Grain refinement in shape casting of aluminium alloys – Part II

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The second part of a two part review is presented here. The paper considers the grain refinement of aluminium alloy shaped castings and particularly Al–Si alloys. It examines the methods of grain refinement, benefits of grain refinement, procedures for assessing grain refinement, the efficiency of different refiners and factors affecting grain refinement. The review is intended to be of practical interest to the foundryman as well as providing an academic background to the subject.

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Factors affecting grain refinement

Type of grain refiner, level of addition, holding time and fade

Boron containing refiners (Al–B and Al–Ti–B)

Several sets of data were reported in the section *'Comparison of effectiveness of different refiners'* in part 1 of this paper (figs. 6-11). This section considers in more detail the effects of boron addition level, Ti/B ratio and holding time. Grain size results are often quoted for holding times such as 2, 5 or 10 min. These times equate to exposure times of substrates in melts during DC casting. However, because of the possibility of 'fade' of the grain refining effect with time, data for holding times up to hours are more relevant to commercial conditions in shape casting foundries.

Spittle *et al.*(28) examined the grain refinement of two Al7Si type alloys, a binary Al7Si alloy and a commercial A356 alloy, having the compositions in Table 1, with refiners of nominal compositions Al5Ti1B, Al3Ti3B and Al4B as shown in Table 2. B additions were made in the range 0.002-0.02%. Grain sizes were determined from castings poured into tapered graphite moulds after a holding time of 2 min.

The results are shown in fig. 12 as a function of total wt-%B (i.e. added B plus the residual B levels in the base alloys). Every data point in the figure has a total Ti content of 0.10 wt-% or less. For the binary Al7Si alloy, it can be seen that grain size decreases with increasing B content and, for the solidification conditions prevailing in the castings, that significant refinement was only achieved with the two highest B levels examined, namely 0.01 and 0.02%. The Al5Si1B and Al4B refiners were also more effective than the Al3Ti3B refiner. The addition of B at these two levels to the commercial A356 alloy, using the Al3Ti3B refiner, produced grain sizes almost identical to those observed in the binary alloy with the other two refiners. In agreement with the data by Sigworth and Guzowski(26) (figs. 8 and 9 - see Part I of this paper), this again appears to demonstrate that, in the presence of sufficient residual Ti to raise the total Ti/B ratio to >2.2:1, Al3Ti3B can refine to the same degree as Al5Ti1B for the same B addition level. Also, in agreement with the more recent data by Kori *et al.*(32) (fig. 11 - see Part I of this paper), at the 0.01%B addition level (Kori *et al.* did not examine as high as 0.02%), Al5Ti1B produced a finer grain size than Al3Ti3B in binary Al7Si alloys.

Cook and Spooner(29) examined the grain refinement of a commercial Al7SiMg type alloy (Table 3) with a variety of Al5Ti1B refiners, two AlTiB refiners with a 1:1 Ti/B ratio and an Al3B refiner (Table 4). The AA-TP1 grain refiner test was used for holding times up to 2 h, with an addition level of 0.006 wt-%B, except for the 1:1b where the addition level was 0.0075%B. The results are shown in fig. 13. Sample 1:1a gave a poor response in comparison with the 5:1

Analysis	Alloy 1	Alloy 2
Si	6·99	6·83
Fe	0·020	0·116
Cu	0·0068	0·002
Mn	0·0019	0·005
Mg	0·0047	0·365
Zn	0·0015	0·008
Ti	0·0023	0·070
B	0·0003	0·0001

Table 1. Analysis of Al-Si alloys (28)

Analysis	Al5Ti1B	Al3Ti3B	Al4B
Ti	4·79	3·14	<0·01
C			
B	0·99	2·92	4·65
Fe	0·11	0·38	0·14
Si	0·05	0·24	0·08
V	0·10	<0·01	<0·01
K	0·04	0·08	0·46
Al	Balance	Balance	Balance

Table 2. Analysis of grain refiner master alloys (28)

Ti	B	Si	Fe	Cu	Mg	Mn	Zn	Rem.	Al
0·017%	0·059%	7·04%	0·35%	0·04%	0·43%	0·19%	0·03%	<0·01% each	Balance

Table 3. Composition of commercial Al7SiMg alloy (29)

Sample	Alloy	Form	%Ti	%B
5:1a	Al–Ti–B	As cast bar	4·86	0·95
5:1b	Al–Ti–B	10 mm rod	4·99	0·99
5:1c	Al–Ti–B	Conformed bar	4·95	1·00
5:1d	Al–Ti–B	Extruded bar	4·80	0·96
1:1a	Al–Ti–B	10 mm rod	1·68	1·59
1:1b	Al–Ti–B	10 mm rod	1·52	1·27
3BAl	Al–B	Waffle plate	<0·01	3·20
6TiAl	Al–Ti	Waffle plate	5·62	<0·01

Table 4. Analysis of grain refiner master alloys (29)

Refiner	Ti, wt-%	B, wt-%
X	3·14	2·92
Y	1·52	1·27
Al2·2Ti1B	2·09	1·03
Al6Ti	5·92	<0·002
Al3B	<0·01	3·2

Table 5. Analysis of grain refiner master alloys (30)

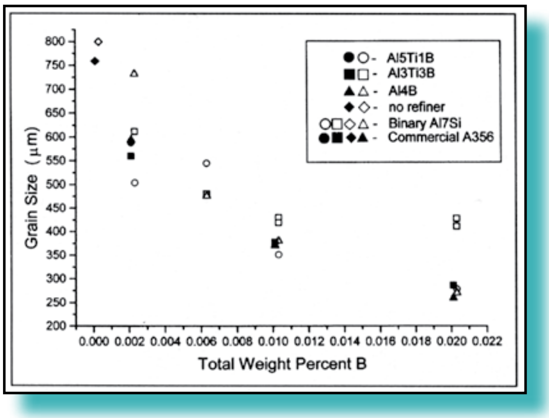

Fig. 12 Influence of B level on grain size of Al7Si type alloys for three B containing refiners(26)

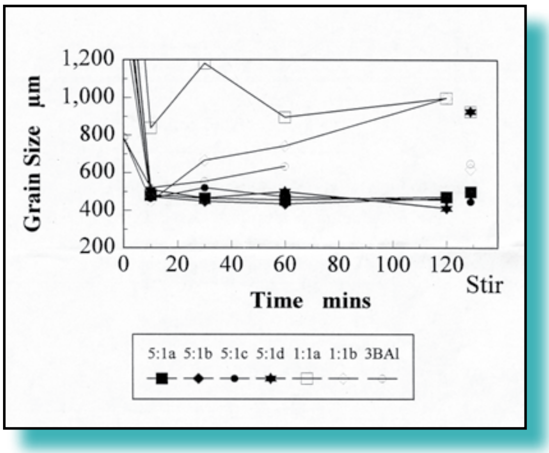

Fig. 13 Grain size data for refinement of Al7SiMg alloy with several B containing refiners(29)

refiners. Increasing the B addition level in 1:1b gave a 10 min holding time grain size equivalent to the 5:1 refiners, however significant coarsening (fade) took place over the 2 h. A similar coarsening effect was seen with Al3B. This emphasises the unreliability of short holding time tests for refiners for use in shape casting foundries.

Spittle and Keeble(30) examined the grain refinement of a binary Al7Si alloy with B containing refiners as a function of holding time. After 2 h of holding, each melt was stirred and a further casting poured. As previously described,(28) the castings were again made in tapered graphite moulds. A range of Ti/B ratios was examined from 0 (Al-B refiner) to 5:1, at two boron addition levels of 0.006% and 0.02%. The analyses of the Al7Si alloy and the Al5Ti1B and Al4B are given in Tables 1 and 2. The analyses of the remaining refiners used are shown in Table 5 and the results are shown in figs. 14 and 15. At the 0.006%B level, it can be seen that, overall, the 5:1 ratio displayed the best characteristics with respect to grain size and stability with holding time. At the 0.02%B level three ratios, including the two 1:1 ratios and the 2.2:1 ratio, showed rapid fade during the first 30 min. At both B concentrations and for all Ti/B ratios, fine grain sizes were returned following stirring of the melt, pointing to settling of nucleant particles in all cases. The observations at the 0.006% level, that there is a greater tendency to fade with sub-stoichiometric Ti/B ratios, is in accord with the observations of Cook and Spooner(29). Schaffer(33) has recently investigated fade when grain refining commercial purity AA 170.9 aluminum with three different master alloy refiners - Al5Ti1B, Al1.6Ti1.4B and Al1.2Ti0.5B. In all three trials, the addition level was 0.05%Ti and 0.01%B. In the case of the latter two refiners, this required addition of extra Ti using an Al–10%Ti master alloy. Again it was observed that fade was more rapid with the sub-stoichiometric refiner than with the other two refiners.

Comparing the data in figs. 14 and 15, it is clear that grain size is determined by both the amount of refiner added (which will determine the number of potential nucleant substrates) and the Ti/B ratio (which will presumably determine the type of nucleant substrate and hence its nucleating efficiency). Depending on the type of boron refiner, the active substrates for nucleation will possibly be AlB_2, TiB_2 or a mixed $(Al,Ti)B_2$ boride. The nature of the nucleant substrates is unknown. However, from analysis of the melts during holding, it is interesting that Cook and Spooner(29) observed that the composition of the particles settling has an excess of B over that required to form TiB_2 in the samples showing poorest grain refinement and significant fade in fig. 13 (fig. 16).

Summarising, from observations on laboratory cast binary Al-Si alloys, the body of evidence would support the fact that, for the same level of boron addition, B containing refiners with above stoichiometric Ti/B ratios of 2.2:1 produce finer grain sizes and are more resistant to fade on holding than sub-stoichiometric refiners. The data also illustrates that the commonly used Al5Ti1B refiner is superior to commercially available refiners with a 1:1 Ti/B ratio. However, as indicated by several data sets, (26, 28, 31) it appears that a 1:1 refiner can also produce fine grain sizes if added to commercial Al-Si alloys containing sufficient residual Ti in the base alloy to raise the overall Ti/B ratio to well in excess of 2.2:1.

Non-boron containing refiners (Al–Ti and Al–Ti–C)

Data already presented(25) (fig. 6 - see Part I of this paper) illustrates that, for the same Ti addition rate, an Al-Ti refiner is less effective than an Al-Ti-B refiner. From observations on the grain refinement of a binary Al7Si alloy for 2 min holding times, Keeble(24) showed that grain size decreased with increasing Ti content (fig. 17). However, Ti levels in excess of that required for the peritectic reaction (0.15 wt-%Ti) were necessary in order to achieve, for the same casting conditions, a grain size equivalent to that obtained with an Al5Ti1B refiner at a ~0.05%Ti addition level, cf. Fig. 12. As suggested by Cibula,1 below 0.15%Ti grain refinement is possibly due to the presence of TiC coupled with 'growth restriction' of the aluminium crystals because of redistribution of Ti on freezing. Fig.18 illustrates that Al–Ti refiners show little tendency to fade for up to 2 h holding time.(24) All samples were taken without prior stirring the melt. However, as shown by the final set of data points, stirring of the melt after 2 h had little effect on grain size.

Based on the original work of Cibula,(1) in recent years there has been renewed interest in the possibility of Al-Ti-C refiners for both wrought and foundry alloys.

Boone *et al.*(27) examined the influence of residual Ti levels up to 0.2%Ti on the grain refinement of an A356 alloy by three refiners, Al5Ti1B, Al2.5Ti2.5B and Al6Ti<0.1C, at additions up to 1.5 kg/1000 kg. On the basis of weight of addition, Al-Ti-C was not as efficient as the other two refiners and was only effective at the 0.2% residual Ti level.

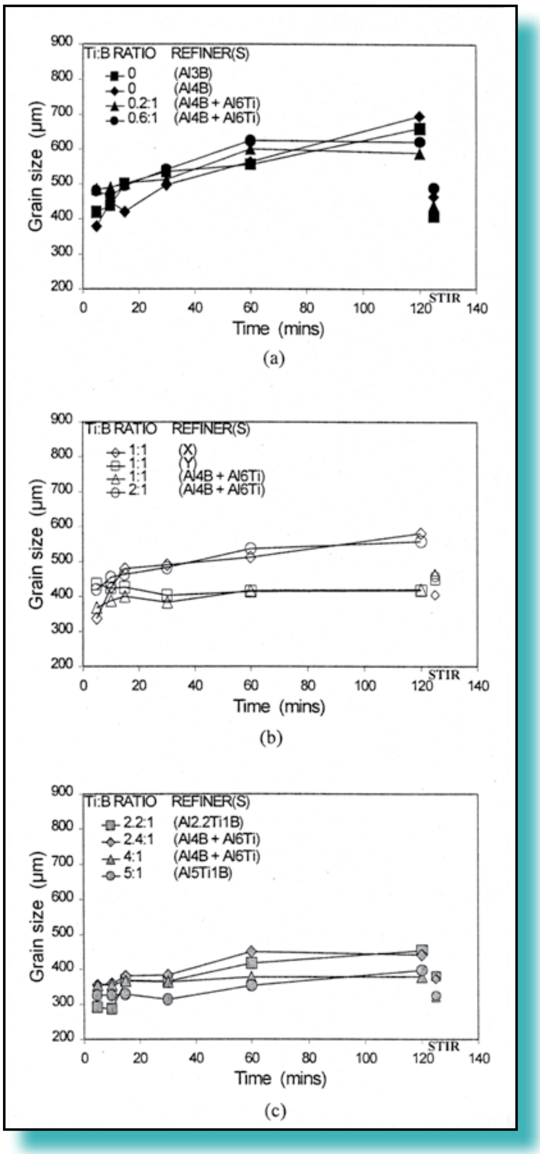

Fig. 14 Grain size as a function of holding time and Ti/B ratio for 0·006%B addition(30)

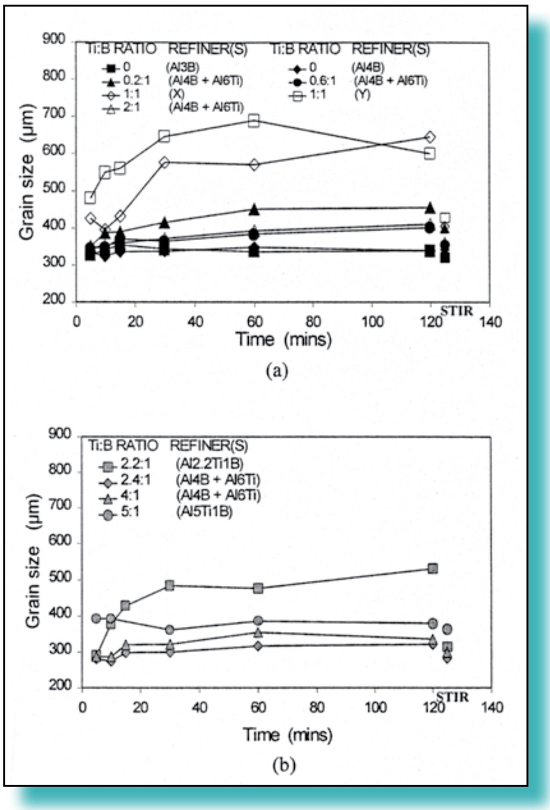

Fig. 15 Grain size as a function of holding time and Ti/B ratio for 0·02%B addition(30)

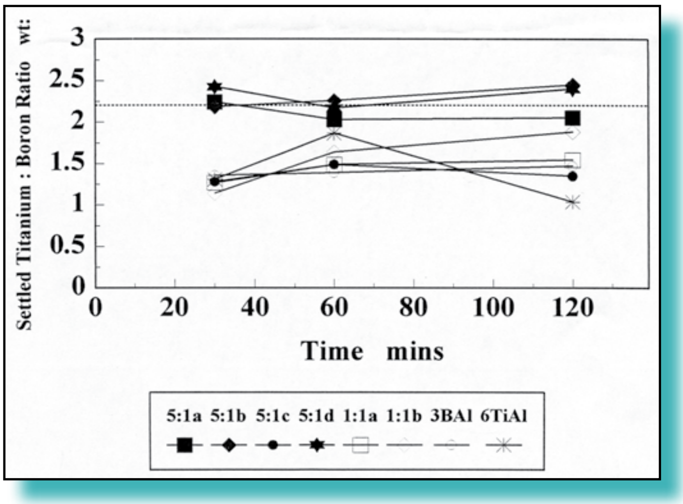

Fig. 16 Ti/B ratio of settled elements(29)

Spittle *et al.*(28) examined the grain refinement of a binary Al7Si alloy and a commercial A356 alloy, using two grain refiners (Al6Ti and Al5Ti0.25C), at different Ti addition levels, for a 2 min holding time. They concluded that the Al5Ti0.25C refiner was no more effective than the Al6Ti refiner, both only producing significant refinement at levels in excess of ~0.15%Ti (fig.19).

Keeble(24) examined the influence of holding times up to 2 h for the same two refiners for the binary Al7Si alloy. As in fig. 18, all samples were again taken without prior stirring of the melt. After 2 h, the melts were stirred and additional castings poured (see final set of data points). Addition levels of 0.01 and 0.1%Ti were selected. The results shown in fig. 20 illustrate that the effect of the Al-Ti-C refiner tends to fade with time.

Summarising, it appears that for Al-Ti and Al-Ti-C refiners, significant refinement is only achieved at Ti addition levels in excess

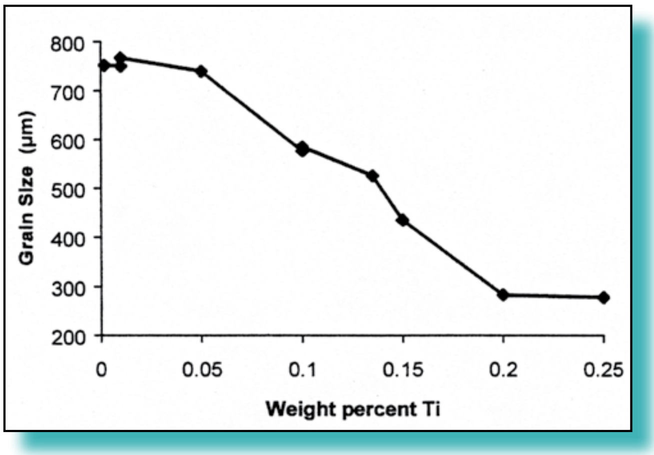

Fig. 17 Influence of Ti level on grain refinement of Al7Si alloy(24)

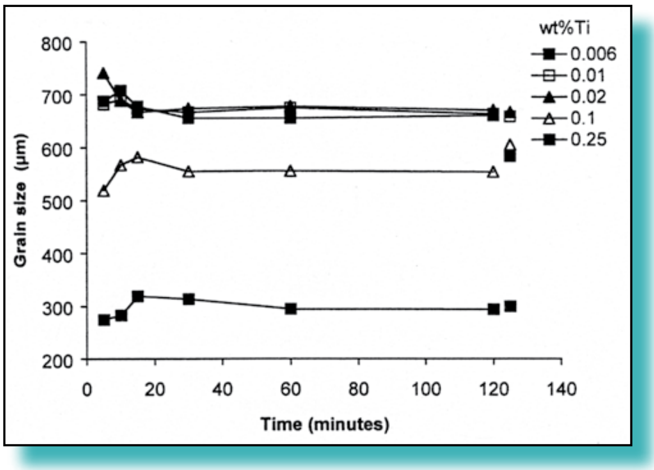

Fig. 18 Influence of holding time and Ti level on refinement of Al7Si alloy with Al-Ti refiner(24)

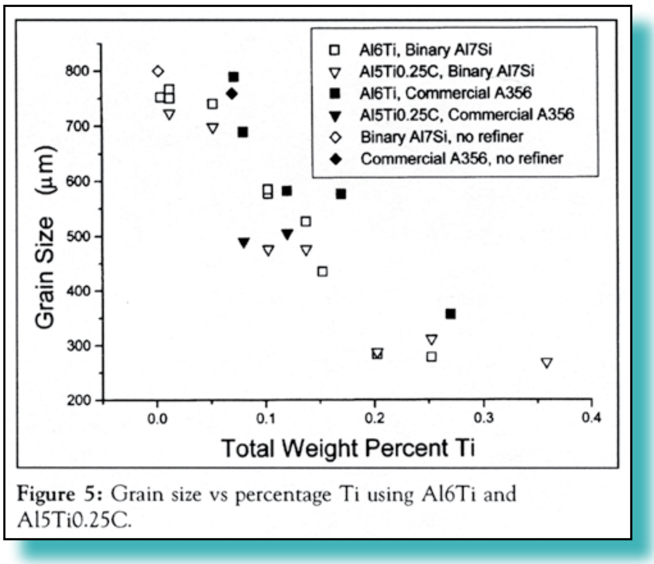

Fig. 19 Grain size versus percentage Ti for Al6Ti and Al5Ti)-25C refiners(28)

of 0.15% and that for the same Ti addition level, there is little difference in the refinement obtained with the two types of refiner.

Residual Ti levels

Sections *'Comparison of the effectiveness of different refiners'* and *'Type of grain refiner, level of addition, holding time and fade'* have alluded to the probable influence of residual Ti in the base alloy on the refiner addition. In the case of Al-Ti-B refiners, this residual Ti is expected to have a greater influence when using refiners with a Ti/B ratio >2.2:1. The residual Ti levels are often sufficient to raise the ratio to >2.2:1, thus favouring TiB$_2$ formation and enhanced refinement. For the same B addition level, a >2.2:1 refiner can therefore achieve an equivalent grain size to a >2.2:1 refiner.

Two studies have been reported that specifically examined the effect of residual Ti. Boone et al.(27) examined the influence of residual Ti at five levels (0.005, 0.5, 0.1, 0.15 and 0.2%), for three refiners Al5Ti1B, Al2.5Ti2.5B and Al6Ti<0.1C, for additions up 1.5 kg/1000 kg, on the grain refinement of A356. As the residual Ti increased from 0.005 to 0.5, a significant decrease in grain size was initially observed for the Al2.5Ti2.5B refiner, but thereafter the size stayed almost constant up to 0. 15%Ti. For the Al5Ti1B and Al6Ti<0.1C refiners, the grain sizes were reasonably constant up to 0.15%Ti. All three refiners showed a definite decrease in grain size on exceeding 0.15% residual Ti indicating a possible additional refining effect of TiAl$_3$.

Young *et al.*(34) examined the grain refinement of A356 and 319, with different residual Ti levels of 0.005%, 0.02% and 0.2%, using three refiners Al5Ti1B,

Al2.5Ti2.5B and Al5B and employing three types of refining test (the AA-TP1 test, the KBA ring test and the Reynolds golf tee test). The refinement was compared for a refiner addition level of 1 g kg^{-1} and, also, an additional test at 2 g kg^{-1} for the latter refiner. The results in fig. 21 are for the A356 using the AA-TP1 test. It can be seen that at low residual levels, there is a clear distinction between the refiners which tends to disappear with increasing residual level. A 0.02% residual would provide sufficient Ti to combine with all the B supplied by the Al5B refiner at the 2 g kg^{-1} addition level to form TiB2. At the lowest residual Ti level, the Al2.5Ti2.5B refiner gave a coarser grain size than the Al5Ti1B refiner.

Type of casting alloy

Attempts to compare the influence of specific grain refiners on different base alloys, from examining different reported literature sources, must be treated with care because of the effects of other factors on grain refinement including residual Ti level and, most importantly, cooling rate. Although individual studies have reported grain refinement differences for pure binary Al7Si type alloys compared with equivalent commercial alloys (A356) (see the section *'Boron containing refiners (Al-B and Al-Ti-B)'*), very few studies have reported the effect of the type of base alloy for the same casting conditions and grain size assessment procedure.

A number of papers from KB Alloys Inc have reported comparisons of the grain refinement of aluminium alloys A356 (Al7SiMg) and A319 (Al5Si3Cu), with different refiners and using different grain refinement tests.(26,27,34) The results are in agreement that A319 is more difficult to grain refine than A356 at low residual Ti levels (<0.15%Ti). Fig. 22a and b show the grain sizes for the two alloys, for a 5 min holding time, as a function of the amount of Ti added using an Al5Ti1B refiner.(26) The KBA ring test was used and there was no residual Ti. Top and bottom in the figure refer to measurements made on the top and bottom faces of the ring, with the cooling rate at the bottom being greater. The reason for the difference between the two alloys is unclear. For a given residual Ti level, the difference in grain refinement decreases with increasing cooling rate associated with the grain refinement test employed(34) (fig. 23).

It is therefore apparent that differences in grain refinement between different base alloys may occur for a given level of refiner addition. However, far more data is required to determine the reasons for these differences.

Cooling rate

Various investigators have referred to the significant influence that cooling rate has on the grain refinement of Al-Si type foundry alloys.(16,26,27,30,34) Apelian *et al.*(16) examined the grain sizes on the top and bottom surfaces of KBA ring test castings for A356 and A319 test castings as a function of $\Delta\theta$. The latter was obtained from castings, poured in tandem, into a thermal analysis mould (see the subsection *'Thermal analysis'* in Part I of this paper). Average grain size was observed to increase with increase in $\Delta\theta$ and, for a given value of $\Delta\theta$, the average grain size at the top of the ring castings was significantly higher than that at the bottom of the castings. The latter observation was confirmed by Sigworth and Guzowski(26) (fig. 22). Boone *et al.*(27) and Young *et al.*(34) examined the grain refinement of A356 and A319 with various grain refiners using the AA-TP1 test, the Reynolds golf tee test and the KBA ring test. These are reported to correspond to cooling rates of 8.5, 2 and 0.3uF s^{-1}, respectively. No detail was given as to how these values were obtained. However, since cooling rates vary with time and location within a solidifying casting, the values must only be used as a guide. Fig. 23 indicates the grain size obtained with each test for the two base alloys, for an Al5Ti1B refiner at an addition rate of 1 g kg^{-1} and a residual Ti level of 0.005%.(34)

Spittle and Keeble(30) reported grain sizes for two cooling rates, 6 and 12 K s^{-1}, for the grain refinement of a pure Al7Si alloy with an Al5Ti1B alloy and a holding time of 1 h. The cooling rates were averages over the time period preceding nucleation of the primary phase and the grain sizes were measured close to the thermocouple positions. For two B addition levels of 0.006 and 0.02%, a 6 K s^{-1} decrease in the cooling rate caused an increase in grain size of ~250 µm.

The above data illustrate that at low cooling rates, e.g. 10 K s^{-1}, small variations in cooling rate can lead to significant variations in grain size. This possibly reflects the influence of cooling rate on the degree of undercooling of the melt and therefore the number of potential nucleant sites that are activated.

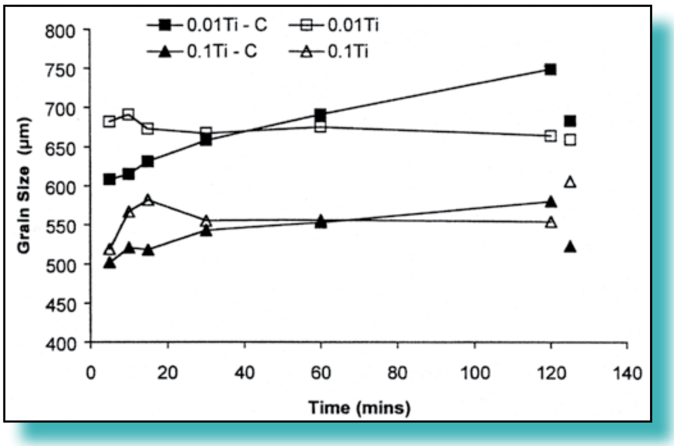

Fig. 20 Grain size versus holding time at two Ti levels for refiners used in Fig.19(24)

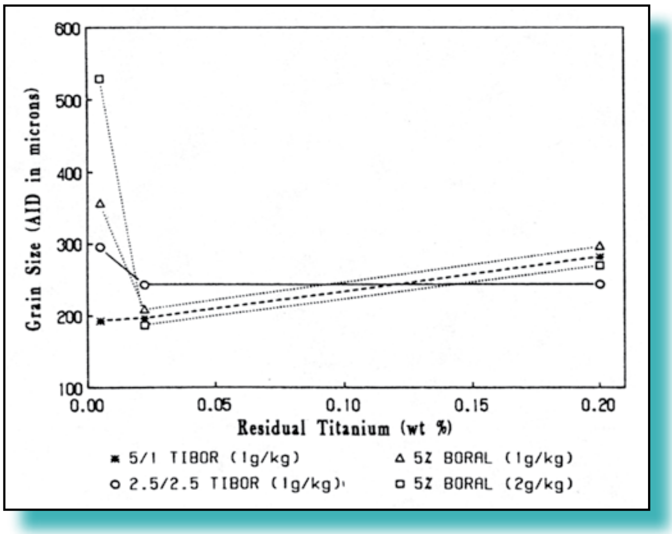

Fig. 21 Influence of residual Ti level on grain refinement of A356 alloy using AA-TP1 test(34)

Summary

The following comments relate to observations on Al-Si type foundry alloys. Over the years, Al5Ti1B has probably become established as the most widely used master alloy refiner in the shaped casting foundry industry. The fact that it is necessary to add larger percentages of this refiner to casting alloys than to wrought alloys, to achieve adequate refinement, has led to the investigation of alternative types of refiner namely Al-B, Al-Ti-C and Al-Ti-B with Ti/B weight ratios <2.2:1 (i.e. less than the stoichiometric ratio for TiB_2). Methods of comparing the effectiveness of different refiners, e.g. on the basis of weight of grain refiner added per unit weight of base alloy, etc., have led to some confusion. It is evident that Al-Ti-C refiners offer little advantage over binary Al-Ti refiners, both being far less effective than Al5Ti1B for the same Ti addition level. In the case of B containing alloys, most effort has been concentrated on comparing Al5Ti1B with refiners with Ti/B ratios <2.2:1 (usually 1:1, e.g. Al2.5Ti2.5B). For low Ti residual levels in the base alloy, it appears that Al5Ti1B exhibits a much more consistent behaviour and resistance to fade with holding time. With high residual Ti levels, it appears, for the same B addition level, that a 1:1 ratio refiner can be as effective as Al5Ti1B. This is presumably because, at normal refiner addition rates, the residual Ti level is raising the ratio to >2.2:1. At low cooling rates, typically from observations at < ~10 K s^{-1}, small variations in cooling rate can have a significant effect on grain size.

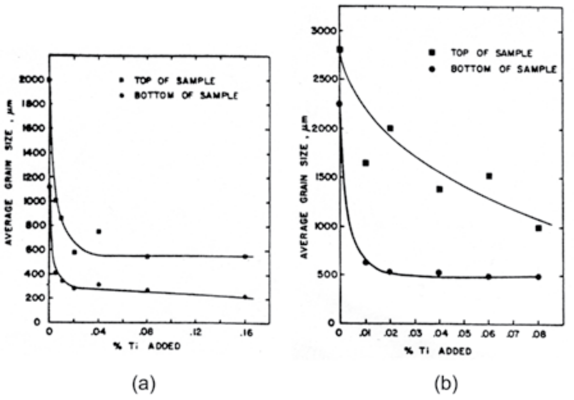

Fig. 22 Grain size as a function of added Ti using Al5Ti1B refiner(26)

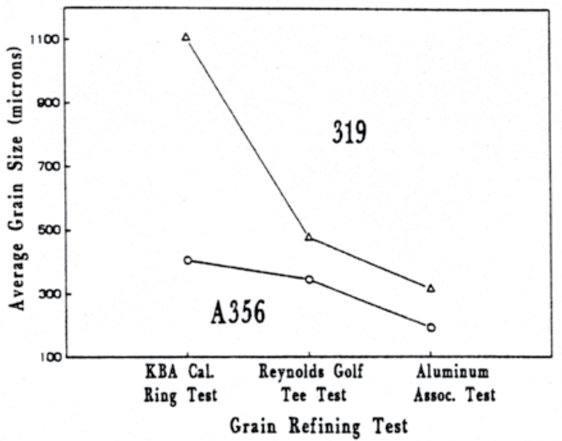

Fig. 23 Grain size data for 356 and 319 alloys using different assessment methods(34)

The grain refinement of a wider range of foundry alloys needs to be investigated as does the interrelationship of grain refiner addition level and cooling rate.

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