

Grain Refiners & Modifiers for the Aluminum Foundry

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Grain refinement plays a vital role in cast and wrought Aluminum alloys. Apart from wrought alloys grain refinement has several benefits in cast alloys like improved mechanical properties that are uniform throughout the casting, distribution of second phase and micro porosity on a fine scale, better feeding to eliminate shrinkage porosity, improved ability to achieve a uniform anodized surface, better strength and fatigue life. The principle grain refiners used in the foundry industry are the same as in the wrought industry, namely Al-5% Ti-1% B or Al-3% Ti-1% B. Grain refinement has been associated with the formation of casting defects. It is generally assumed that an increase in the level of grain refinement is beneficial for castability. However, there are some casting configurations where the addition of extra grain refiner causes an increase in porosity. It was found that the amount of hot cracking decreased as the refiner level increased, while the amount of localized porosity increased. Therefore, there is an optimum level of refiner required to obtain castings of optimum quality. In the past two decades, various modification and heat-treatment techniques have been developed to refine the microstructure of cast Al-Si alloys. Generally, chemical modification and thermal treatment have been adopted to modify the coarse acicular Si to fine and globular particles. Chemical modification methods involve adding very small amounts of sodium, strontium, or antimony, known as eutectic modifiers.

**Behaviour of Grain Refiner
Contact Time and Fade**

Fig.1 shows the grain size vs. time curve after grain refiner addition. The curve is characterized by initial rapid decline in grain size to ultimate grain size (UGS) at contact time t_c , followed by a rise in grain size at longer times. This loss of refinement is termed as 'fade'. Fade can be ameliorated in part by stirring the melt, through the degree of recover depends on the melt compositions [6]. It is known that grain refinement can be lost if a melt is held above 750°C, but that this can be regained if more titanium is added and melt is stirred.

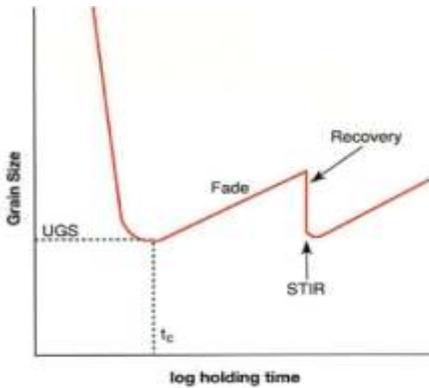


Fig. 1 : Schematic form of grain size vs. log time behaviour following addition of grain refiner to Al alloy melt [6]

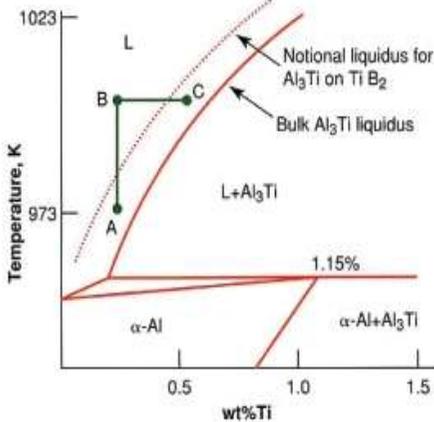


Fig. 2 : Schematic representation of dilute Al-Ti phase diagram showing liquidus for TiAl3 on TiB2. Sequence A to B to c shows how potency may be lost and regained [6]

Effect of Refining Particles

Following the rod addition, TiAl3 particles dissolves rapidly (40µm/min) and with good stirring 90% Ti will be in solution within 10s for a typical distribution of aluminum sizes. Depending on the melt temperature and composition, the TiAl3 overlayers on TiB2 may grow slightly, remain

stable, desorbs or undergo site competitive substitution with other transition metal elements present in the alloy melt. Fig.2 (Fig.3) demonstrates how the absorbed TiAl3 layer may be lost and reformed. Substitution and site competition effects may be estimated from dilute Al-X binary phase diagrams which are shown super imposed in Fig.4 from this fig. it is possible to see Zr and V compete strongly with Ti at particularly lower temperatures and that Ta will form a stable layer. Whilst aluminide dissolution and TiB2 interfacial chemistry changes are in progress, some degree of particle collision, sticking and settling will occur. If holding times are long then there will be fewer particles remaining in the melt to nucleate grains. It will also be likely that those remaining in the suspension will be smaller on average than immediately after addition as larger particles settle first.

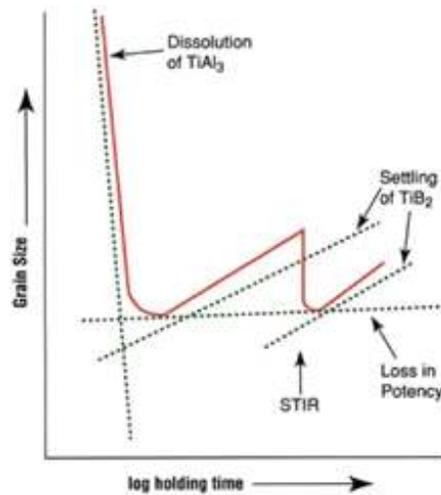


Fig. 3 : Schematic representation of processes occurring on addition of TiBAl grain refiner to aluminum melt showing how the characteristic form of behavior emerges [6]

Solidification

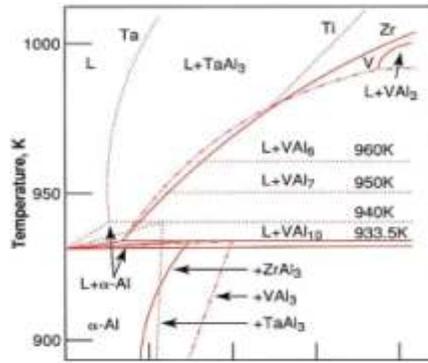


Fig. 4 : Dilute portions of Al-Ti, Al-Zr, Al-V and Al-Ta phase diagrams showing relative stabilities of aluminides which affects preferred adsorption behavior on TiB2 [6]

Grain refinement can be understood to be directly related to the nucleation and growth process of aluminum grains. This is based on Volmer and Weber ideas for homogeneous and heterogeneous nucleation [10]. Fig. 5 shows the solid nucleating on the substrate on liquid. The critical free energy for heterogeneous nucleation is always less than or equal to that for homogenous nucleation. The values of undercooling, ΔT is of order of 1 – 2 K for observable nucleation rates in commercial aluminum alloy with grain refiners. Therefore clearly heterogeneous nucleation is taking place. The expression for heterogeneous nucleation rate per unit volume in m-3s-1 by equation (1).

$$I_{\text{heterogeneous}}^v = 10^{18} N_v^0 \exp \left[\frac{-16\pi\gamma_{SL}^3 f(\theta)}{3K_B \Delta S^2 \Delta T^3} \right]$$

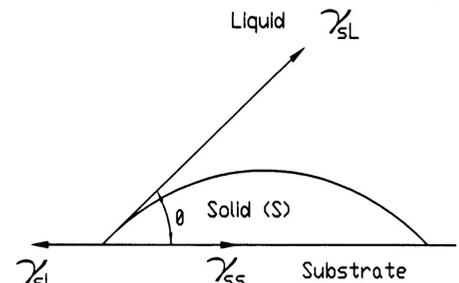


Fig. 5 : Schematic representation showing the formation of spherical cap of solid (s) on a

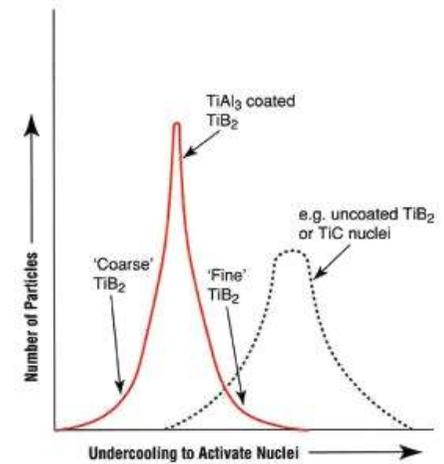


Fig. 6 : Schematic distribution of undercoolings required substrate, contact angle and surface tension by different nuclei within a grain refined melt. [6] forces [10]

Under the heat flow conditions prevailing during solidification, the melt becomes undercooled until sufficient undercooling is achieved for particles to nucleate α -Al by the peritectic reaction (Fig. 6). In order to achieve finest grain size, it will be necessary to activate the median portion of the undercooling

distribution. In reality undercooling will vary from positions to positions because of local heat flow and constitutional effects.

Behaviour of Grain Modifier & its Selection for Al Casting

Comparison of Sodium & Strontium Modifier

Modifiers are added to eutectic and hyper eutectic Al-Si alloys to refine the eutectic Si phase from one of angular platelets to fine fibers. This change in microstructure results in improved mechanical properties, particularly strength and ductility [01]. Modification also leads to refined porosity which leads to an additional improvement in mechanical properties.

The first hypoeutectic modifiers were based on Na, and are added as Na metal or encapsulated Na in Al foil. Due to high reactivity and low solubility of Na in aluminum (recovers low up to ~ 20%) with gradual loss of Na with time (fade) results in a process that is difficult to control.

In sodium modified melt the eutectic growth front is typically planar, thus allowing regular solidification through the dendritic network and minimal entrapment of liquid pockets [14]. With Sr modification however, the growth front is more irregular, allowing the possibility of liquid areas becoming trapped leading to shrinkage microporosity. The modifying action of Na practically disappears after only few remelts. On the other hand, the modifying effect of strontium does not fade on holding at elevated temperature [11].

However, longer holding time is required at 750 C due to the difficulty in dissolution of strontium, resulting in increased gas pickup. Finally, although antimony has no fading effect and the improvement in elongation and impact strength is greater than that achieved by sodium, its use has been precluded in most countries because of environmental and safety reasons. Thermal modification involves heat-treatment of cast alloys at high temperature; usually at the solid solution temperature around 540 C for long times [12]. Solution heat treatment results in a substantial degree of spheroidization of second phase particles.

Variation of Silicon particles morphology with modification [15]

In unmodified alloy, the silicon grows as plates that can be lamellar or acicular. Lamellar structures are nearly parallel and thin plates, while acicular structures are randomly distributed plates with much massive structure. At an unmodified condition, thin silicon plates

TABLE 1 : COMPARISON OF SODIUM & STRONTIUM MODIFIER [11]		
	Sodium Metal	Al-Sr Alloy
Recovery	Low, Variable & Operator Dependent	High and Consistent
Contact Time	Immediate	Up to 10-20 min.
Fade	Fast (20-40 min)	Slow (> 2 hours)
Environmental	Fumes and Refractory Attack	Clean and fume free
Overmodification	Possible Due to Difficulty of Control	Unlikely
Potency	Very High	High
Addition Level (Typical)	50 ppm	250 ppm
Ease of Handling	Must be Protected from Moisture	Unreactive with Moisture if <20% Strontium Master Alloy

can be seen cutting through the aluminum matrix (Fig.7).

Partially modified structures are the coexistence of flake and fibrous silicon mixed, cellular or banded structure. They can be obtained by a combination of slow solidification rates (bet. 1 & 25 μ m/s) and low strontium concentration. At low strontium concentration and during slow growth, the eutectic is able to reject enough strontium ahead its interface to avoid transforming to fibrous morphology (Fig.8).

In well modified structure silicon grows in a coral-like form (fibrous) that looks like small individual round-shaped particles in polished surface. The modification treatment affects not only size and shape of the particle, but also its distribution. Ideal concentration of strontium results in a fibrous eutectic structure, well refined and homogenous (Fig.9).

When the addition of strontium exceeds the amount necessary to produce a fully modified structure, it exerts a deleterious effect on the mechanical properties of the alloy. Strontium overmodification is much more subtle and difficult to identify by microstructural analysis.

In overmodified alloys, elongated silicon particles that no longer grow as well as refined fibers can be observed. However the formation of Sr-rich phase is reported in strontium concentration above 0.03% and the eutectic silicon grows in coarser fibrous form. Although the morphologies of a well modified alloy and an overmodified alloy are mostly coral-like ones, their thickness are considerably different (Fig.10).

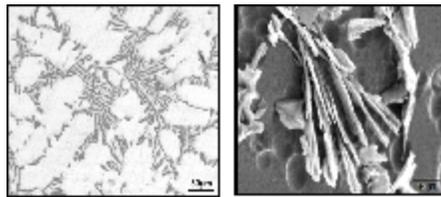


Fig. 7 : Unmodified Alloy (0.0003% Sr) Lamellar Structure (a) 200X (b) 1500X

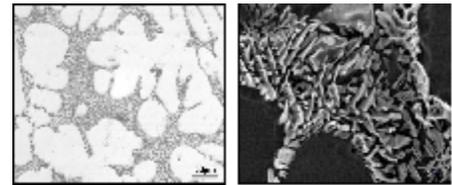


Fig. 8 : Partially Modified Structure (Mixed) (0.0026% Sr) (a) 200X (b) SEM Deep Etched 1500X

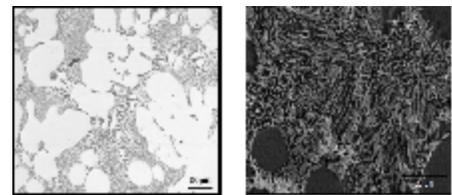


Fig. 9 : Fully Modified Structure (0.0075% Sr) (a) 200x (b) SEM Deep Etched 1000x

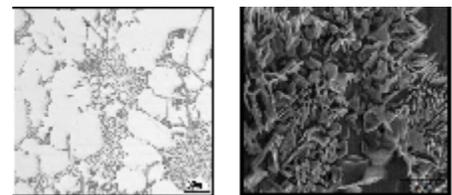


Fig.10 : Over Modified Structure (0.0130% Sr) (a) 200x (b) SEM Deep Etched 1000x

Effect Of Strontium on Reliability Of Castings

The average mechanical property results after the various treatments are shown in Fig. 12 these show that the melt treatments lead to improved mechanical properties in GDC A319 alloy. The addition of modifier gives an increase in UTS and elongation values, treatments have resulted in reduction in scatter as evidenced by an increases in Weibull modulus from 5.9 (untreated) to 17.6 (modified) [05]. Similarly the Fig.11 shows an increased fracture toughness value for Sr-modified alloy A357 compared to unmodified alloy.

Selection of Grain Refiners

Grain refiners are added to Al-Alloy to improve the melt processability and to reduce the size of primary Al grains. These grain

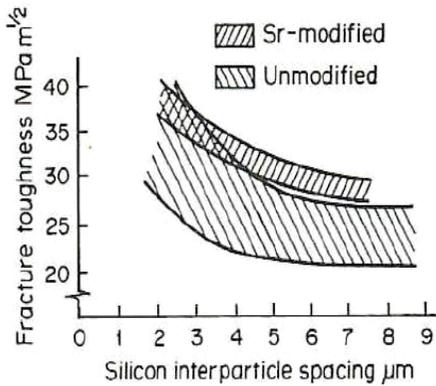


Fig.11 : Fracture Toughness of Alloy A357(al-7si-0.5mg) with and without Sr Modification [14]

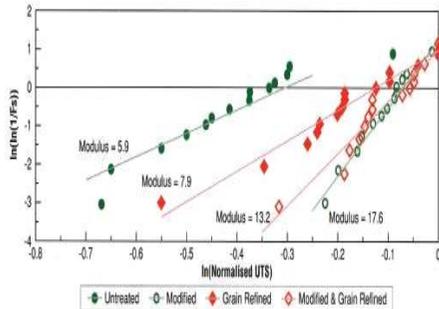
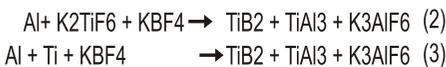


Fig.12 : Effect of Melt Treatment on Weibull Plots of UTS of Gravity Die Castings A319 [05]

refiners can be in various forms. The most suitable form is master alloys as AlTiB and AlTiC, it contains TiAl3 particles and TiB2 particle which are responsible for grain refinement as discussed earlier. Originally these particles were created into the melt by addition of compacted powder tablets i.e. compacted mixture of K2TiF6 and KBF4 salts. The tablets works as simple dissolution and reaction of titanium boron tablets or by dissolution and reaction of titanium and boron salts in titanium boron tablets as indicated below.



Because these reactions have to occur in the melt to form TiB2 nuclei, this addition method is not as quick or as controllable as TiBAl master alloy approach, as comparison shown below :

TABLE 2 : COMPARISON OF TIBAL & SALT TABLET AS GRAIN REFINER IN FOUNDRY [5]

	TiBAl Rod	Salt Tablets
Recovery	High and Consistent	Variable and Operator Dependent
Contact Time	Short (30 sec.)	Long (5-10 min)
Efficiency	High	Low

To be Cont..

Fade	2-4 hours	1-1.5 hours
Dissolution	Fast (<30 sec.)	Slow (2-5 min.)
Addition	Clean and Fume Free	Fumes and Flux Residues
Cost Comparison	High	Low

Industrial Application of TiCaI & TiBaI

TiCaI refiners (Al-3Ti-0.15C) have been used industrially in aerospace plate (AA7xxx), bright trim (AA5xxx), lithographic (AA1xxx), canstock (AA5xxx) and foil (AA8xxx) alloy applications. Operationally, the higher sensitivity of TiCaI to temperature makes it more suitable for slowly cooled products e.g. large rolling slabs where the undercooling driving grain growth is primary [08]. TiCaI offers advantages in alloy containing Zr, Cr which can otherwise poison TiBaI refiners. At a given addition rate and low temperature TiCaI master alloy is as efficient as TiBaI alloys in grain refining AA6063. In terms of quantity of particles added however, both TiCaI and Al5Ti-0.2B are more potent than Al-3Ti-1B. TiBaI is used for strip cast application with addition rate of 0.15 to 0.4 wt% of grain refiner. [03]. Recycling test demonstrates that TiBaI is more robust than TiCaI during the thermal cycling of AA3004 at 800°C [02]. TiBaI and TiCaI bearing 3xxx and 5xxx alloys can be recycled effectively with modest addition of TiBaI after exposure to 800°C.

Comparison of Grain Refiners TiCaI and TiBaI

It has been estimated typically only 1 in 500 TiB2 particles nucleates grain. Fig. 13 shows relation between no. of particles required per grain and grain refiner addition rate for AA1050 at different temp. In general, with fewer particles present, the nucleation efficiency of each particle becomes greater. The loss of potency displayed by TiCaI at higher temp. may be caused by poisoning. Conversion of the surface of TiC particles to Ti2AlC or Al4C3 would destroy the excellent lattice matching between TiC and α-Al which is basis of TiC's effectiveness as a nucleant for aluminum [09].

Thermal cooling dominates at the edges of castings and constitutional undercooling is greatest at the centre of cast sections. AlTiB produces finer grain sizes at billet edges and therefore responds better to thermal undercooling (Fig.14). The nuclei generated near the mould walls will be relatively mobile and rejected solutes will tend to be dispersed leading to relatively low constitutional undercooling. Under such condition most potent

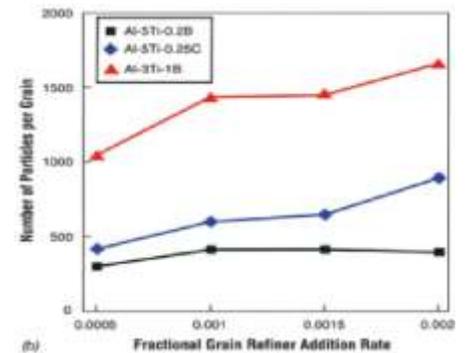
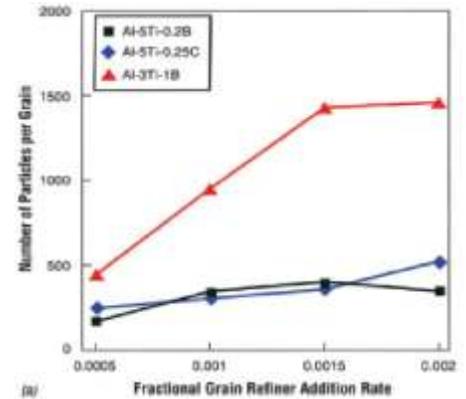
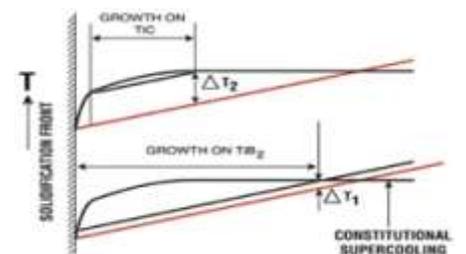


Fig.13 : No of Particles (Calculated) Needed to Nucleate A Grain in Aa1050 as a Function of Refiner Type, Addition Rate and Temperature (a) 670°c (b) 700°c [09]



nucleant will dominate solidification behavior and so TiB2/TiAl3 produces finer grains at the mould walls.

Fig. 14 Schematic of the constitutionally-Conversely at billet centre, thermal gradient supercooled region ahead of the solidification will be low and the constitutionally-front showing different behaviour of AlTiC and AlTiB [10] supercooled zone will be large. The zone of activation of TiB2 nucleants will be larger than that for TiC and the opportunity for nucleation well in advance of growth front will be greater for TiBaI [09]. The relatively fine grain size at billet centre is obtained with TiCaI is therefore suggested to be due to combination of its greater constitutional supercooling to become active and its tighter particle size distribution. For TiCaI there is no change observed in grain size with increasing



mould temperature in the range 25500°C. Whereas, TiBA1 showed coarsening of grain with rising mould temperature. Thus TiCA1 is more effective in situations where thermal gradient are low.

**Poisoning Effect
Influence of Zr/Cr on Grain Refiners**

Zirconium has a poisoning effect (especially in TiBA1, not in TiCA1) on the grain refiner efficiency more obvious at higher melting temperature. G.P. Jones and J. Pearson suggest that the fading mechanism is mainly due to the formation of a thin layer of ZrB2 on TiB2 particles in the melt They claim that the nucleation is on TiB2 particles adsorbing of Ti, when Zr element is present, the titanium borides will be covered with a monolayer of zirconium borides preventing the dissolved Ti from being adsorbed [13].

On the contrary, when 0.12%Zr is added into the melt, the grain refinement performance of AlTiC refiner with 0.2% addition level was affected at higher temp. (i.e. 800°C)[13]. Zr element interact with both TiAl3 and TiC phases, if both of them are present, Zr preferentially reacts with TiAl3 phase. Thus TiCA1 is a effective grain refiner at lower refining temperatures.

A combination of small quantities of Fe, Cr, Si (0.2 wt% Cr) has shown early and significant fading. At higher Cr concentration (Cr 2wt %) has adverse effect of coarse ring grain size [07].

Agglomeration

The boride agglomeration takes place only in case of AlTiB grain refiner. The user can not be certain that the agglomerate will disperse on addition to aluminum. It is also possible that the agglomerate may form within the customer’s own process. The causes of boride agglomeration are: TiB2 particles collide with

each other, TiB2 particles are attracted to oxide films, to form complex agglomerate, halogen elements “wet” TiB2 particles causing them to easily agglomerate and TiAl3 layers on TiB2 can stick the particles together.

Inclusions, in grain refining master alloys and aluminum alloys as TiB2 agglomerates, manifest themselves in various forms such as rings, clusters and strings. Boride agglomerates are generally classified as defects when they are above 5 micron in size. They are often observed to be tiny clusters of much smaller particles (½ to 1 micron).

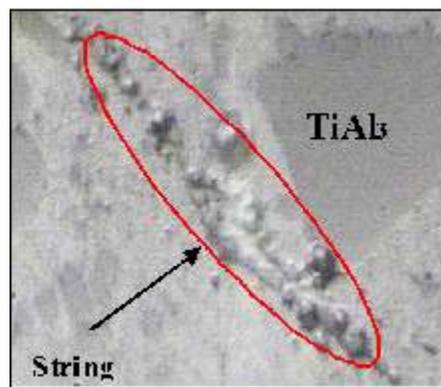
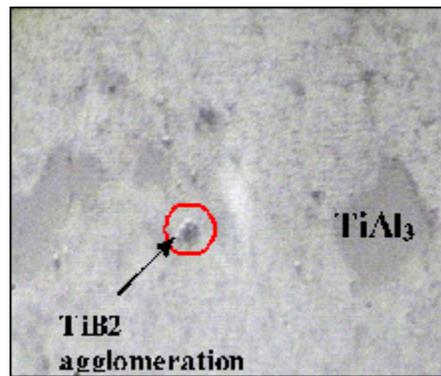


Fig.13 : Optical Microstructure of TiBA1 5/1 at 1000x having TiB2 Agglomeration and String Type Defects

Examination of fractured samples to investigate the boride agglomeration (as strings) contains fluorine at relatively higher levels. TiB2 particles are susceptible to wetting by fluorides [04]. This can also be identified in grain refiner microstructure as shown (grain refiner with defects)

The chances of agglomeration of TiB2 particles in lower boron containing grain refiner is less (e.g. TiBA1 5/0.2). Reduced TiB2 agglomeration to allow thinner foils and brighter trim alloys to be produced. In case of TiCA1, TiC a particle doesn't agglomerate, thus TiCA1 is suitable for all applications.

Conclusion

- Grain refiners play a crucial role in aluminum alloys; it improves mechanical properties that are uniform throughout the casting, better feeding to eliminate shrinkage porosity, better strength and fatigue life and is achieved by heterogeneous nucleation and growth of grains.
- TiCA1 offers advantages in alloys containing Zr/Cr which can otherwise poison TiBA1 refiner. Al-3% Ti-0.15% C improves melt fluidity and finished cast appearance in comparison to Al-3% Ti-1% B in 5XXX series alloys in particular, but also in 6XXX alloys
- For lithographic/Strip casting/foil grade application Al-5%Ti-0.2%B is more effective grain refiner than compared to Al-3%Ti-0.2%C and 3%TiAl. As lower boron concentration leads to less agglomeration of TiB2 particles
- And in modifiers Sr is preferred over Na metal modifier in Al-foundry due to environmental restrictions. But excess amount of Sr cause overmodification by coarsening of Silicon structure which is not easily assesjed by optical microstructure study.