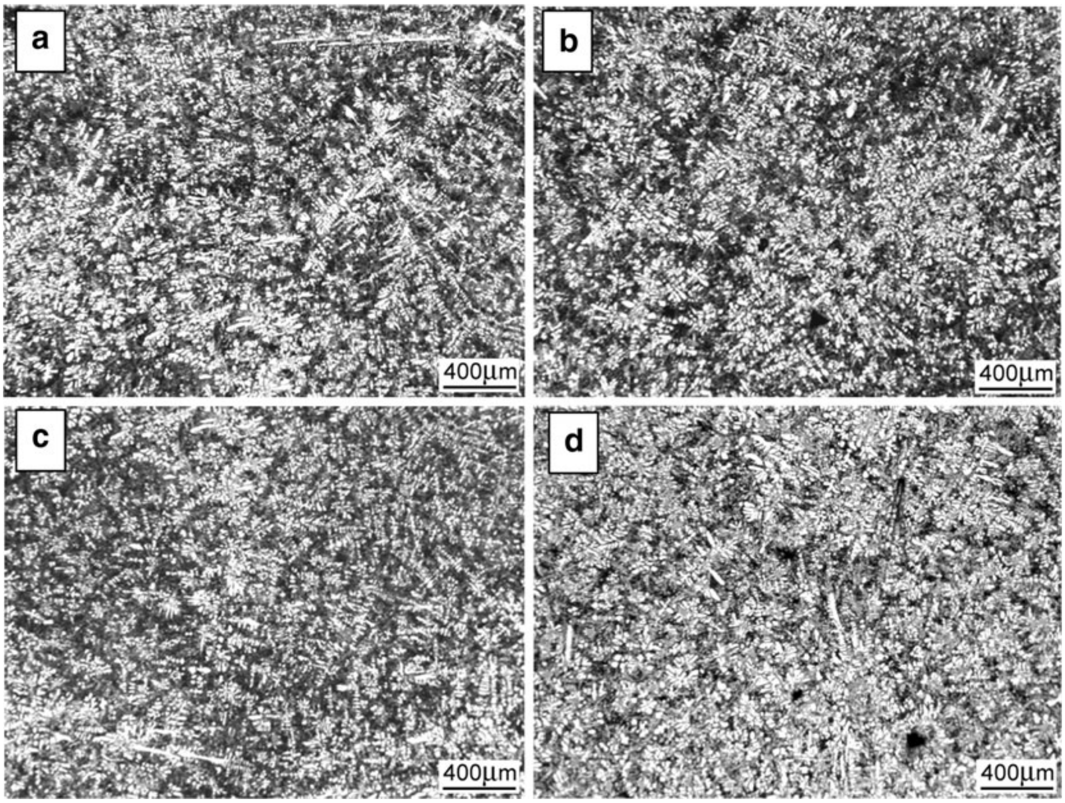

Fig. 4—Microstructure of alloy 1 grain refined with (*a*) 0.2, (*b*) 0.5, (*c*) 1.0, and (*d*) 2.0 wt pct Al-1Ti-3B master alloy.

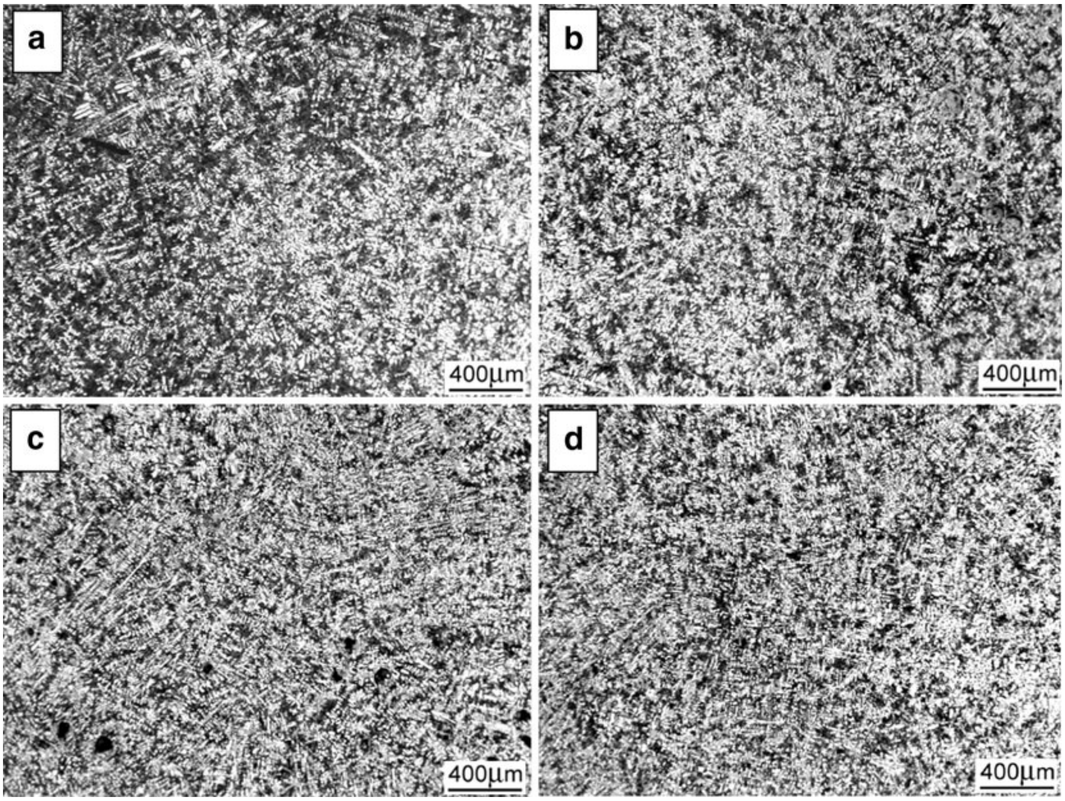

Fig. 5—Microstructure of alloy 2 grain refined with (*a*) 0.2, (*b*) 0.5, (*c*) 1.0, and (*d*) 2.0 wt pct Al-5Ti-1B master alloy.

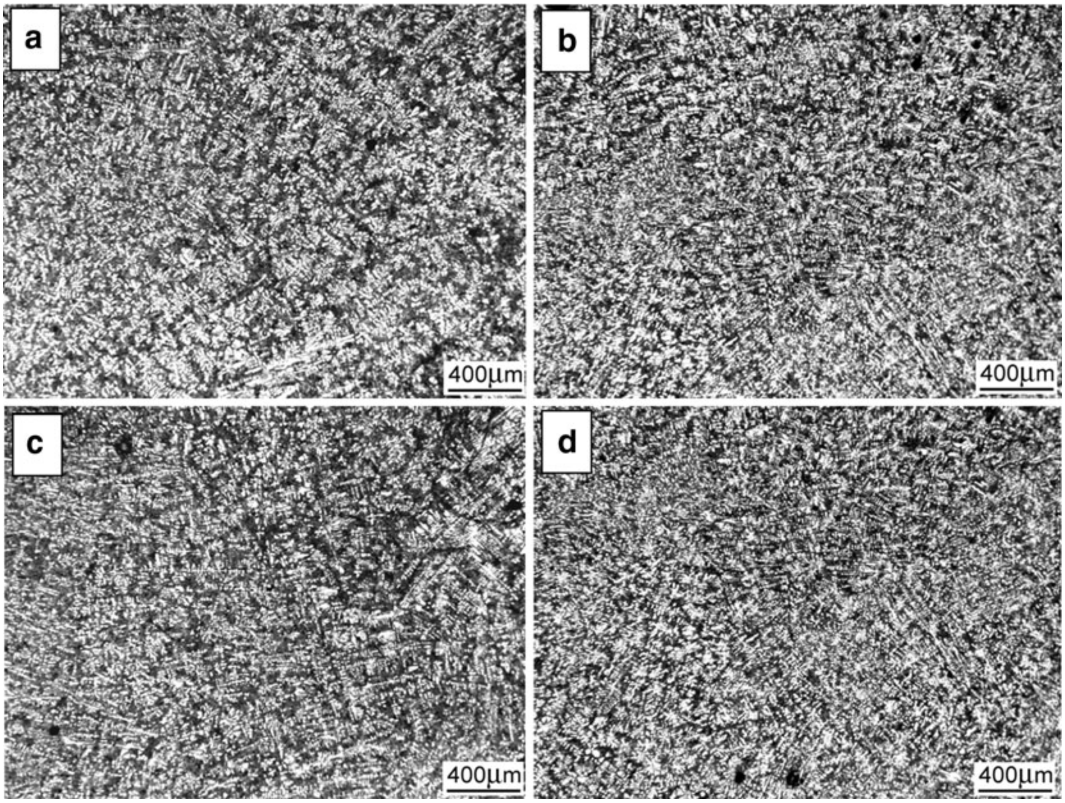

Fig. 6—Microstructure of alloy 2 grain refined with (*a*) 0.2, (*b*) 0.5, (*c*) 1.0, and (*d*) 2.0 wt pct Al-1Ti-3B master alloy.

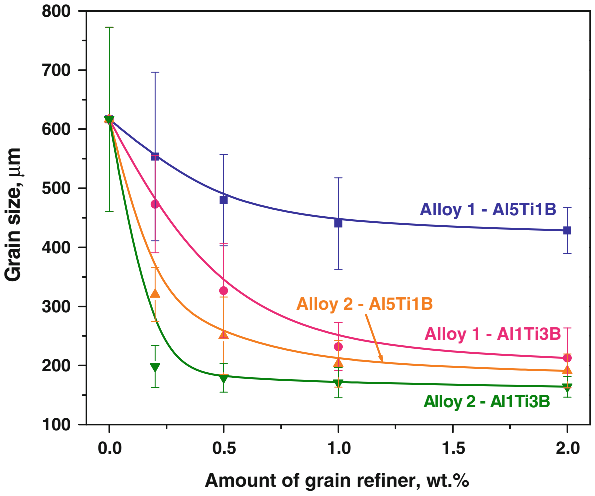

Fig. 7—Grain size analysis of alloys 1 and 2 treated with various amounts and types of grain refiner.

refiners confirms the qualitative observations from the SEM micrographs. Additions of 0.2 pct of Al-5Ti-1B and Al-1Ti-3B master alloy marginally reduced the grain size of alloy 1 from ~600 to ~550 and ~470 μm, respectively. Addition of the same amount of Al-5Ti-1B and Al-1Ti-3B master alloy to alloy 2 resulted in significant decreases in grain size from ~600 to ~320 and 200 μm, respectively. Further increases in Al-1Ti-3B master alloy addition level to alloy 2 resulted only in marginal grain refinement. On the other hand, the increase in the addition levels of both Al-5Ti-1B and Al-1Ti-3B master alloys significantly decreases the grain size of alloy 1 up to 1 pct, thereafter showing only a marginal decrease in grain size. Similar results are also observed in alloy 2 treated with Al-5Ti-1B master alloy. Although the grain refinement of alloy 1 increases with the master alloy addition levels, the grain size of alloy 2 treated with 0.2 pct Al-1Ti-3B master alloy is lower than that of alloy 1 treated with 2 pct of either Al-5Ti-1B or Al-1Ti-3B master alloys.

Figure 8 shows the size of primary Si in alloys 1 and 2 for varying levels of Al-5Ti-1B and Al-1Ti-3B master alloy additions. With 0.2 pct Al-5Ti-1B master alloy additions, a decrease in the primary Si size of alloys 1 and 2 from ~55 to ~35 and 24 μm, respectively, is observed. This further decreases to ~22 and 18 μm, respectively, at 0.5 pct addition levels. The size of primary Si does not change significantly with further additions up to 2 pct Al-5Ti-1B master alloy. We have observed a more pronounced refinement of primary Si size from ~55 to ~18 μm in alloy 1 when it is treated with 0.2 pct of Al-1Ti-3B master alloy additions, beyond which there is no significant effect. A similar result has been observed in alloy 2 treated with varying additions of Al-1Ti-3B master alloy.

The effects of varying additions of master alloys on the hardness of alloys 1 and 2 are presented in Figure 9. It is found that the hardness of alloy 1 remains constant up to 0.5 pct of Al-5Ti-1B master alloy addition. Thereafter, the hardness increases with further additions of the Al-5Ti-1B master alloy. On the other hand, the

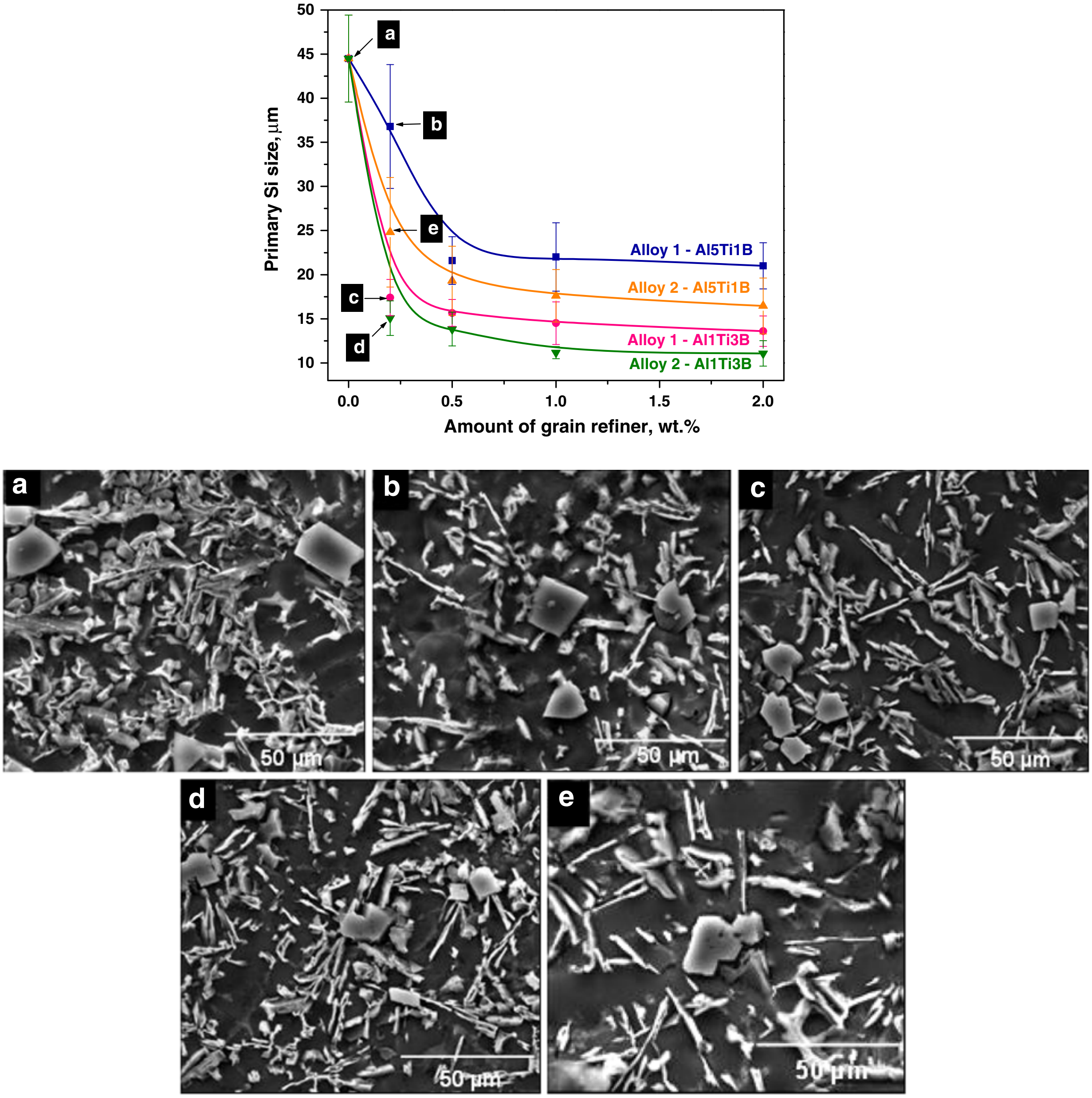

Fig. 8—Refinement of primary Si size in alloys 1 and 2 treated with various amounts and types of grain refiner.

addition of Al-1Ti-3B master alloy to alloy 1 increases the hardness value almost linearly with increased addition levels. A sharp increase in hardness of about 25 pct compared to the base alloy is observed when up to 0.5 pct Al-1Ti-3B master alloy is added to alloy 2. The hardness values then remained constant with further additions of this Al-1Ti-3B master alloy. The hardness of alloy 2 having 0.2 pct Al-1Ti-3B alloy was found to be higher than that of alloy 1 even with 2 pct Al-1Ti-3B alloy additions. It is to be noted that the change in hardness levels of alloys 1 and 2 treated with varying amounts of Al-5Ti-1B and Al-1Ti-3B master alloys follow a similar trend compared with the grain refinement trends reported in Figure 7.

Figure 10 shows the hardness and grain size data in a Hall–Petch form for varying amounts of Al-5Ti-1B and Al-1Ti-3B master alloy added to alloys 1 and 2. It is evident that, irrespective of the chemical composition and the type of master alloy additions, there exists a linear relationship between hardness and (grain size)$^{-1/2}$; *i.e.*,

$$\text{hardness} = 66.35 + 527 \times (\text{grain size}, \mu\text{m})^{-1/2} \quad [1]$$

The tensile strength values also reflect the increased hardness levels of alloy 2 with Al-1Ti-3B master alloy additions (Figure 11). The tensile strength of alloy 1 increases from 170 MPa to 190 and 203 MPa with 2.0 pct addition of Al-5Ti-1B and Al-1Ti-3B master alloys, respectively. On the other hand, the tensile strength of alloy 2 increases to 227 MPa (from 175 MPa) with 0.5 pct additions of Al-1Ti-3B master alloy (an almost 30 pct increase in strength compared to

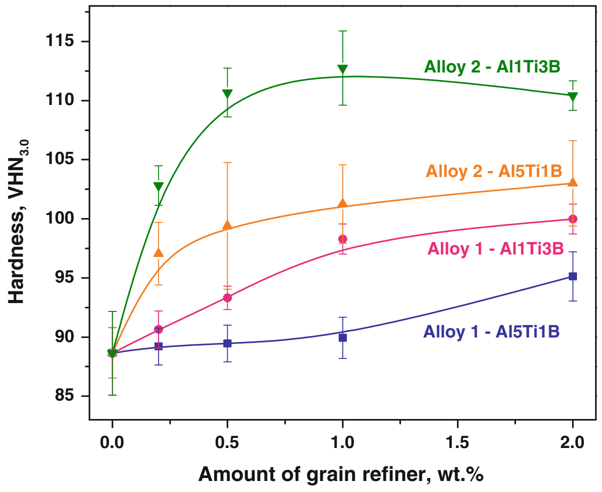

Fig. 9—Hardness of alloys 1 and 2 treated with various amounts and types of grain refiner.

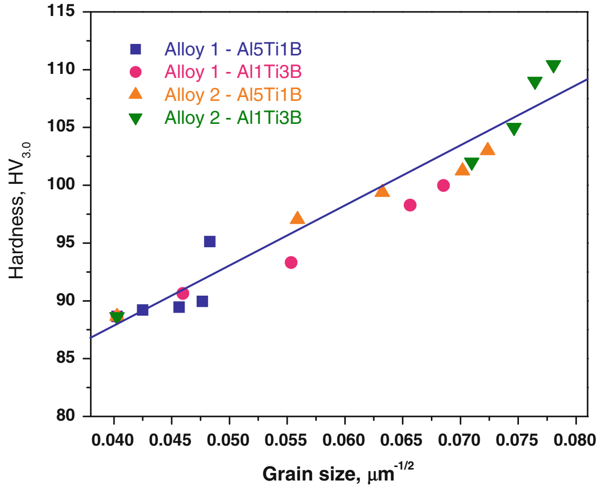

Fig. 10—Hall–Petch plot for alloys 1 and 2 treated with various amounts and types of grain refiner.

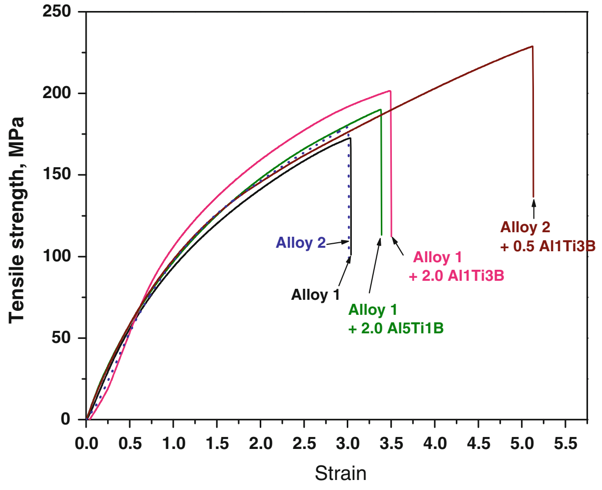

Fig. 11—Tensile properties of alloys 1 and 2 treated with various amounts and types of grain refiner.

alloy 1). Also, the elongation of alloy 2 increases from 3 to 5.2 pct with 2 pct additions of Al-1Ti-3B master alloy. Significant improvements in mechanical properties of alloy 2 are observed in the presence of Al-1Ti-3B alloy and 0.2 pct Mg additions.

IV. DISCUSSION

The role of Mg on the grain refining performance of Al-1Ti-3B master alloy in the near eutectic Al-Si alloy is discussed in this section.

A. *Role of Mg as Modifier*

Joenoes *et al.*[33] suggested that the addition of Mg to eutectic alloys modifies the eutectic Si and shifts the eutectic composition toward higher Si content. It is thus possible to produce near eutectic alloys containing a greater amount of α-Al grains, which are more amenable for grain refinement. However, our results suggest that the size of eutectic Si increased from ~15 to ~37 μm in alloy 1 treated with 0.2 pct of Al-5Ti-1B master alloy (Figure 12). Further, increase in addition levels of Al-5Ti-1B master alloy to alloy 1, decreases the eutectic size gradually to a value of ~20 μm corresponding to a 2.0 pct addition of Al-5Ti-1B master alloy. A similar behavior is also observed in alloy 1 treated with varying amounts of Al-1Ti-3B master alloy. However, the extent of increase in the eutectic Si size is observed to be lower in the case of alloy 1 treated with Al-1Ti-3B master alloy when compared to Al-5Ti-1B master alloy. The degree of increase in eutectic Si size is further reduced in alloy 2 treated with Al-5Ti-1B and Al-1Ti-3B master alloys. Notably, at lower levels of grain refiner additions up to 0.5 wt pct, these differences in the extent of increase in eutectic Si size are much higher. This suggests that, at lower grain refiner levels, alloy 2 has a much larger amount of α-Al grains when compared to alloy 1 when these alloys are treated with Al-5Ti-1B or Al-1Ti-3B master alloy additions.

B. *Role of Mg as Wetting Promoter*

According to classical nucleation theory, the formation of a stable nucleus depends on the competition between the driving force for the phase change from liquid to solid (the volume free energy) and the energy that is required for the formation of a new interface. The free energy barrier for nucleation on a heterogeneous substrate is:

$$\Delta G_n^o = \left(\frac{16\pi}{3}\right)\left(\frac{\sigma^3}{\Delta s_f \Delta T^2}\right) f(\theta) \qquad [2]$$

where σ is the energy of the new interface, Δs_f is the entropy of fusion, ΔT is the undercooling below the liquidus temperature, and θ is the wetting angle between the liquid phase and the substrate.

According to Eq. [2], the free energy barrier for nucleation can be decreased by increasing the undercooling

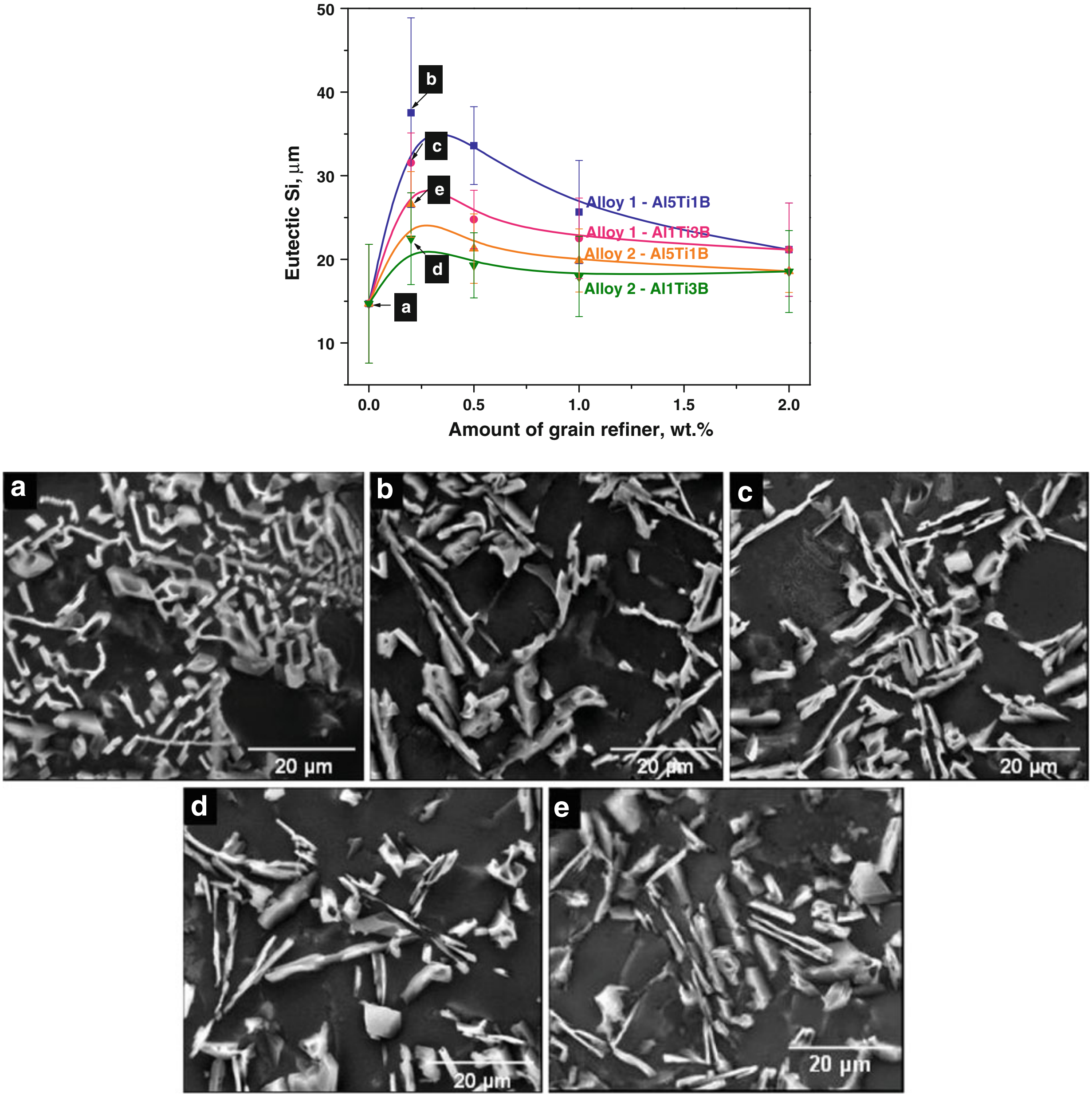

Fig. 12—Eutectic Si size in alloys 1 and 2 treated with various amounts and types of grain refiner.

or by decreasing the wetting angle of the heterogeneous substrate, which is related to the interfacial energy between the substrate and the liquid melt. Therefore, when substrates present in the melt have a lower wetting angle with respect to the melt, the thermodynamic barrier to nucleation is lower, even at a relatively lower undercoolings. Thus, there is a higher probability of a nucleation event occurring at a lower undercooling for smaller wetting angles. It is well known from Korolkov's review[34] that the interfacial tension of molten aluminum decreases significantly with the addition of solute elements, especially magnesium. At a concentration of 0.5 pct of Mg, the surface tension of pure aluminum at its melting point drops from 0.92 to 0.72 N/m,[35] thereby improving the wetting between nucleant particles and liquid aluminum. This increases the probability of the nucleation event, leading to increased grain refinement efficiency.

C. *Role of Mg as Oxygen Scavenger*

In the grain-refining master alloy production process, the fluoride flux is melted in air together with aluminum metal and is cast in a mold under normal atmospheric conditions where some moisture may be present. The presence of moisture in the flux and in air adversely affects the dispersion of the ceramic phase due to the formation of a detrimental layer of alumina; and the extent of dispersion then is inversely proportional to the concentration of moisture in the melting atmosphere and that of the flux during the casting process. The fact that alumina is thermodynamically more stable than

TiB_2 is detrimental to the grain refinement process. On the other hand, magnesium reacts with alumina, thereby removing it preferentially and making the liquid melt conducive for grain refinement. Studies on ceramic particle reinforced Al-Mg, Al-Si-Mg alloy metal matrix composites show that magnesium reduces the agglomeration tendency of the reinforced particles by scavenging the oxygen from the particle surface and preferentially reacting with the alumina layer.[36] This scavenging process also helps in cleaning the particle surface and exposes a fresh nascent surface to the liquid aluminum leading to effective grain refinement.

D. *Role of Mg on the Stability of Al_3Ti, AlB_2, and TiB_2 in Al Melt*

As stated earlier, Al_3Ti is considered as an effective nucleant for wrought Al alloys. However, the presence of Si in commercial foundry Al alloys poisons its effectiveness by forming titanium silicide ($TiSi_2$) on the Al_3Ti surface. AlB_2 and TiB_2 particles are considered as potent nucleation sites for foundry aluminum alloys. Hence, for effective grain refinement of near eutectic Al-Si alloys, AlB_2 and TiB_2 particles should be made more stable in molten aluminum. Recently, Fan *et al.*[37] found that the presence of alloying elements affects the stability of Al_3Ti, AlB_2, and TiB_2 particles. To evaluate the role of Mg on the stability of Al_3Ti, AlB_2, and TiB_2 in Al melt, the excess free energy after Mg addition, *i.e.*, $\Delta G_{\text{Al-Mg alloy}}$-$\Delta G_{\text{pure Al}}$ for each precipitate, is calculated. Fan *et al.*[36] calculated the free energy associated with the formation of Al_3Ti, AlB_2, and TiB_2 in Al-Ti-B and Al-Ti-B-Mg melt by combining the Wilson equation[38] with the Miedema model.[39] According to their model,[37] addition of Mg in Al decreases the excess energy of Al_3Ti and TiB_2 and increases the excess free energy of formation of AlB_2. However, the change in excess free energy with the Mg additions in the Al melt is rather very low. For example, when 1 pct of Mg is added to Al, the excess free energy of Al_3Ti, TiB_2, and AlB_2 is –5, –2.2, and 2.2 kJ, respectively. This finding suggests that Mg in small amounts does not significantly alter the stability of Al_3Ti, AlB_2, and TiB_2 in Al melt.

E. *Role of Mg in Dispersing the Boride Agglomerates in AlTiB Grain Refiner*

Most of the commercially available Al-Ti-B grain refiner master alloys are prepared by reaction of the KBF_4 and K_2TiF_6 salts with molten aluminum. Gudmundsson *et al.*[40] used a novel approach to investigate the boride agglomeration in fractured AlTiB grain refiners. They found strings/clouds of particles existing in the fractured samples of AlTiB grain refiners. The strings were seen to contain fluoride at relatively high levels when compared to the rest of the sample. They proposed a theory that suggests that the boride particles are susceptible to wetting of fluorides such as potassium aluminum fluoride (K_3AlF_6), which is the spent salt from the reaction of KBF_4 and K_2TiF_6 with aluminum while producing Al-Ti-B master alloy. If this is the cause of agglomeration in Al-Ti-B master alloys, then it is possible that a similar mechanism could operate when casting aluminum alloys with these grain refiners. Our initial attempts made to prepare Al-10Mg-1Ti-3B master alloy by reacting the KBF_4 and K_2TiF_6 salt fluxes to Al-10Mg alloy were not successful and led to many powder agglomerates on the melt surface. An XRD analysis of these powders identified these compounds as MgF_2 and KF (Figure 13). While preparing the Al-10Mg-1Ti-3B master alloy, the following reactions can occur between salt flux and Al-Mg melt:

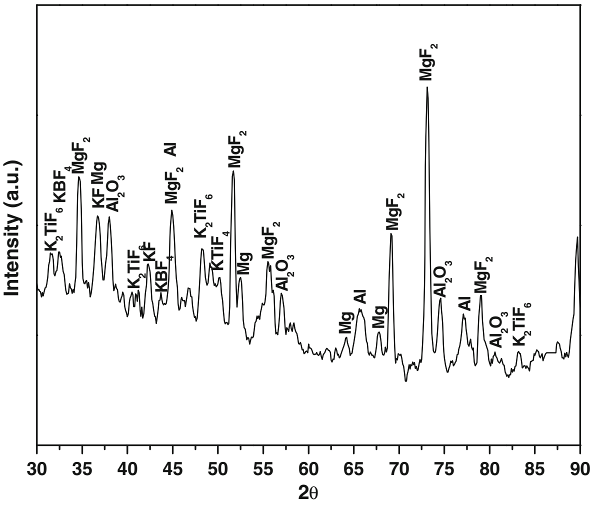

Fig. 13—XRD analysis of powders obtained during preparation of Al10Mg1Ti3B master alloy.

$$K_2TiF_{6(1)} + 2KBF_{4(1)} + 5[Mg] \rightarrow 5MgF_2 + 4KF_{(1)}TiB_2 \qquad [3]$$

$$K_2TiF_{6(1)} + 2KBF_{4(1)} + 3^1/_3[Al] \rightarrow 3^1/_3AlF_{3(1)} + 4KF_{(1)}TiB_2 \qquad [4]$$

Fan *et al.*[37] found that when Mg content is more than 0.1 pct at 993 K (720 °C), ΔG for reaction [4] is <<0. This indicates that Mg easily reacts with the fluorides to form MgF_2, KF, and TiB_2 particles, as is also evident from our XRD analysis (Figure 13).

In view of this, an alternative approach was attempted for preparing the Al-10Mg-1Ti-3B master alloy. In this process, at first, Al-1Ti-3B master alloy was prepared by reacting the KBF_4 and K_2TiF_6 with pure aluminum. Thereafter, 10 wt pct of Mg was added to the Al-1Ti-3B to obtain the master alloy. An SEM micrograph of Al-10Mg-1Ti-3B master alloy shows a good distribution of boride particles when compared to Al-1Ti-3B master alloy (Figure 14). The boride agglomeration in AlTiB grain refiner could occur possibly due to the presence of either unreacted salt fluxes or due to the contamination of spent salt of potassium aluminum fluoride (K_3AlF_6) in the AlTiB grain refiner. The addition of Mg to AlTiB grain refiner results in a reaction between Mg and either unreacted salt fluxes or with the spent potassium aluminum fluoride (K_3AlF_6) salt. This reaction scavenges the fluoride, thereby reducing the boride agglomeration in

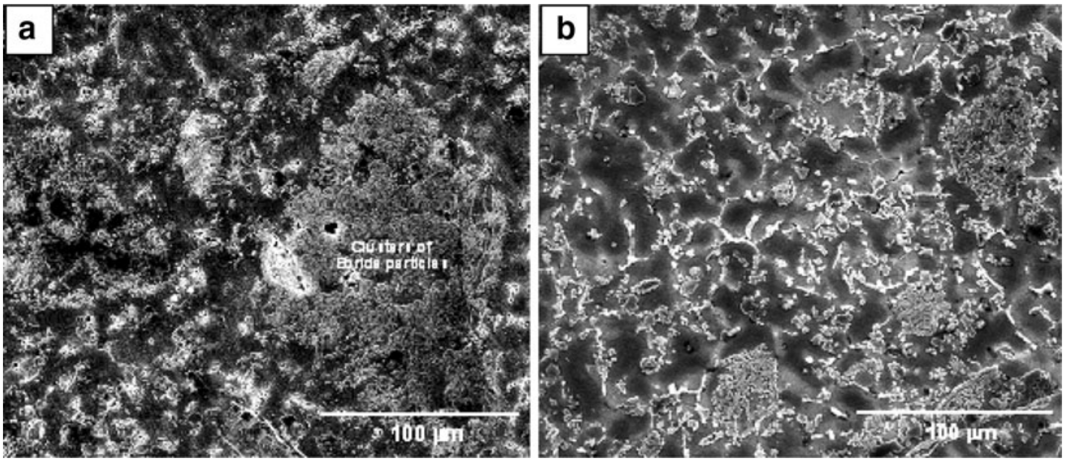

Fig. 14—SEM micrographs of (*a*) Al-1Ti-3B master alloy and (*b*) Al-10Mg-1Ti-3B master alloy.

AlTiB grain refiner. Moreover, the reaction between Mg and the unreacted salt fluxes introduces additional TiB_2 nucleant particles, which further enhances the grain refining efficiency of AlTiB grain refiner.

F. *Role of Grain Refiner in Refinement of Primary Si*

According to the literature, there is no direct evidence to support either TiB_2 or AlB_2 particles in refinement of primary Si in near eutectic or hypereutectic alloys. Data from the literature indicate that AlP and Si are both diamond cubic with very similar lattice parameters. Prior work shows that primary Si nucleates heterogeneously on the solid AlP particles with a cubic-cubic orientation relationship and solidifies, thereby promoting the refinement of primary silicon.[41–43] Most of the commercial Al-Si alloys invariably contain small amounts of phosphorus leading to the formation of AlP particles. Many of the AlP particles cannot be absorbed by the Al melt because of the lower solubility of phosphorus as well as the density differences. The undissolved AlP particles do not act as nuclei for the primary Si formation during solidification but rather combine with the dross and float up to the melt surface. When AlTiB grain refiner is added to the melt, the AlP compound can be absorbed by either TiB_2 or AlB_2 compounds, coupled with a peritectic-like reaction to form an AlP-rich transition layer around these particles, which can then act as heterogeneous nucleation sites for primary Si formation during solidification.[44] It can be concluded that the addition of AlTiB grain refiner could significantly increase the absorptivity of P in the melt, thereby improving the refinement of primary Si in near eutectic Al-Si alloys.

V. CONCLUSIONS

1. Near eutectic Al-Si alloy shows better grain-refining response to high B containing Al-1Ti-3B master alloys when compared to the conventional Al-5Ti-1B grain refiners with higher Ti levels.
2. Grain refining response of Al-1Ti-3B master alloy is substantially improved by the addition of 0.2 pct of Mg to near eutectic Al-Si alloy.
3. Combined additions of Al-1Ti-3B grain refiner and 0.2 pct of Mg to near eutectic Al-Si alloy results in significant improvements in the mechanical properties.
4. Magnesium in near eutectic Al-Si alloy scavenges the oxygen present on the surface of nucleant particles, improves wettability, and reduces the agglomeration tendency. This allows the nucleant particles to act as potent nucleating sites even at reduced levels of about 0.2 pct Al-1Ti-3B master alloy additions.
5. In both cases, Al-5Ti-1B and Al-1Ti-3B master alloys, added to near eutectic Al-Si alloy, refine the primary Si size by increasing the absorptivity of phosphorus in the melt.
6. It is important to note that several interactions (positive or negative) are possible in Al alloys, due to the presence of trace or impurity elements. Hence, when dealing with multicomponent Al alloys, the effect of trace elements on the grain refinement aspects also needs to be carefully studied.

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