



Characterisation of a New Generation of Grain Refiners for the Foundry Industry

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CHARACTERISATION OF A NEW GENERATION OF GRAIN REFINERS FOR THE FOUNDRY INDUSTRY

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Abstract

There have been a number of studies in recent years relating to the mechanisms of grain refinement, poisoning and fade of Al-Ti-B refiners. In addition there have been several new grain refining products introduced for the foundry sector, such as TiBAlloy and Strobloy, for which studies have also been performed, albeit in a more limited way. The new generation of grain refiners have a number of specific beneficial attributes, which distinguish them from the traditional Al-Ti-B refiners. These benefits are explored by characterising the refiner particle types in terms of composition, size, poisoning tendency and fade characteristics.

Introduction

The Al- (3 or 5)%Ti-1%B and Al- (3 or 5)% Ti-0.2%B grain refiners of the Al-Ti-B system have dominated the grain refining market for several decades. Whilst this position has not changed dramatically in recent years, the foundry market has seen increased use of TiBAlloy in particular, but also Strobloy. Grain refinement of hypoeutectic Al-Si alloys appears to be quite different to that of wrought alloys, in that sub-stoichiometric refiners are quite successful. The use of TiBAlloy for the hypoeutectic alloys used in the foundry sector has been shown to provide benefits in terms of effect on porosity and lack of fade^[1-3]. Strobloy has been described as combining the benefits of grain refinement of TiBAlloy with the modification effects of Sr^[4].

Review of literature

Ideal Refiner Particle Size

There have been several studies modelling the nucleation stage of grain refinement^[5-11]. These have explored the relationships between nucleant particle potency, number and volume efficiencies and hence overall refiner performance. A grain refiner is more effective if a greater number of nucleant particles is activated at smaller undercooling ΔT . Importantly, activation at smaller ΔT makes equiaxed growth more likely to relict columnar growth from cooler regions of the casting^[12]. Not all particles in a refiner can become active^[13], because latent heat release from growing grains nucleated early can limit the ΔT available to activate later nucleation events. Thus the effectiveness of a refiner depends on the spectrum of undercoolings at which grain initiation occurs.

The performance of a refiner must depend on the population of nucleant particles and their spectrum of potencies^[10]. It has been speculated^[10] that with free-growth ΔT dominant, the spectrum of

potency can be derived from the particle size distribution. A key point is that this characteristic of a refiner is directly measurable, unlike parameters such as contact angle, which would be relevant for a nucleation analysis. Although there is no simple relation between refiner effectiveness and individual particle potencies, the models suggest that refiner performance would be improved by a narrower particle size distribution, but that for realistic ranges this is not a dominant influence^[7]. It is suggested that the average particle size of the refiner is of greater importance. The models also suggest that it is only the larger refiner particles in the size distribution, which play a part in nucleation events^[7]. One result of the modelling^[10] work suggests that the ideal mean particle size is of the order of approximately 0.7 μm .

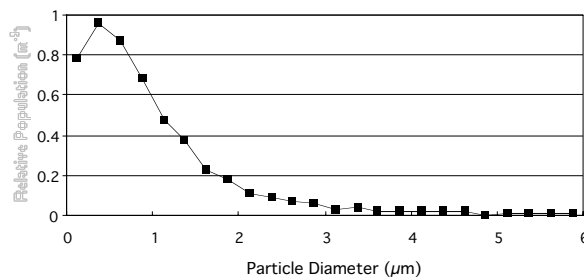


Figure 1: TiB_2 particle size distribution, from reference 10 (mean particle size is approximately 1.0 μm).

Refiner Particle Chemistry

Further key issues to successful formation of α -Al on particulate substrates are their crystallographic matching^[14] and their chemical composition at the nucleating interface^[15]. It has been suggested^[16] that lattice mismatches below 10 to 12% are required to promote nucleation. For this reason TiAl_3 is considered to be a better nucleant than TiB_2 .

It has been stated^[1] that most of the boride particles in TiBAlloy are of the $(\text{Al,Ti})\text{B}_2$ type. The chemical composition of the diboride $(\text{Al}_x\text{Ti}_{1-x})\text{B}_2$ in TiBAlloy was said to have $x = 0.35$, which represents the average for the refiner composition. In practice it is expected that x will vary from 0 to 1^[17].

Thermodynamic studies^[18] suggest that these particles convert to TiB_2 if given sufficient time in the melt, such that in the melt Ti would diffuse into the $(\text{Al,Ti})\text{B}_2$ particles while Al diffuses out, resulting in the formation of TiB_2 (at least in the surface layers). $(\text{Al, Ti})\text{B}_2$ and Al_4Sr have been described as the dominant particle

types in Strobloy, although clearly the possibility of SrB_6 cannot be discounted.

Porosity Formation

It is generally accepted that, grain refinement delays the onset of coherency during solidification, and so allows easier mass feeding into shrinkage prone areas. However, it is not clear why grain refiners should impact on porosity formation. It has been suggested^[19,20] that grain refiner particles may nucleate gas bubbles, and one finding^[19] reported that the threshold hydrogen level for the onset of porosity decreases considerably with grain refinement. There has been some research aimed at improving the understanding of pore nucleation and growth^[21-26]. Lee^[23] developed a technique to examine pore formation in-situ in real time, and also speculated^[26] on the possibility of TiB_2 particles acting as nucleants for pores. The reasons for the beneficial effects on porosity of TiB_2 alloy over other refiners are likely to be linked to either the finer particle size distribution or the different refiner particle type (in particular the surface chemistry). There is also a possibility that there are different effects for TiB_2 and $(\text{Al,Ti})\text{B}_2$ when combined with a strontium modification addition. It has been suggested^[26] that Sr and TiB_2 combine to alter the nature of any oxide present, and so alter the formation of porosity (industrial experience is that Sr redistributes porosity).

Fade and Particle Agglomeration

The fade characteristics of the super-stoichiometric Al-Ti-B ^[27-30] refiners are well documented. It is well established that fade in the Al-Ti-B system occurs as a result of TiB_2 particles (agglomerating and) settling.

The TiB_2 alloy refiner has been shown to exhibit superior fade characteristics^[1]. This is probably linked to the relatively small boride particle size and lower density. In terms of refining mechanism it is thought that the surface of the $(\text{Al,Ti})\text{B}_2$ particles requires a TiB_2 surface layer. This would be achieved by reacting with Ti in solution in the melt. This idea is supported by the fact that Ti in solution is required for TiB_2 alloy to perform (a level of 0.08% Ti has been quoted as necessary; foundry alloys tend to be specified above this level. However it is important not to have too high a level or TiAl_3 particles may form). It is also notable that TiB_2 alloy added to foundry ingot also provides superior performance to the casting foundry, indicating incomplete reaction of $(\text{Al,Ti})\text{B}_2$ to TiB_2 , when exposed in the melt for extended periods. This theory is supported by evidence^[31] of settled particles from TiB_2 alloy treatment containing an excess of boron for that required for TiB_2 . (In a similar way to BaAl_2 treatment for improving electrical conductivity, leading to settled borides with an unreacted aluminium boride core^[32]).

The grain refining efficiency of Strobloy appears to be similar to that of TiB_2 alloy^[3,4], although there is less experience and literature on its fade characteristics.

Particle agglomeration for foundry grain refiners has not been widely discussed in the literature, probably as it is generally not considered to be critical in these applications.

Poisoning

At low addition levels of Si to Al, Si behaves as expected in reducing the grain size by what is termed constitutional or growth restriction effects. However above approximately 3 wt.% Si the opposite is true and coarsening occurs^[33-38]. It has been suggested^[39,40] that the TiB_2 interface is an energetically favourable site for Si atoms, compared to the matrix subgrain/grain boundaries. Another factor, which could be of importance, is that the solubility of Ti in solid Al decreases with the presence of Si^[41]. The surface chemistry and hence surface energy are thought^[42] to adversely affect TiB_2 as a nucleation site.

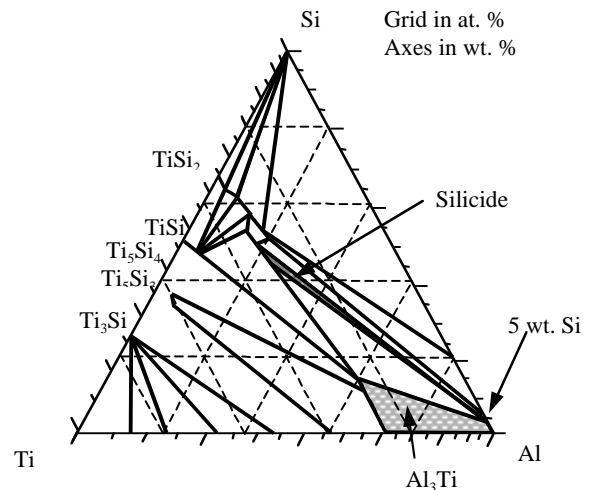


Figure 2: Isothermal section at 973K from Al-Ti-Si ternary phase diagram.

To study the Si poisoning phenomena in Al-Si alloys, the techniques developed for producing glassy forming alloys (to study nucleation phenomena) have been used^[43]. A deliberately high Si content alloy was designed^[44,45], in which the effect of extended holding times (30 minutes at 900°C) was assessed. Under these conditions the TiB_2 particles were surrounded by a TiSi_2 phase. There have been a number of studies on the Al rich end of the ternary phase diagram of the Al-Ti-Si system^[46-57], from an isothermal section at 973K is shown in figure 2.

TiSi_2 is dimorphous with the resultant structure depending on the method of synthesis. One of the forms of TiSi_2 is metastable^[47], but is stabilised by Al^[49], leading to a continuous solid solution from $\text{Ti}(\text{Si}_{0.85}\text{Al}_{0.15})_2$ to $\text{Ti}(\text{Si}_{0.7}\text{Al}_{0.3})_2$. The lattice parameters for this phase^[57] indicate it is not suitable as a nucleant for $\alpha\text{-Al}$. Another phase which can exist in this system^[49] is $\text{Ti}(\text{Al,Si})_3$, with Si soluble in TiAl_3 up to a composition of $\text{Ti}(\text{Al}_{-0.8}\text{Si}_{-0.2})_3$, which may also impact negatively on refiner performance, by altering the favourable lattice parameter of TiAl_3 .

The nucleation of this silicide phase by boride particles from the refiner may help explain the Si poisoning phenomena in Al-Si alloys. In addition excess Ti, which would strongly affect growth restriction, will be bound in TiSi_2 so a reduction in growth restriction would be expected. This may also explain why sub-stoichiometric refiners perform well, as the driving force for the

reaction to form the silicide will be reduced (as Ti will diffuse into the (Al,Ti)B₂ particle promoting the reaction to TiB₂). Clearly the effect of Ti at the boride interface is a key issue in both the nucleation of α -Al (through its role in the possible formation of TiAl₃^[43]) and the poisoning effect of Si.

Experimental

In order to “complete the picture” in terms of the characteristics of this new generation of grain refiners, and how they compare to the traditional Al-Ti-B refiners, the following work was carried out:

- (1) Characterisation of particle types in terms of chemistry.
- (2) Characterisation of particle types in terms of size distribution.
- (3) Fade tests on Strobloy.

Chemistry of Particles

0.3g samples of the refiners were dissolved in butanol^[58]. The solution was then passed through a filter with a pore size of 0.2 μ m. Undissolved intermetallic particles and inclusions remained on the filter. The amount of particles was determined using a microbalance. The structure of the particles was determined using X-ray diffraction, mixing with a small amount of reference material. This technique reveals of the order of 50,000 to 100,000 particles for the sample size stated.

Size Distribution of Particles

The size distribution of particles was determined by centrifuging and light scattering. The master alloys investigated contained several types of particles. Each phase had different densities and thus moved with different speeds during centrifuging. (The densities were assumed to be ^[59]: TiB₂: 4.520g/cm³; TiAl₃: 3.350g/cm³; SrB₆: 3.420g/cm³ and Sr Al₄: 2.980g/cm³). First the particles were analysed from 0.1 - 100 μ m assuming a density of 4.520g/cm³ in order to determine the size range for more detailed analysis. Then, based on the X-ray diffraction results, three parallel analyses were carried out for each phase in the material. If the particles in a sample were from two different phases, there were several peaks in the size distribution. Assumptions were then made as to which peak belonged to which phase based on previous experience.

Fade Characteristics

Fade tests were carried out on Strobloy using a modified version of the Aluminium Association TP-1 test ^[60]. 10kg of A356 alloy (Table I) was heated to 720°C in a small resistance furnace and allowed to stabilise. The grain refiner was then added to the melt and stirred for 30 seconds until dissolved. For the purposes of this study the Strobloy addition (2.2kg/tonne) was calculated to give an equivalent B level to a 2kg/tonne addition of TiBAlloy. A static bath was maintained throughout the test with samples carefully withdrawn from the melt and water quenched after 2, 10 and 30 minutes, then at 30-minute intervals up to a total of 360 minutes. Samples were sectioned and prepared for evaluation using standard techniques. Grain size was determined using the comparison technique outlined in ASTM-E112 ^[61].

Table I Chemistry of A356 Alloy Used for Strobloy Fade Tests

Alloy ID	%Si	%Mg	%Ti	%Fe
10857/0	6.90	0.31	0.10	0.06

Results and discussion

Chemistry of Particles

The techniques used revealed that the refiners contain the particles as summarised in Table II. The findings are in line with the literature, with the exception of the Strobloy sample. SrB₆ has not been reported previously as a phase present in this refiner. In addition, the presence of TiB₂ in Strobloy rather than (Al, Ti)B₂ is in contradiction to previous literature. Of the boride particle types in Strobloy, the one most likely to be primarily responsible for grain nucleation, based on their particle sizes is TiB₂. The boride phase in TiBAlloy is quoted in the literature^[1] as being (Al_x, Ti_{1-x})B₂. This is confirmed in the present study, although the value for x has not been established, the values for the lattice parameters (see Table III) indicate that x is likely to be closer to 1 than zero (the literature^[1,4] suggests x ~ 0.35). The presence of SrAl₄ in Strobloy will also play a key role in nucleation of eutectic Al-Si colonies within dendrite branches. In this way Sr may cause reduced feeding distances in alloys such as A356 with the resultant tendency to redistribute porosity.

Table II Nominal Composition of Intermetallic Particles in Common Grain Refiners

Refiner	%Ti	%B	%Sr	Boride Phases	Alumini de Phases
Al-5%Ti-1%B	5.0	1.0	0	TiB ₂	TiAl ₃
TiBAlloy	1.6	1.4	0	(Al,Ti)B ₂	-
Strobloy	1.6	1.4	10	TiB ₂ , SrB ₆	SrAl ₄

Size Distribution of Particles

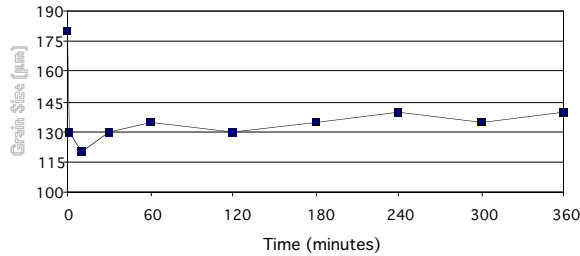
The technique used to establish particle sizes allows a ready assessment of the boride sizes in TiBAlloy, as it contains only small (Al, Ti)B₂ particles. These are of average size 0.8 μ m, with most below 1 μ m, and a maximum at 3 μ m. The current study therefore suggests that the boride refiner particles in TiBAlloy are significantly smaller than those found in conventional Al-Ti-B refiners (mean size of 0.8 μ m compared to 1.0 μ m). In comparison to the model of the ideal refiner particle size, the size distribution in TiBAlloy is much closer to the theoretical ideal.

The data for Strobloy is less easily interpreted as it contains TiB₂, SrB₆ and SrAl₄ particles. It is suggested that the TiB₂ particles are of a size between the boride sizes of TiBAlloy and Al-5%Ti-1%B refiners. The SrB₆ particle size is probably larger than the other boride phases, although again this is not readily distinguished due to the presence of SrAl₄ particles, so some intuitive interpretation of the data has been made.

Fade characteristics

Figure 3: Strobloy Fade Curve

The results of the fade tests on Strobloy are shown in figure 3, which indicates some fading, although a good performance is still achieved after 6 hours in the melt.



Some degree of fade might normally be expected from a grain refiner after 6 hours. Of the boride types present in Strobloy, SrB_6 is less dense than TiB_2 . It could then be speculated that the role of SrB_6 becomes more important during the holding period, but this would require further research to be confirmed.

TABLE III

Refiner Alloy	Particle Density (g/cm^3) lattice parameter (Å)	Mean Size (μm)	Agglomeration Behaviour	Stability/ effect on porosity	Poisoning Mechanisms	Fade Characteristics
5/1 & 3/1	TiB_2 (4.52) a = 3.03 c = 3.23	Typical 5 Maximum 1-2	Agglomerates by particle collision, halogens (F, Cl), affinity to oxide films and $TiAl_3$ stable layer	$T_m = 3225$. High stability in molten Al. Nucleates pores?	1.Zr: competes with Ti in TiB_2 2. Cr: not studied 3. Si in foundry alloys: formation of $TiSi_2$, ?	Significant fade only after several hours, due to particle agglomeration and settling
	$TiAl_3$ (3.35) a = 3.85 c = 8.60	Typical 30 - 50	No tendency as it dissolves, but see above for role of stable layer on TiB_2	Dissolves rapidly (at approx. 40 μm per minute). Thin layer thought to remain stable on TiB_2 particle. Little effect on porosity?	Loss of potency may be associated with loss of stable layer on TiB_2 particles	Not applicable as phase dissolves, although stable $TiAl_3$ layer on TiB_2 particles may play a role in particle agglomeration
BAI	AlB_2 (2.55) a = 3.01 c = 3.26	Typical 20 - 40	Not studied	Tendency to form TiB_2 on outside if Ti in solution in melt. Effect on porosity not studied.	Not applicable as transforms to TiB_2	Rapid as large (TiB_2) particles form in melt.
TiBAlloy	$(Al,Ti)B_2$ ($2.55 < x < 4.52$) a = 3.01 c = 3.27	Majority <1 Maximum ~ 3	Not studied but likely to be similar or less compared to TiB_2 (no superficial $TiAl_3$ layer)	Tendency to form TiB_2 on outside if Ti in solution in melt. Significant effect on porosity.	Less prone to Si effect of $TiSi_2$ formation?	Very low fade due to relatively small particle size and low density
Strobloy	SrB_6 (3.42) a = 4.20	Not readily assessed but larger than TiB_2	Not studied	$T_m = 2235$. High stability in molten Al. Effect on porosity not studied.	Not studied	Likely to fade more rapidly than TiB_2 due to larger particle size
	TiB_2 (4.52) a = 3.03 c = 3.23	Similar to that in 5/1?	Agglomerates by particle collision, halogens (F, Cl), affinity to oxide films and $TiAl_3$ stable layer	$T_m = 3225$. High stability in molten Al. Nucleates pores?	Formation of $TiSi_2$ in foundry alloys?	Significant fade only after several hours, due to particle agglomeration and settling

	SrAl ₄ (2.98) a = 4.46 c = 11.07	Similar to TiAl ₃	No tendency as it dissolves	Dissolves rapidly. Redistributes porosity.	No refining effect (modifies Al-Si eutectic)	Not applicable as phase dissolves
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Conclusions

The particles created during the manufacture of grain refiner master alloys are responsible for a multitude of effects in the foundry.

The current work has summarised the characteristics of a range of grain refiner master alloys, shown in table III. This has enabled a more ready understanding of the nucleation of *a*-Al, agglomeration behaviour, poisoning tendency and fade characteristics.

The boride particles in TiBAlloy are of the (Al, Ti)B₂ type, and are smaller than the TiB₂ particles found in conventional Al-Ti-B refiners. There are two boride types in Strobloy: TiB₂ and SrB₆. Their individual roles in grain refinement has not been well established.

The different behaviour of TiBAlloy with regard to porosity formation is probably linked to either its unique particle size distribution or surface chemistry. The relatively lower density of these boride particles (and probably also surface chemistry) also helps contribute to the excellent fade characteristics of TiBAlloy.

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