

# ANOMALOUS GRAIN COARSENING BEHAVIOUR IN GRAIN-REFINED ALUMINIUM ALLOYS CAST USING LOW SUPERHEAT

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## Abstract

Chemical grain refinement of aluminium alloys has been commercially practiced for many years. Low superheat casting has also been recognised as a means of inducing grain refinement in aluminium alloys. However, the present study indicates that when both techniques are used in combination, the result is not always a further improvement in overall refinement, in fact, even grain coarsening can occur. Grain sizes were measured in test castings made from 356, 6063 and 2024 alloys poured at low superheats using various grain refiners (Al-5Ti-1B, Al-6Ti and Al-4B) at a range of addition levels. High addition levels of the Al-Ti-B and Al-Ti grain refiners sometimes yielded marginal improvements in grain size compared to non grain-refined low superheat samples. However, grain coarsening was also observed particularly at the lower addition levels of the Al-B master alloy. The mechanism proposed for this latter phenomenon carries implications for impurity control and recycling.

## Introduction

Chemical grain refining agents are commonly added to commercial wrought aluminium alloys to control the grain size and grain morphology in extrusion billets and rolling slabs so that good, reproducible processing and mechanical properties can be achieved. The most common of these refining agents contain titanium, e.g. Al-Ti-B, Al-Ti-C and Al-Ti master alloys, and are usually supplied in rod or ingot form. The addition of grain refiners to commercial aluminium foundry alloys is a less common practice than with wrought alloys. However, when it is employed, it is usually added to improve the alloy's castability (e.g. in terms of reducing hot tearing or redistributing shrinkage porosity) rather than to specifically control the grain size for property improvement [1].

Easton and StJohn [2] proposed that for wrought alloys with relatively low solute concentrations, the optimum chemical grain refiner needs to include both solute titanium (with its very high growth restriction factor, GRF) and nucleant particles (e.g. TiB<sub>2</sub> or TiC) in order to produce effective grain refinement. For this reason, the Al-5Ti-1B type of refiner is extremely effective.

The beneficial effect of boron in conjunction with titanium to grain refine aluminium alloys has also been explored by others [3, 4] and alternative mechanisms have been proposed. These have involved various permutations of mixed (Al,Ti)B<sub>2</sub> borides and TiAl<sub>3</sub> that become stabilised at sub-peritectic compositions.

The GRF of any solute element is given by the factor,  $mc_0(k-1)$ , where  $m$  is the gradient of the liquidus line in the binary alloy phase diagram,  $c_0$  is the concentration of the solute in the alloy, and  $k$  is the partition coefficient. It is generally assumed that individual GRFs are additive in multi-component alloy systems, however this method can grossly overestimate the value of GRF [5].

Easton and StJohn [2] also suggested that because aluminium casting alloys, such as 356 (Al-7%Si-0.3%Mg), already contain high solute levels and a high GRF (the GRF of 7%Si is equivalent to that of 0.17%Ti), the optimum grain refiner really only needs to contain nucleant particles. This means that master alloys such as Al-2.2Ti-1B (i.e. TiB<sub>2</sub> particles with no extra solute Ti) or Al-4B (i.e. containing AlB<sub>2</sub> and/or AlB<sub>12</sub> particles) are quite suitable as grain refiners for foundry alloys [6, 7, 8]. The Al-4B master alloy is actually more commonly used as an addition to electrical conductivity (EC) grade aluminium to remove Ti, V and Cr from solution and to precipitate them out as their respective borides [9]. Titanium, vanadium and chromium in solution are deleterious to electrical conductivity whereas their borides are not.

It should be noted that AlB<sub>2</sub> particles are much less stable than TiB<sub>2</sub> particles in an aluminium melt. In the pure Al-B binary system, there is a eutectic reaction at 0.022 wt% B and 659.7°C [6, 10]. Below this concentration, AlB<sub>2</sub> is not in equilibrium with liquid aluminium. However, the eutectic reaction occurs at lower B levels in hypoeutectic Al-Si alloys [10], meaning that AlB<sub>2</sub> stability is increased in these alloys.

Grain coarsening is known to occur when chemical grain refiners become "poisoned" by other elements present as alloying elements or impurities in the melt [11]. For instance, the effectiveness of Ti-based grain refiners is known to be severely diminished in the presence of Zr (another grain refining element in its own right). Grain coarsening may also result from "fade" which has been associated with extended holding times [12]. Such fade may occur because the nucleating particles either settle out, agglomerate or undergo some chemical transformation to another compound.

It is also known that grain refinement can be achieved by the use of low superheat pouring in conjunction with a “chill” casting surface [13]. The practice of low superheat pouring has been demonstrated to be effective not only for controlling grain size. It also induces rosette-like or non-dendritic grain morphologies (useful for thixotropic casting) rather than columnar or equiaxed dendritic structures more typically formed from higher pouring temperatures [13, 14, 15].

It seems logical that the combined use of low superheat pouring with additions of chemical grain refiners could offer even greater reductions in grain size. However this does not appear to have been the subject of much detailed study. The effects of individual parameters that affect grain size can be isolated to some degree by the use of simple gauze barrier casting experiments [16], described in the following section. By pouring metal inside a gauze barrier to prevent initial contact of the melt with the “chill” mould wall, the influence of crystals, nucleated by the various “wall” mechanisms [17], on the overall grain size can be constrained to the region outside the gauze. As a result, the inner region becomes sensitised (see Figure 1) to the variable under study, e.g. superheat or grain refiner addition type/level.

### Experimental

The average compositions of the three alloys (356, 6063 and 2024), used for the present grain size studies, were measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) and are presented in Table I. The 356 alloy was commercial foundry ingot, while the 6063 and 2024 were prepared using 99.7% aluminium ingot with additions of commercial purity materials (Si, Mg and Cu) and 75%Mn-25%Al master alloy, as required. Each melt was prepared in a clay-bonded graphite crucible using a 20 kW induction furnace. Three types of grain refiner were added at four different levels, or else no addition was made to the melt; see Table II. Two castings were prepared for each condition by pouring the melts at the required superheat values into a set of preheated cylindrical moulds with gauze barriers, as described below. The range of experimental conditions tested in this work are given in Table II.

Table I: Measured average alloy compositions using ICP-AES analysis

Alloy	Concentration (wt%)					Concentration (ppm)			
	Si	Mg	Cu	Fe	Mn	Ti	V	B	
<b>356</b>	6.76	0.36	<.01	0.08	<.01	150	50	<10	
<b>6063</b>	0.40	0.61	0.02	0.13	<.01	<50	<10	30	
<b>2024</b>	0.05	1.48	3.89	0.12	0.32	<50	<10	20	

Note: The chromium content of each alloy is < 50ppm.



Figure 1: Etched cross-section of a cylindrical casting with a gauze barrier, showing the different grain structures generated inside and outside the gauze when internal pouring is employed.

The steel casting moulds used in this work are of the split-half type with a cylindrical cavity. Within the cavity, an open cylinder of fine mesh stainless steel gauze (made of 0.28mm wire with 0.56mm aperture) was suspended so that a gap of ~10mm existed between the gauze and the floor of the cavity. The geometry and dimensions of this arrangement are shown in Figure 2. The moulds were preheated to 200°C prior to casting. At this temperature, when metal was poured on the inside of the gauze, there was no penetration through the gauze to the outside, rather the metal ran under the gauze and then filled upwards into the outside mould wall region.

The cylindrical cast samples were sectioned along the horizontal mid-line and then specimens were cut from regions representing both outside and inside the gauze. These samples were ground, polished and anodised, before observation under polarised light microscopy to reveal the grain structure. The 356 and 6063 alloys were anodised in a solution of 6ml HBF<sub>4</sub>, 6ml HF, 144ml ethanol and 444ml H<sub>2</sub>O at 30 volts for 2 minutes, while the 2024 alloy was anodised in a solution of 16ml HBF<sub>4</sub> and 760ml H<sub>2</sub>O at 25 volts for 2 minutes. Grain size measurements were conducted on representative optical micrographs, according to the lineal intercept method described in ASTM standard E112-88. At least 100 grains were measured in each sample, along several lines.

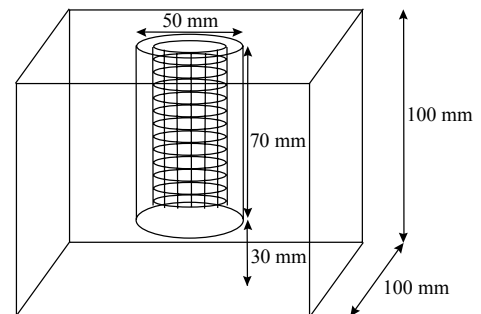


Figure 2: Geometry and dimensions of the cylindrical cavity casting mould used to produce the gauze-insert castings.

Table II: The range of experimental conditions used for each of the three alloys (356, 6063 and 2024)

Type of grain refiner	Addition level (wt%)		Superheat (°C)
	Ti *	B	
None	-	-	15, 30, 45, 60
Al-5Ti-1B	0.025	0.005	15, 60
Al-5Ti-1B	0.05	0.01	15, 60
Al-5Ti-1B	0.1	0.02	15, 60
Al-5Ti-1B	0.2	0.04	15, 60
Al-6Ti	0.025	-	15
Al-6Ti	0.05	-	15
Al-6Ti	0.1	-	15
Al-6Ti	0.2	-	15
Al-4B	-	0.005	15
Al-4B	-	0.01	15
Al-4B	-	0.02	15
Al-4B	-	0.04	15

\* Although the nominal Ti addition levels for the Al-5Ti-1B and Al-6Ti grain refiners are the same, they represent different Ti solute levels. All of the Ti from Al-6Ti will form solute (after the  $Al_3Ti$  intermetallic particles dissolve), whereas only about 56% of the Ti from the Al-5Ti-1B will form solute, the remainder being tied up in the  $TiB_2$  particles.

### Results

The grain size measurements reported in this paper represent only a portion of a much larger body of experimental work. The overall trends are presented and discussed only insofar as they pertain to the observed anomalous grain coarsening behaviour.

#### Low superheat pouring without the addition of grain refiners

For each of the three alloys, it was observed that the grain size was much larger (and also tended to be more dendritic and sometimes more columnar) in the samples cast with the higher superheats (60 and 45°C), than in samples cast with the lowest superheat (15°C). A typical set of grain size measurements is shown for 356 alloy in Figure 3. From this figure, it can be seen that the effect of superheat temperature is greater for the region inside the gauze than it is outside the gauze. This indicates that at low superheats, there is an increasing likelihood of grain nucleation from the gauze and subsequent survival of embryonic grains within the inside region. This is in addition to the expected improved survival rate of “wall” crystals nucleated from the “chill” mould wall in the region outside the gauze.

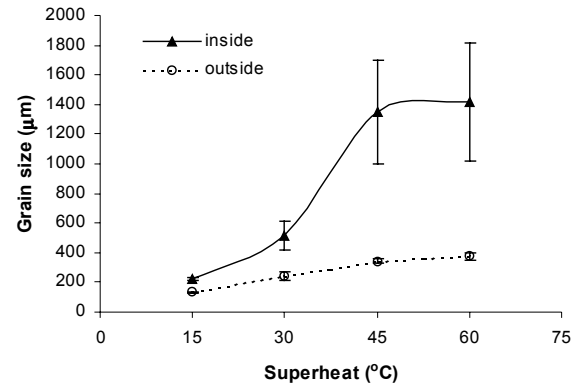
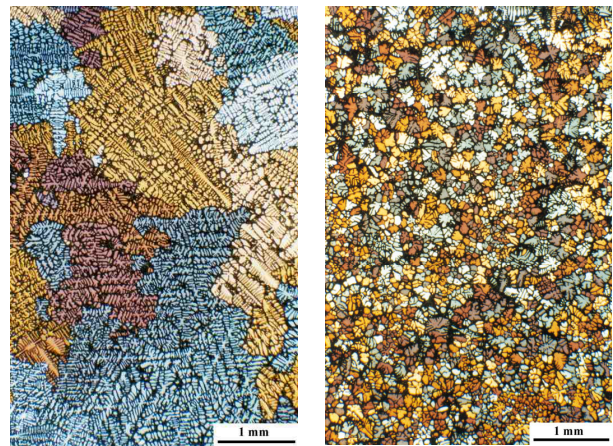


Figure 3: Graph showing the average measured grain sizes in non-grain-refined 356 alloy, both inside and outside of the gauze barrier, versus pouring superheat. The error bars are standard deviations based on the average values from five intercept lines.

Typical microstructures of the 60°C and 15°C superheat 356 alloy castings from the region from inside the gauze are shown in Figure 4. It can be seen that at low superheat, the grain morphology has become rosette-like, compared to fully dendritic structures obtained at the higher superheat. The corresponding grain structure changes of non-grain-refined 6063 and 2024 alloys were more extreme than for 356 for these superheat temperatures. The 6063 alloy grain structure was columnar in the 60°C superheat sample, while both 6063 and 2024 became almost completely non-dendritic at 15°C superheat.

#### Low superheat pouring with the addition of grain refiners

**Al-5Ti-1B master alloy** The use of Al-5Ti-1B master alloy was observed to generate potent grain refining effects in each of the three alloys at the 60°C superheat, especially in the sensitised region inside the gauze barrier (Figure 5). In addition, the grain morphologies of the 6063 and 2024 alloys were transformed to rosette-like and then to fully non-dendritic as Ti levels increased to 0.2% Ti, while the 356 alloy morphology remained as fine equiaxed dendrites.



(a)

(b)

Figure 4: Micrographs of 356 alloy samples, inside the gauze, without the addition of chemical grain refiner and cast with (a) 60°C, and (b) 15°C superheats.

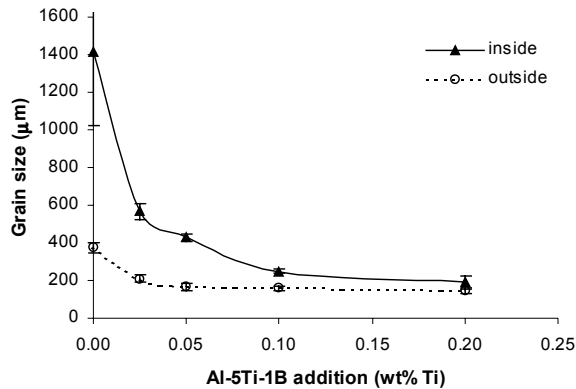


Figure 5: The effect of Al-5Ti-1B additions on the grain size of 356 alloy cast with 60°C superheat.

However, at the lower 15°C superheat, the grain refining effect observed was much less (Figure 6) than at 60°C, presumably because of the reduced starting grain size that results from low superheats alone. In 356 alloy at low superheat, the effect of Al-5Ti-1B additions is essentially non-existent, however for 6063 and 2024 alloys there were some useful grain size reductions achieved. For example, in 6063 alloy, the grain size was reduced from 259 to 110 μm with the addition of 0.05%Ti (as Al-5Ti-1B grain refiner) in the low superheat condition. Morphological changes associated with increased Ti additions in all three alloys were minimal, as the structures were already significantly altered by application of low superheat pouring.

**Al-6Ti master alloy** When the Al-6Ti grain refiner was added to the 356 alloy cast with low superheat (15°C), the effect on grain size was minimal, both inside and outside of the gauze barrier. There appeared to be only a slight reduction in grain size inside the gauze at addition levels of 0.1% and above. Below this level, there was essentially no response. In each of the 356 samples, the grain morphologies remained rosette-like at all Ti levels.

In the 6063 and 2024 alloys, the addition of Al-6Ti master alloy was observed to cause some grain refining effect, particularly in the region inside the gauze and at the lower Ti addition levels, i.e. 0.025 and 0.05%. Above these levels, no further decreases in grain size were obtained. In both of these alloys, all samples regardless of added Ti level displayed non-dendritic grain morphologies.

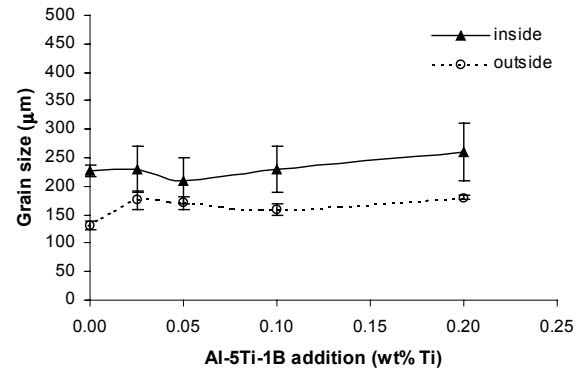


Figure 6: The effect of Al-5Ti-1B additions on the grain size of 356 alloy cast with 15°C superheat.

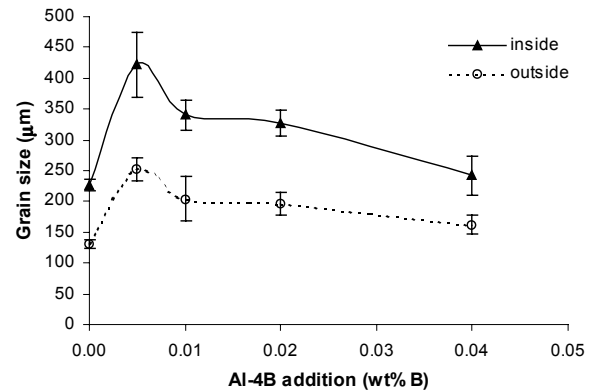


Figure 7: The effect of Al-4B additions on the grain size of 356 alloy cast with 15°C superheat.

**Al-4B master alloy** The effect of the Al-4B grain refiner was somewhat surprising compared with that of either the Al-5Ti-1B or Al-6Ti master alloys. For each of the three alloys cast with 15°C superheat, there was a distinct incidence of grain coarsening at the lower levels of Al-4B addition, particularly at 0.005%B. The coarsening was observed both inside and outside the gauze but was more pronounced inside the gauze. Figure 7 shows the effect of Al-4B additions on the grain size of 356 alloy, while Figure 8 shows the effect in 2024 alloy. The grain coarsening was also associated with an increased tendency to form dendritic grain structures rather than rosette-like or non-dendritic structures that formed in the samples without the Al-4B additions (Figure 9). Although further B additions tended to reverse the grain coarsening effects in each of the three alloys, it should be noted that even the highest B addition levels (0.04%) did not improve on the grain sizes obtained in the non-grain-refined condition.

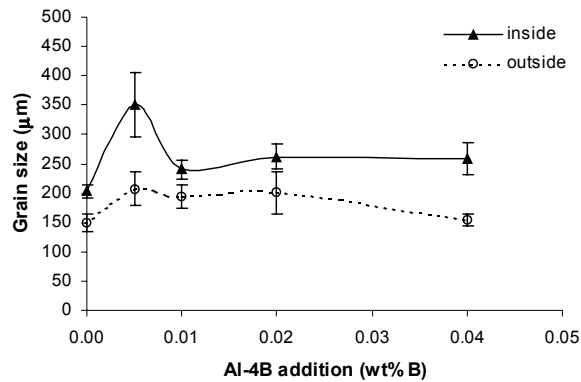


Figure 8: The effect of Al-4B additions on the grain size of 2024 alloy cast with 15°C superheat.

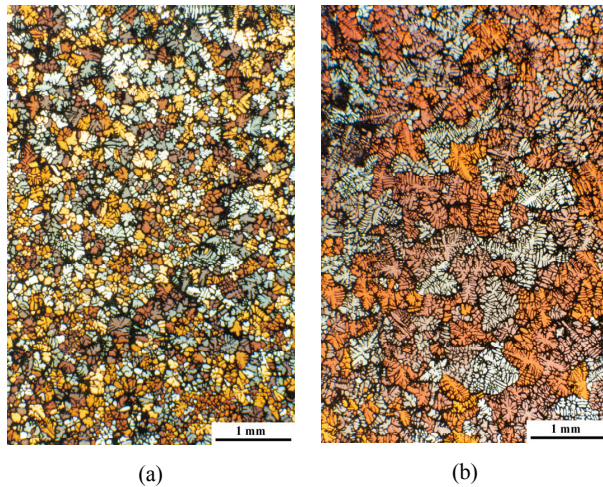


Figure 9: Micrographs showing the increase in grain size and the change in grain morphology of 356 alloy samples, inside the gauze, with small Al-4B additions: (a) no addition; (b) 0.005%B.

### Discussion

It is well known [18] that chill crystals nucleate at “cold” mould walls and this is evidenced by the relatively fine grain size observed in all three alloys in the regions outside the gauze barriers for all pouring superheats (15-60°C) tested. The gauze barrier has a low thermal mass and certainly at the higher pouring superheats is incapable of generating massive numbers of chill crystals. However, at the lower superheats, the gauze does appear to be capable of nucleating crystals that can survive in the region inside the gauze. This would appear to be the reason for the wide difference in grain sizes between the inside and outside of the gauze at high superheats and for the much narrower difference in size observed at low superheats.

Reduction in casting superheat in alloys without chemical grain refiner additions was accompanied by grain size reductions and an increased tendency towards a non-dendritic grain structure (Figure 3 and Figure 4). This was evident both inside and

outside the gauze for each of the three alloys, although 356 alloy appeared to be slightly less responsive to refinement and more prone to preserve its dendritic character than either the 6063 and 2024 alloys, both of which formed very fine, fully non-dendritic structures at 15°C superheat.

Grain refinement by the addition of Al-5Ti-1B master alloy (containing solute Ti plus nucleant particles) to alloys cast from the higher superheat was strong (Figure 5). Small amounts of grain refiner produced significant grain size reductions, with further additions only producing minimal additional benefit. These effects were more pronounced in the region inside the gauze where the “wall” effects were suppressed and the constitutional effects could be magnified. It is assumed that the other grain refiners, Al-6Ti and Al-4B might behave in a similar manner at the higher superheat but with different efficiencies. Further work is required to test this assumption.

The normally potent Al-5Ti-1B grain refiner became effectively powerless in each of the three alloys (both inside and outside the gauze) when it was used at the lowest casting superheat (15°C), regardless of the addition level (see Figure 6). Clearly, there could be potential cost savings in situations where casting conditions produce massive wall crystal nucleation/survival and where grain refiners are nevertheless used routinely. Of course, the question remains unanswered as to how the grain sizes and morphologies change at the intermediate superheats between 15 and 60°C. So too, how the results from the experimental superheats and mould arrangement actually correspond to the effects of the working superheats used in a typical distribution launder above a VDC billet mould table. Further work is also required to address these important issues.

The addition of Al-6Ti master alloy to the three alloys in the low casting superheat condition was generally predictable. As Easton and StJohn [2] suggested, wrought alloys with lower solute levels (and hence lower GRFs) than foundry alloys require nucleant particles as well as additional solute Ti to grain refine effectively. Assuming that there are some suitable residual nuclei present within each alloy, the Al-6Ti grain refiner adds the necessary extra Ti solute (and perhaps some stabilised  $TiAl_3$  particles) and therefore induces grain refinement in 6063 and 2024 alloy to a similar extent as was observed with the Al-5Ti-1B refiner.

The effect of Al-6Ti grain refiner additions in 356 alloy was also similar to that of Al-5Ti-1B additions producing essentially no refinement in the low superheat condition regardless of the addition level. It was anticipated from the literature [2] that the Al-5Ti-1B refiner would produce some reduction in grain size in this alloy because of the presence of  $TiB_2$  nucleant particles, however it was not surprising that Al-6Ti (without nucleant particles) had no effect additional to that of the low pouring superheat.

The work of Easton and StJohn [2] would also suggest that Al-4B master alloy (containing nucleant particles, but with no high GRF solute such as Ti) should be an effective grain refiner in high solute foundry alloys such as 356, but be less effective in the lower solute wrought alloys. This is supported by the work of others [6, 7, 8] on the efficacy of boron-based grain refiners for Al-Si foundry alloys. A strong grain refining effect might have occurred if normal high superheat pouring had been employed, but it was not observed at the 15°C superheat. In fact, the behaviour at 15°C superheat was quite dissimilar to the

minimal or zero refining effects observed for both the Al-5Ti-1B and Al-6Ti master alloy additions. Instead, for each of the three alloys, an initial grain coarsening was observed, followed by a gradual recovery of grain refinement as addition levels were increased but not improving on the initial starting grain size obtained without any addition (Figure 7 and Figure 8).

As stated earlier, it is known that one effect of boron (as an Al-x%B master alloy) in aluminium alloys is to remove solute Ti and V by precipitating them out as the respective boride particles. Boron additions may also react with other elements to form different boride particles [11] but since those elements are not involved in conductivity issues (as are Ti, V and Cr) their formation is overlooked. The mechanism by which these borides are formed is unclear. AlB<sub>2</sub> particles are unstable at the hypoeutectic B concentrations (i.e. <0.022%) in pure aluminium melts (but stabilised at lower concentrations in Al-Si alloys) [6, 10] and therefore B atoms will become available to react with these other species after the aluminium boride dissolves. However Marcantonio and Mondolfo [3] indicate that complex borides such as (Al,Ti)B<sub>2</sub> may also form and this clouds the issue. The grain refining potency of the various particle combinations is likely to depend on the types of particle present, possibly on the manner in which they form (particularly whether they form as discrete particles or as agglomerated clusters), and also on any interactions that occur with “poisoning” elements [11]. The possibility for unpredictable scenarios is quite apparent.

Since the levels of Ti and V in the base alloys were not generally high in the experimental alloys (see Table II), the amount of B that is required to react with them to form borides will also be relatively low. The 356 alloy had the highest levels of Ti and V (150 and 50 ppm respectively; the amount of Cr is below the detection limit of 50 ppm) of the three alloys. If this were all initially solute (rather than some of it already being in the form of aluminides, carbides and borides), it would require only 90 ppm of B to convert it all to the simple TiB<sub>2</sub> and VB<sub>2</sub> forms. In the three experimental alloys, the grain coarsening effect peaked at 50 ppm or 0.005% B additions, after which grain refinement restarted.

This value of B addition appears consistent with a mechanism that might involve two consecutive actions. First, the initial low boron addition probably reacts with the various solute element species present in the alloy thereby altering the balance of the nucleating particle population while at the same time reducing the GRF arising from the reduced total solute level. Second, further additions of aluminium-boron master alloy result in a direct increase in the number of active AlB<sub>2</sub> particles (which are presumably stabilised in some way at hypoeutectic B concentrations, e.g. ~ 0.01%) and that these then start to induce their own cumulative refining action. It seems unlikely that the increased B levels are capable of causing an increase in GRF sufficient to induce the observed grain refining recovery.

Since the use of low superheat casting is capable of inducing a small grain size even in the absence of grain refiners, the further Al-4B additions (at least up to 0.04% B levels) do not provide sufficient refining power to improve on the grain size obtained without grain refiner. At even higher levels, the grain size may reduce further, however a cube root relationship exists (i.e. a law of diminishing returns) between the number of active nuclei and measured grain size and therefore it becomes more difficult to observe and measure a change in the average grain size. This is

also consistent with the inability of Al-5Ti-1B and Al-6Ti to induce significant refining actions in alloys cast from the low 15°C superheat.

As noted earlier, it is assumed that Al-4B might produce some useful grain refining action for some alloys (especially foundry alloys) cast from higher superheats. Whether the same coarsening behaviour would also be apparent at the high and intermediate superheats remains unknown and is clearly an avenue for further work. The grain coarsening behaviour observed also has implications for its effective application and use in alloys with variable background impurity element levels. Alloys prepared from various sources or with a high use of recycled materials in the furnace charge may need particular care to ensure grain refining results are consistent over time.

### Conclusions

1. A reduction in casting superheat from 60 to 15°C for 356, 6063 and 2024 alloys without any chemical grain refiner additions resulted in large reductions in grain size and a change in grain morphology from dendritic towards non-dendritic structure.
2. Al-5Ti-1B master alloy additions made to 356, 6063 and 2024 alloys that were then cast from 60°C superheat induced significant changes to grain morphology and grain size, similar to those produced by low superheat pouring alone.
3. The effects of chemical grain refiner additions on grain size and morphology of 356, 6063 and 2024 alloys when using low superheat (15°C) pouring techniques were generally much less than those observed when using higher superheats.
4. The Al-5Ti-1B and Al-6Ti master alloys were found to produce either minimal or negligible grain refining effect in the three alloys at 15°C pouring superheat.
5. The Al-4B master alloy was found to induce grain coarsening at low addition levels (0.005%B) in each of the three alloys at 15°C superheat, but for higher addition levels (up to 0.04%B) gradual reductions in grain size were observed but only back to the non-grain refined level.

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### References

1. J. A. Taylor, “Metal-related castability effects in aluminium foundry alloys,” *Cast Metals*, 8 (4) (1995), 225-252.
2. M. Easton and D. StJohn, “Grain refinement of aluminum alloys: Part II. Confirmation of, and a mechanism for the solute paradigm,” *Metallurgical and Materials Transactions*, 30A (1999) 1625-1633.

3. J. A. Marcantonio and L. F. Mondolfo, "Grain refinement in aluminum alloyed with titanium and boron," Metallurgical Transactions, 2 (1971), 465-471.
4. M. M. Guzowski, G. K. Sigworth and D. A. Sentner, "The role of boron in the grain refinement of aluminium with titanium," Metallurgical Transactions, 18A (1987), 603-619.
5. M. A. Easton and D. H. StJohn, "A model of grain refinement incorporating alloy constitution and potency of heterogeneous nucleant particles," Acta Materialia, accepted for publication.
6. G.K. Sigworth and M.M. Guzowski, "Grain refining of hypoeutectic Al-Si casting alloys," Transactions of American Foundryman's Society, 92 (1985), 907-912.
7. S. A. Kori, B. S. Murthy and M. Chakraborty, "Development of an efficient grain refiner for Al-7Si alloy," Materials Science & Engineering, A280 (2000), 58-61.
8. K. Yaguchi et al., "Grain refinement of cast Al alloys by Al-B master alloy," Materials Science Forum, 331-337 (2000), 391-396.
9. F. King, Aluminium and its alloys (Chichester, UK: Ellis Horwood Ltd, 1987), 23.
10. P.A. Tondel, "Grain refinement of hypoeutectic Al-Si foundry alloys," (Ph.D. thesis, University of Trondheim, 1994), 39-44.
11. A. A. Abdel-Hamid, "Effect of other elements on the grain refinement of Al by Ti and B," Zeitschrift für Metallkunde, 80 (8) (1989), 566-569.
12. J. A. Spittle and J. M. Keeble, The grain refinement of Al7Si alloys with boron containing refiners," Light Metals 1999, ed. C. Edward Eckert (Warrendale, PA: The Mining, Minerals and Materials Society, 1999), 673-677.
13. R. Shibata, "SSM activities in Japan," Proceedings of 5<sup>th</sup> International Conference on Semi-Solid Processing of Alloys and Composites, Golden, Colorado, 23-25 June 1998, li-lvi.
14. H. Wang et al., "Characterisation and shear behaviour of semisolid Al-7Si-0.35Mg alloy microstructures," Aluminum Transactions, 2 (1) (2000), 57-66.
15. K. Xia and G. Tausig, "Liquidus casting of a wrought aluminium alloy 2618 for thixoforming," Materials Science & Engineering, A246 (1998), 1-10.
16. J. Hutt et al., "The effect of nucleant particles and alloy chemistry on the grain structure of aluminium castings," Proceedings of 4<sup>th</sup> Decennial Conference on Solidification Processing (SP97), Sheffield, UK, 7-10 July 1997, 268-272.
17. J. Hutt and D. StJohn, "The origins of the equiaxed zone – review of theoretical and experimental work," International Journal of Cast Metals Research, 11 (1998), 13-22.
18. B. Chalmers, "The structure of ingots," Journal of Australian Institute of Metals, 8 (3) (1963), 255-263.