Grain refinment in Al-Si alloys

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Abstract- Grain refinement of aluminum alloys has been used commercially since the first half of this century and it has been a main feature in the control of quality products manufactured from wrought aluminum alloys. The increase in resistance to hot cracking, the homogeneity of the micro structural features leading to improved mechanical properties and the reduction of macro porosity were the main reasons for the aluminum casting producers to adopt the technology of grain refinement. Grain refinement of AI-Si casting alloys is commonly assessed by the presence of Ti and B in the melt.

Grain refinement in Al-Si casting alloys improves the mass feeding characteristics during solidification, resulting in reduced shrinkage porosity and the promotion of smaller and improved porosity dispersion. Also, a fine grain size creates a more uniform distribution of secondary intermetallic phases in addition to pores which form from the evolution of dissolved gas in the melt. The resultant increase in casting integrity is accompanied by improvements in both mechanical properties and pressure tightness. An incremental improvement in the ultimate tensile strength and the yield strength of A356.

I. INTRODUCTION

The global market for automobile parts aluminum die casting registered revenue $5.08 billion in 2015 and is expected to touch $6.64 billion by 2020 with an estimated CAGR of 5.52% over the forecasted period. Increased automation in the die casting industry spiked the productivity and a parallel demand for the former from the automotive industry is dragging the attention of automotive manufacturers towards highly durable aluminum die casting parts..

Automobile industry is highly dependent on the environmental protection agency regulations, owing to the high emissions by the automotive units. The move by EPA of raising the mile per gallons standards to 35.5 miles per gallon by 2016 and then 54.5 mpg by 2025 actually helped the die casting industry as the auto industry concluded the only way they can get to those mileage standards is by light weighting the vehicles. Aluminum, and specifically aluminum die castings, in many of the power train and engine areas, are the only way they've concluded they could achieve this. This is one of the major reasons for the predicted growth of the industry in the area of structural die-castings too. Further, aluminum is becoming increasingly popular material for this purpose due to its ability to be easily recycled. Approximately 75% of aluminum consumed can be reused, and reclaimed aluminum can be recycled indefinitely, making it's the most popular material for automotive part die-casting.

In order to rneet these growth expectations, aluminum casting producers rely on the technology that has been developing since about 1980 to manufacture quality aluminurn alloys. Alurninium-silicon alloys comprise 90 % of the total cast alurninium production, due to their excellent castability and good corrosion resistance. Liquid metal treatment to control the melt chemistry, cleanliness and hydrogen content, as well as micro structural control, are critical in attaining optimum physical and mechanical properties in a casting. In the case of aluminum casting alloys, the control of grain size has been important to improve the feeding capability of the melt. to improve the mechanical properties, and to ensure proper pressure tightness in automotive applications as well as an acceptable surface appearance. In addition to the grain size, the eutectic Silicon morphology as well as the dendrite arm spacing of the primary a (Al) phase play a major role in the production of high quality aluminum castings.

Additions of certain elements to aluminum alloy melts can provide nuclei for grain growth. Titanium, particularly in association with boron, has a powerful nucleating effect and is the most commonly used grain refiner. Titanium alone, added at the rate of 0.02–0.15% as a master alloy, can be used but the effect fades within 40 minutes. The addition of boron together with titanium produces finer grains and reduces fade.

It is also important to appreciate that the effects of grain refinement in aluminum castings can be further enhanced when varying other production parameters such as pouring temperature, cooling rate, silicon morphology and heat treatments. Figure 1 shows the combined effect of hydrogen content, silicon modification and grain refinement on microporosity of Al alloy 356.

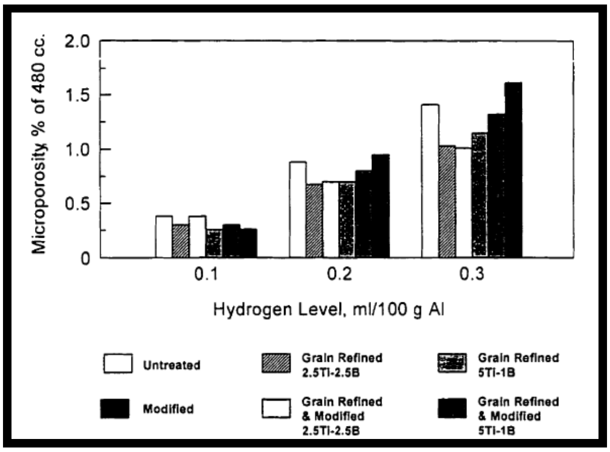


Figure 1 Effect of hydrogen content, Silicon modification and grain refinement on micro porosity of 356 alloy

II. GRAIN REFINEMENT MECHANISM

Chernical refinement by controlled heterogeneous nucleation has been accomplished in the aluminum industry by the addition of AI-Ti and Al-Ti-B master alloys and more recently by Al-B and Si-B master alloys for cast Al-Si alloys. Various theories have emerged from this practice and the exact mechanism of grain size reduction is still in dispute. Here, some of the main theories will be described briefly in order to outline the physical aspects of grain refinement and to be able to correlate them later with the parameters of the thermal analysis.

2.1 Peritectic theory:-

Among the various theories presented by several authors. The Peritectic Theory has been taken as a base mechanism in the explanation of grain refinement of alurninurn alloys by titanium addition.

Titanium, when present in sufficient arnounts (>0.15%), forms primary crystals of TiA13 which react peritectically with the liquid forming a (Al). Compositions are usually in the hypoperitectic range and the transformation takes place according to reaction.

$$\text{Liquid} + \text{TiAl}_3 \rightarrow \alpha\,(\text{Al}) + \text{Liquid}$$

The α (Al) particles then act as nucleants for the remaining liquid. The degree of refinement being dependent on the number of primary crystals formed (Figure 2). Al- Ti master alloys contain TiA13 particles in an alurninum matrix and when added to the molten metal to be refined. The matrix dissolves, distributing the TiAl3 particles in the melt and so generating heterogeneous sites for nucleation. Even at concentrations of Ti< 0.15 Wt. % grain refinement is achieved in commercial aluminum alloys. But this effect fades with time due to dissolution of the TiAI3 particles.

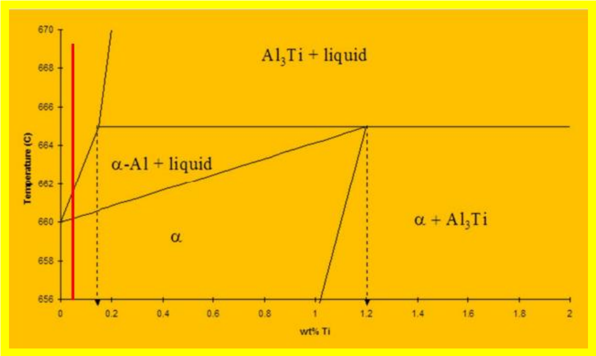


Figure 2 Addition of boron has little effect on Al-Ti phase diagram

The Peritectic Theory has been confirmed by other authors who have found particles of TiA13 at the center of aluminum grains and observed orientation relationships between this compound (TiA13) and the surrounding aluminum.

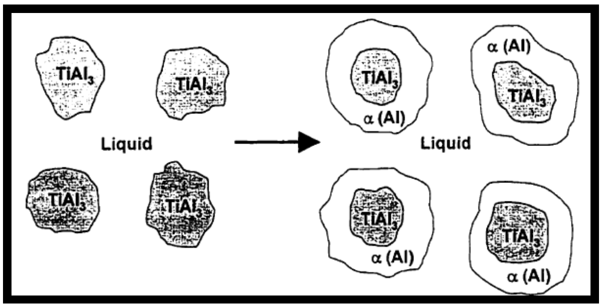


Figure 3 Nucleation of α (Al) by the Peritectic reaction in the Al-Ti system

For AI-Ti master alloys, it has been found that at titanium levels below the peritectic. The refining effect fades due to dissolution of the TiA13 particles in the melt

2.2 Grain refinement by titanium & boron addition:

Titanium and boron additions may be added as a master alloy or as a flux. In the wrought aluminum industry, the benefits of Ti-B-Al master alloys are well known, with alloy rod used in continuous applications. The majority of foundries use smaller melting and holding furnaces and continuous application is not possible so batch applications are used. While the master alloy approach has benefits of precision and controllability. The level of silicon in the alloy affects the grain-refining response to Ti and B. Higher silicon casting alloys require higher additions of grain refiner.

Several studies have been done in this respect and the literature is abundant with thermodynamic studies (sometimes contradictory) and experimental findings. This can be sumrnarized in three main theories that are reviewed here.

2.2.1 Boride theory:-

The boride/carbide theory was first postulated by Cibula in 1949. Cibula postulated that when a metal refined by titanium is remelted, the nuclei of titanium carbide dissolve but do not readily re-precipitate on cooling due to the great dispersion of titanium and carbon atoms which make nucleation with titanium carbide more difficult. Similarly, in melts treated with Borone the aluminum boride also dissolve if heated above the aluminum –boron liquidus (660°C) but the re-formation of aluminum boride on cooling should be less liable to suppression since aluminum is the main constituent of the melt.

Contrary to this idea. Marcantonio and Mondolfo proposed that the boron addition reduced the solubility of titanium in molten alurninurn, and expanded the peritectic reaction of the AI-Ti system towards the Al-rich end, allowing TiA13 crystals to exist even at very low titanium concentrations. Other researchers have also contradicted the Boride Theory of Cibula by noting that boron containing particles are found at grain boundaries, and not at grain centers.

Despite these contradictions, these authors have definitely established the presence of the following particles in the grain refined rnetal, Ti-Al3, TiB2, AlB2 and a mixture of (A1.Ti) B2. From these observations two theories have emerged. Neither of these, which are described below, has been proven conclusively.

2.2.2 Peritectic Hulk theory:-

The peritectic hulk theory, proposed by Backerud, this theory proposes that the nucleation occurs inside a boride shell via the peritectic reaction. The titanium is present inside the boride shell after TiAl3 dissolution at the peritectic concentration. While recognizing TiAl3 as a better nucleants than TiB2, the peritectic hulk theory explains how the boride slows down the dissolution of aluminide. It suggests that borides form a shell around the dissolving aluminides, thus slowing down the dissolution of the latter as diffusion needs to proceed through the boride shell. The aluminide finally dissolves leaving a cell of approximately peritectic composition inside the boride shell. The peritectic reaction takes place to form α-aluminum and growth occurs from there. It has been observed that Al-Ti-B master alloys contain a mixture of borides surrounding the aluminide phase (and sometimes found within the phase), which can improve the protection against dissolution of Ti-Al,. The grain refining effect of these duplex particles seems to fade with time due to the cornplete dissolution of the aluminide but other authors claim that the loss of refining efficiency is due to the settlement of boride particles. Another important aspect considered in this theory is that the presence of excess titanium (above the stoichiometric Ti/B = 2.21) has a critical significance in the grain refinement.

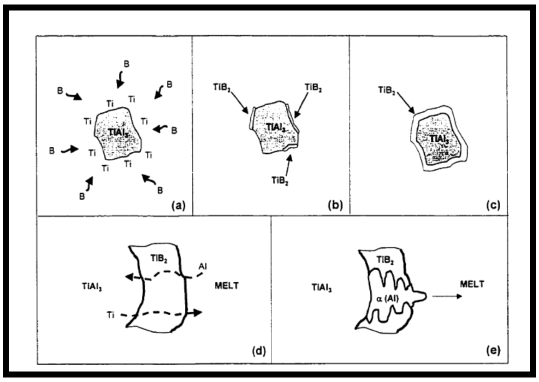


Figure 4 Model for Peritectic Hulk theory (a) Partial dissolution of TiAl3 and diffusion of B towards TiAl3, (b) Solubility product of TiB2 is exceeded, (c) Protective shell of TiB2 on TiAl3 is formed, (d) Simultaneous diffusion of Al and Ti through protective shell, (e) Nucleation & growth of α (Al).

2.2.3 Hypernucleation Theory :

The Hypernucleation theory was proposed by Jones and Pearson and named as such because of the disproportionate effect that very small amounts of titanium and boron have on the grain size of aluminum. Hypernucleation theory proposes that nucleation occurs on the borides. Titanium segregates down the activity gradient to the borides (TiB2) particles, thus forming a suitable interface for nucleation of α-aluminum. Solutes of similar atomic size to aluminum lead to Hypernucleation whereas solutes of grossly mismatching size will destroy the Hypernucleation process. The atomic size of titanium is very similar to that of aluminum and hence promotes Hypernucleation.

When there is excess titanium (above the ratio TiA3 = 2.21) in the molten aluminum, solute titanium segregates from the melt to the TiB2-melt interface, forming a thin layer of TiAl3, which on cooling, reacts peritectically to nucleate α (Al), Figure-5 Fading, according to this mechanism is due to the agglomeration and settling of boride particles. Experirnental evidence supports this theory based on fading recovery but the thermodynarnics of this theory have yet to be precisely established.

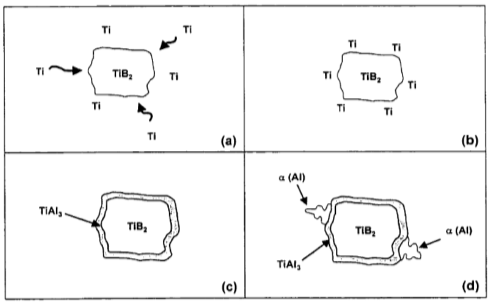


Figure 5 Model for the Hypernucleation theory (a) Excess Ti (Ti/B>2.21) in solution, (b) Ti segregated to

the TiB2-melt interface, (c) Formation of TiAL3 layer on TiB2, (d) Nucleation of α (Al) by peritectic reaction.

2.3 Duplex Theory:

The duplex nucleation theory suggests that nucleation takes place on TiAl3 particles that surround TiB2 particles. The basic idea is that, in the absence of titanium in the aluminum melt, TiB2 does not act as a nucleating site and is pushed to the grain boundaries. However, with the titanium at the peritectic concentration, TiB2 was observed at the centre of aluminum grains with a TiAl3 layer on the boride.

2.4 New Understanding of Nucleation of Aluminium by Inoculation:

A new approach has been set forward to explain which of the two compounds, TiAl3 and TiB2, is the primary nucleants. Based on the quantities of grains of aluminum and of TiB2 and TiAl3 particles added in the grain refining process, Lee and Chen concluded that TiAl3 particles couldn't be the primary nucleating substrate for grain refinement using Al-Ti-B grain refiners. This explanation is based on the fact that the introduced quantities of TiAl3 are much lower than the amount of grains and the number of grains was lower than that of TiB2 particles. Furthermore, when only TiB2 is used, the grain refining performance is very poor or even nil. It was thus concluded that the nucleation mechanism for Al-Ti-B grain refiners must be based on TiB2 as the nucleating substrate while the titanium in excess has some effect on the surface of TiB2 particles. TiB2 is then said to be the primary substrate.

2.5 Grain refinement of Al-Si alloys:

The practice of grain refining Al-Si alloys has largely been adopted from the wrought aluminum industry without considering the effects of the main alloying elements (Si, Cu, Zn and Mg) on the final grain size. Experimentation on Al-Si alloys has show the importance of boron in AI-Ti-B master alloys. Again the Ti/B ratio becomes important, since an excess of boron will generate the formation of AlB2 particles. There is considerable controversy over the effectiveness of AIB2 as a nucleant for alurninum. According to Cibula, AB2 particles are able to nucleate aluminum. but Maxwell and Hellawell contend that AIB2 is not an effective nucleant for pure aluminurn. AIB2 and TiB2 have nearly identical structures and sirnilar properties may be supposed for each of these phases. If experimental findings have found undissolved TiB2 particles on grain boundaries of solidified samples. There is no reason to suppose that AIB2 will become a site for heterogeneous nucleation of primary aluminum.

In general the different classes of master alloys have been produced for the refinement of the grain structure of Al-Si foundry alloys. These are binary Al-Ti. Binary Al-B and ternary Al-Ti-B alloys with titanium or boron in excess of the TiB2 stoichiometry (Ti/B=2.21)

The performance of these master alloys has been tested in 356 and 319 Al-Si alloys and several factors have been proven to affect the results. It has been found that refiners of the type Al-Ti-B, containing solute boron, provide the best results in Al-Si foundry alloys and that differences in performance of the refiners is magnified by the lack of residual titanium in the melt.

Al-Ti refiners, originally used in the wrought alurninum industry, are found to be the least effective among the products tested in Al-Si foundry alloys, possibly due to some kind of interference of silicon with the grain refining effect of titaniurn. It is suggested that in casting alloys with high silicon content, the system Al-Ti becomes an Al-Ti-Si system, still a peritectic one, but involving new aluminide phases such as indicated in reaction.

$$\text{Liquid} + \text{Ti}_x\text{Si}_y\text{Al}_{1-(x+y)} \rightarrow \alpha\ (\text{Al}) + \text{Liquid}$$

This Ti-Si-Al phase has been found in the center of aluminum grains and it is believed that, for silicon contents of 6 %, reaction occurs at approximately 600°C, just below the liquidus temperature of 356 and 319 Al-Si casting alloys.

Sigworth and Guzowski found that the Al-3%Ti-3%B master alloy gave powerful refinement in an Al-Si melt with primary aluminum nucleating on (Al.Ti) B2 particles (having a composition close to AIB2). Other authors have proposed that excess boron forms a layer on TiB2 particles and nucleates α (Al) by a eutectic reaction at 659.7°C reaction.

$$\text{Liquid} \rightarrow \alpha\ (\text{Al}) + \text{AlB}_2$$

Also, in Al-Si alloys, Mohanty and Gruzleski Found that an Al-Ti-Si phase forms on TiB2 when titanium is in excess. This Al-Ti-Si phase subsequently nucleates primary aluminum by means of the peritectic reaction.

In early experiments, AIB2 was believed to nucleate pure aluminum, based on X-ray diffraction results of centrifuged samples. Also, Sigworth reported superior grain refinement obtained by the addition of boron alone (as A1-4% B master alloy) over the conventional Al-Ti and Al-Ti-B additions (Figure 6). It has been proposed that the effect of boron alone in the grain refinement of pure aluminum is virtually nil, but for Al-Si alloys, it becornes very significant due to the eutectic reaction at 0.02 wt. % B. If a eutectic reaction does take place at this temperature, no nucleus of α (Al)) is formed above the freezing temperature of pure aluminum (660 °C) since some undercooling will be necessary for reaction itself. For Al-Si alloys, the eutectic reaction takes place well above the liquidus temperature (615°C for 356 alloy), ensuring the presence of solid heterogeneous sites for nucleation.

Tondel, present an alternative method of introducing boron into Al-Si alloys by a B-Si master alloy. They claim that this type of alloy contains boron in solution within the silicon and when in the melt, boron is homogeneously distributed as a solute and not as a compound, avoiding the problems generated due to settling, floating or agglomeration of particles. Their study also supports the eutectic theory for the nucleation of aluminum with boron in Al-Si alloys.

Boron containing master alloys produces good refinement in Al-Si alloys and the presence of AIB2, rather than AIB12 ensures a degree of grain refinement similar or superior to the titanium containing master alloys.

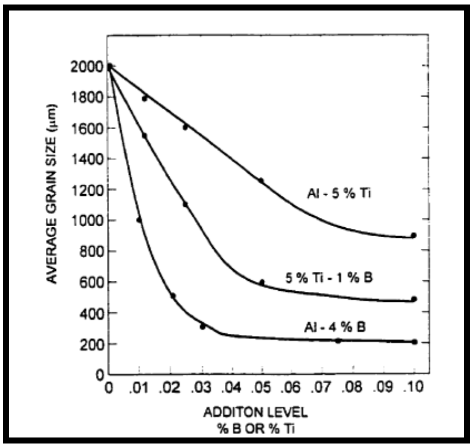


Figure 6 Grain refining of 356 AI-Si alloy with Al-Ti, Al-Ti-B and AI-B

2.6 Effect of growth restriction on grain refinement.

In the study of the grain refining mechanisms of aluminum and its alloys, there has been a considerable concentration of effort towards the heterogeneous nucleation of primary crystals of aluminum, while only a few authors have referred to the influence of the other elements present in the alloy, According to Jones and Pearson. The effect of Zn, Mg and Si in aluminum alloys is to restrict grain growth by constitutional undercooling. Backerud and coauthors have established that there is a growth restriction factor that at least for low concentrations of alloying elements seems to be additive. With the increase in solute build-up in front of the solidifying interface, the added constitutional undercooling causes the dendrite tips to become finer and to branch side-wise. As a consequence, growth rate increases, and coarser grains result.

Stlohn have shown the presence of two nucleation mechanisms in Al-Si alloys, One involves nucleation at the mold wall with crystals transported through the melt by turbulence and convection, while the other implies the activation of substrates in the melt by constitutional undercooling. Successive additions of silicon or titanium to pure aluminum decrease the grain size by constitutional undercooling in the melt and growth restriction at the solid/liquid interface. The rate of nucleation is then enhanced by the presence of potent nucleants. In the Al-Si system, a critical degree of constitutional undercooling is reached, leading to a minimum in grain size (Figure 7), followed by an increase associated with a change in the growth mode of the interface, as reported by Backerud.

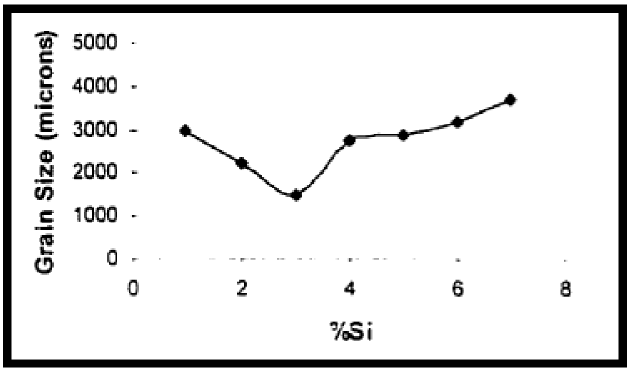
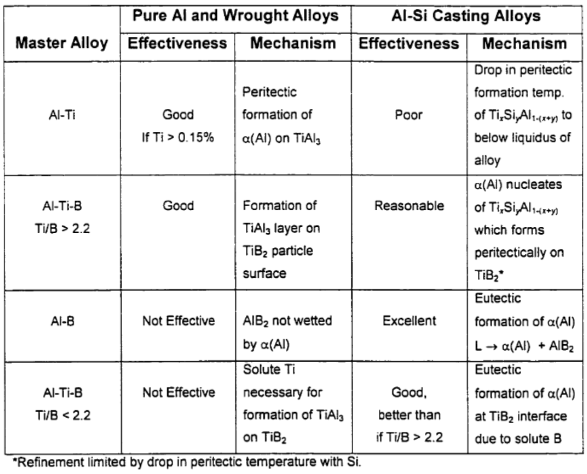


Figure 6 Effect of silicon addition on grain refinement of Aluminum.

III. CONCLUSION

To conclude this review, Table is presented to provide a summary of the mechanisms of grain refinement in aluminum with the main observations for each of the different master alloys.



Master Alloy	Pure Al and Wrought Alloys		Al-Si Casting Alloys	
	Effectiveness	Mechanism	Effectiveness	Mechanism
Al-Ti	Good If Ti > 0.15%	Peritectic formation of α(Al) on $TiAl_3$	Poor	Drop in peritectic formation temp. of $Ti_xSi_yAl_{1-(x+y)}$ to below liquidus of alloy
Al-Ti-B Ti/B > 2.2	Good	Formation of $TiAl_3$ layer on TiB_2 particle surface	Reasonable	α(Al) nucleates of $Ti_xSi_yAl_{1-(x+y)}$ which forms peritectically on TiB_2*
Al-B	Not Effective	AlB_2 not wetted by α(Al)	Excellent	Eutectic formation of α(Al) $L \rightarrow \alpha(Al) + AlB_2$
Al-Ti-B Ti/B < 2.2	Not Effective	Solute Ti necessary for formation of $TiAl_3$ on TiB_2	Good, better than if Ti/B > 2.2	Eutectic formation of α(Al) at TiB_2 interface due to solute B

*Refinement limited by drop in peritectic temperature with Si.

Table 1 Sumary of grain refinement mechanism in aluminum

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