Review of Grain Refinement Performance of Aluminium Cast Alloys

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Abstract: Improving the utilization of aluminum grain refinement in industrial settings is a continual point of focus for research. Grain refinement serves the dual purpose of not only achieving a fine grain size, but also enhancing the mechanical properties of materials. Numerous researchers have dedicated significant efforts over the last decades to explore the grain refinement of aluminium alloys. There has been a numerous research conducted regarding the mechanisms that explain the observed phenomena associated with grain refinement. The most employed are grain refiners based on Al–Ti–B system. However, the limited efficiency of these grain refiners on aluminium silicon alloys with excessive Si and the effect of alloying elements have been noticed. The review examines the impact of the factors influencing grain refining behaviour of master alloys, including the effects of poisoning elements such as Si, Mg, Zr, and Sr. A large grain refiners used for enhancing the properties of aluminium silicon alloys are reviewed. An overview of the new refiners has been given. Also, procedures for the assessment of grain refinement have been examined.

Keywords: Grain refinement, aluminium alloys, casting, solidification, trace elements.

1. Introduction

Aluminium silicon alloys are one of the most aluminium foundry alloys widely used for their light weight, excellent castability, high specific strength and resistance to corrosive attack [1-3]. Typically, in the as-cast Al-Si alloys, the microstructure consists of coarse and flake–like brittle eutectic Silicon and coarse columnar primary α–Al. This structure will significantly deteriorate the mechanical characteristics of Al–Si cast alloys. In the last decades, significant efforts have been undertaken to modify plate–like eutectic Silicon into fibrous structure by adding modifiers and refine grain size by grain refiners' addition [4, 5]. This addition to molten aluminium in small quantities, without affecting the chemical composition of the alloy, will cause a different solidification mode and therefore will improve the mechanical properties [6]. Grain refinement plays a crucial role in the casting of aluminum alloy as it effectively reduces casting defects and enhances the properties of the casting. Nowadays, adding a grain refiner to aluminium alloy is a widespread technique employed in industry to obtain grain refinement in the casting process of aluminium alloy [7].

Grain size in aluminum alloys is controlled by the solidification process, which includes the nucleation and growth of α–Al. During the nucleation phase, numerous sites of heterogeneous nucleation where α–Al can nucleate are introduced into the molten aluminium alloy by using a grain refiner. As the α–Al grains grow, solution elements can aggregate between the grains, thereby restricting the grain growth. Consequently, the grain size becomes smaller due to two factors. The first factor is the heterogeneous nucleation enhanced by high nucleation rate while the second one is the restriction of grain growth caused by constitutional undercooling.

2.   Nucleant additions using master alloys

2.1. Role of Titanuim and Boron in grain refining of Al alloys

Grain refiner based on master alloys of Al–Ti–B is generally used in foundries. Many researchers have established the mechanism of grain refinement [8]. It is agreed that the addition of master alloys leads to the dissolution of the aluminum matrix, resulting in the release of various intermetallic particles (TiB_2, $TiAl_3$, $(Al, Ti)B_2$, or AlB_2) into the molten alloy. These particles then serve as nucleants [9]. The relative amount of these phases in the grain refiner differs as its chemical composition is altered. Therefore, the grain refiner's composition, specifically its Ti:B ratio, plays a crucial role in the process of grain refinement by inoculation. Al–Ti–B refiners that have an excess of Titanium are typically effective for enhancing the properties of wrought aluminium alloys, except when the alloy being treated contains one or more elements that have borides which are more stable than TiB_2. Although there are various Al–Ti–B alloys that have an excess of boron, as well as binary Al–B alloys available for use in foundry alloys, these alloys depend on insoluble particles of $(Al,Ti)B_2$ or AlB_2 for refining the grain, and hence do not benefit from the growth inhibition provided by titanium solutes [10].

The most used compositions for the available master alloys added to hypoeutectic Al-Si foundry alloys are derived from the Al-Ti-B system. These alloys, namely Al-5Ti-1B, Al-3Ti-1B, Al-3Ti-3B, and Al-5Ti-0.2B, belong to different classes and are known for their high refining potency [11, 12].

Extensive research has been conducted to determine the impact of different factors, including the amount of titanium (Ti), the ratio of titanium to boron (Ti:B), the contact time, and the temperature, on the effectiveness of grain refinement in aluminum alloys. In addidtion, the refiner particle characteristics such as density, size, agglomeration behaviour, poisoning mechanisms and fade characteristics are important parameters to select the refiners [10-13]. These characteristics are highly noted in the reviews of G.P. Jones et al. [11] and Murty et al. [14].

An important feature of grain refiner that impacts its quality is fading. This latter refers to the decrease of effectiveness of grain refiners over time with prolonged contact with the melted alloy.

Table 1. *An overview of various chemistries and types of refining particles.*

Refiner	%Ti	%B	%C	Borides	Aluminides
Al5TiB	5.0	1.0	0	TiB_2	$TiAl_3$
Al3TiB	3.0	1.0	0	TiB_2	$TiAl_3$
Al5Ti0.2B	5.0	0.2	0	TiB_2	$TiAl_3$
Al3Ti0.2B	3.0	0.2	0	TiB_2	$TiAl_3$
Al3Ti0.15C	3.0	0	0.15	TiC	$TiAl_3$

C. Limmaneevichitr et al. [15] found that the agglomerations, the settlements and varying density of both $TiAl_3$ and TiB_2 particles are the primary factors influencing the fading mechanism. Vinud Kumar et al. [16] showed that at different reaction temperatures for 60

minutes, TiAl$_3$ particles with varying sizes and distributions are generated in Al–5Ti master alloys. As the reaction temperature rises from 750°C to 850°C, the size of TiAl$_3$ particles increases and the size distribution becomes wider. However, even at shorter holding time the particles produced at 850°C show significant settling tendency.

P.L. Schaffer et al. [17] reported the settling behaviour of three different Al–Ti–B master alloys, namely Al–1.2Ti–0.5B, Al–1.6Ti–1.4B and Al–5Ti–1B, containing particles of different size distribution and composition for grain refinement of aluminium alloys. It was found that the particles settled rapidly, and agglomeration of the refining particles also had a significant impact on the settling rate. S.A. Kori et al. [12] studied a ternary Al–Ti–B master alloys with different Ti–B ratios of 1:3, 3:1, 3:3, 1:5 and 5:1. The researchers confirmed that high boron containing master alloys are more effective at refining of the grain of Al7Si alloy when compared to traditional grain refiners such as Al–5Ti–lB master alloys. For more than six decades, researchers have conducted thorough investigations in order to comprehend the mechanism of grain refinement through the utilization of grain refiners based on Al-Ti-B. Numerous review papers have focused on the investigation of the grain refinement mechanism [18-20], but a definite understanding of the grain refinement mechanism resulting from the use of Al–Ti–B based grain refiners has not been reached yet.

The most agreed mechanism of α–Al grain refinement through the addition of Al5Ti1B confirmed that the refinement of α–Al grains through a process whereby an atomic layer of TiAl$_3$ on TiB$_2$ substrates initiates the formation of α–Al grains, and the accumulation of Ti at the interface between solid and liquid phases inhibits the growth of the α–Al phase [19]. Respectively, T. Wang et al. [21] produced Al–3Ti–3B grain refiner by combining separately synthesized Al–Ti and Al–B master alloys, in which TiB$_2$, TiAl$_3$ and AlB$_{12}$ particles were dispersed. They noticed a superior grain refining performance with respect to the Al–3B master alloys. They concluded that AlB$_{12}$ played an important role in improving performances of grain refinement.

2.2. Role of Silicon content in grain refining of Al–Si alloys

The effect of Silicon content on the grain refinement of hypoeutectic Al–Si alloys was subject of many investigations. Typically, Ti is added to foundry alloys to regulate the size of the cast grains. However, recent research has demonstrated that the positive impact of Ti on grain refinement is significantly hindered when the Si content exceeds 5 wt% [22]. Although solute Ti has been identified as the most potent growth inhibitor for aluminum [23], it becomes ineffective when it reacts with Si to form Ti–Si compounds and then precipitates out of the melt. Unfortunately, most foundry alloys contain a higher Si content and must bear the consequences. Even the addition of soluble TiAl$_3$ and insoluble TiB$_2$ particles to the melt through the use of AlTi5B grain refiners does not provide noticeable improvement. Additionally, Si coats the surfaces of TiB$_2$ particles with Ti–Si compounds, which leads them to be poisoned.

It is well known that TiAl$_3$ particles dissolve quickly in the melt. In aluminium silicon foundry alloys, it is reported that the TiB$_2$ particles are rendered less potent because of the presence of a high concentration of silicon in the melts, TiSi compounds are created on the surface of TiB$_2$ particles. To eliminate TiAl$_3$ particles in master alloys, a new form of grain refining master alloy was experimented by L. Lu et al. [24]. The composition of the alloy consists of a combination of titanium (Ti) and boron (B) in a weight ratio that is slightly less than or near 2.2. This ratio is comparable to the stoichiometric value required to form titanium diboride (TiB$_2$). Examples of such alloys include Al1.5Ti1.5B and Al1.2Ti0.5B. By reacting with Ti in the molten metal, the extra B in the master alloy forms TiB$_2$ and creates more potential nucleant particles.

Moreover, Yucel Birol [25] suggested that when there is insufficient Titanium (Ti) present in the molten alloy, it enables the complete formation of TiB_2 particles. These particles serve as ideal substrates shortly before the crystallization of α–Al begins. He studied the solidification of the AlSi10Mg and AlSi12Cu alloys without Ti, when treated with the AlB_3 master alloy. Adding 200 ppm B into the Ti–free melt offers an impressive efficiency in refining its grains, resulting in uniformly fine and nearly spherical grains and offers the added benefit of a long–lasting grain refinement effect. Based on that, it can be inferred that to achieve exceptional grain refinement with just 200 ppm B, it is necessary to manufacture foundry alloy ingots without Ti. The utilization of Al–B binary grain refiners can bypass the insufficient grain refinement observed in foundry alloys during casting, as an alternative to Al–Ti–B ternary grain refiners.

In addition, Z. Chen et al. [26] studied how high Si concentrations impacts the grain refinement effectiveness of AlB_2. According to their findings, the addition of AlB_2 in the absence of Si does not significantly refine the grain. The presence of high concentrations of Si leads to an enhanced efficiency in grain refinement. This is because a layer of SiB_6 forms at the interface between AlB_2 and Al, reducing the crystallographic mismatch. As a result, the nucleating power of AlB_2 is significantly increased. However, it is important to note that the SiB_6 layer is transient and may exist for a short time in the Al-Si melt before transforming into another stable phase (such as Si).

2.3. Role of Carbon as inoculant in grain refining of Al alloys

Numerous issues have been identified in usage of Al–Ti–B master alloys, resulting in the creation of Al–Ti–C master alloys. Gezer et al. [27] studied the effect of different Ti:C ratios on microstructure of AA 1080 alloys. They stated that Al–3Ti–0.60C and Al–3Ti–0.75C compositions are determined as the most effective grain refiners. And $TiAl_3$ and TiC compounds were detected as effective acting phases in grain refinement process. Typically, numerous factors, including the size, morphology, distribution and the quantity of nucleant particles, impact both the effectiveness and stability of master alloys in refining grains.

Tao Wang et al. [28] examined the impact of carbon source on the microstructure of an Al-Ti-C master alloy and its effectiveness in grain refining. They reported that Al–5Ti–0.3C master alloy with a uniform microstructure prepared by using Al–5C alloy as a carbon source compared with commercial Al–5Ti–0.3C master alloy exhibits high grain refining potency on pure aluminium. Additionally, the effective refinement efficiency does not clearly fade within 30 min.

Moreover, W. Schneider et al. [29] discussed the mechanisms of grain refinement with the observed differences in the behavior with AlTiC and AlTiB. They investigated the potency of AlTiC master alloys as an alternative to AlTiB grain refiners. They demonstrated that when specific casting conditions are met, AlTiC proves to be a more efficient grain refiner compared to AlTiB. It is less susceptible to agglomeration and exhibits greater resistance to poisoning by Zr and Cr.

The combined grain refining effect of TiC and TiB_2 particles is suggested to improve the refining performance. The introduction of a novel Al–Ti–C–B master alloy is expected to significantly enhance the refinement if TiC and TiB_2 particles work together properly in the melt. According to J. Nie et al. [30] adding 0.2 wt.% of the prepared Al–5Ti–0.3C–0.2B alloy can decrease the average grain size of α–Al from 3500 to 170 μm. The refining efficiency remains stable for up to 60 minutes. The excellent grain refining performance is attributed to the TiC_xB_y and TiB_2-mC_n particles, which serve as reliable and stable nucleating substrates for α–Al when it solidifies at center of the grain.

2.4. Effect of alloying elements on Al alloys grain refining efficiency

L. Zhou et al. [31] have stated that in pure aluminum alloys, the presence of solutes is necessary for TiB_2 particles to effectively promote an equiaxed grain refinement while the presence of impurities which provides a growth restricting factor in the inoculated commercial Al melt plays a significant role in restricting the grain growth. These findings demonstrated that the presence of impurities in commercially available aluminum plays a crucial part in enhancing the refining the grain structures. On the other hand according to the literature, the alloying elements can affect the efficiency of grain refinement of aluminum alloy. This phenomenon is referred to as the poisoning effect. The presence of Cr, Zr, and Li elements in the alloy resulted in a reduction of the grain refinement effects of Al–Ti–B, indicating the occurrence of poisoning [32]. G. Mao et al. [33] reported that adding Sc or Zr in Al–Si–Mg alloy with Ti–B leads to the apparition of several intermetallic compounds containing Sc and Ti or Zr and Ti. The concentration of Ti as nucleation centers in the molten metal is reduced, leading to poisoning during the nucleation phase of grains.

Besides, W. Liu et al. [34] evaluated the synergistic effects of alternate less expensive RE element Gd and Zr on the grain refinement of A356 cast Al–Si alloy. The combined addition of Gd and Zr clearly improved the mechanical properties of A356 cast alloy as a result of refining the grain structure and modifying the eutectic silicon.

2.5. Role of Strontium and Al–Ti–B grain refiners on Al alloys

Many researchers reported that grain refinement can not only refine the grain size but also can achieve partial modified microstructure from coarse silicon particles to broken up into smaller pieces. According to a study conducted by S.G. Shabestari et al. [35], there are two reasons for that change of silicon morphology. Firstly, the presence of additional $TiAl_3$ or TiB_2 particles within grain boundaries serves as sites for the formation of eutectic silicon, resulting in a modified silicon structure. Secondly, grain refiners indirectly impact the morphology of the eutectic. They reduce the volume of molten material between dendrites and restrict the areas where silicon nucleates. As a result, the silicon particles undergo fragmentation during the eutectic transformation.

In fact, many scholars tried to clarify the effect of combined addition of silicon modifier and grain refiners [36]. A.M. Samuel et al. [37], for example, investigated the impact behaviour of the Sr–modified A356.2 alloy in conjunction with five different grain refiners/aluminum master alloys, namely, Al–10Ti, Al–5Ti–1B, Al–2.5Ti–2.5B, Al–1.7Ti–1.4B and Al–4B. They found that when the grain refiner master alloy is added in smaller amounts, the eutectic Si particles remain mostly the same. This is likely due to the low amount of B (<0.1%) in each addition of the master alloy. However, if the Boron content increases beyond 0.1%, there will be changes in the length and area of the Si particles, indicating that the interaction between Sr and B becomes stronger and leads to the demodification of Si particles.

On the other hand, J. Lee et al. [38] investigated the simultaneous addition of a Sr modifier and an Al–Ti–B grain refiner to an Al–7Si–0.35Mg cast alloy as well as the interaction between Al–5Ti–1B and Sr. However, they found that by adding both 100 ppm Sr and 500 ppm Ti, the α–Al grain was refined and the eutectic Si was modified. The frequency at which Al–Si eutectic grains nucleate was increased compared to an alloy with only Sr addition. Analysis using TEM showed that Al_2Si_2Sr phases were present along with either TiB_2 or AlP and TiB_2 coupling particles. This indicates that preexisting TiB_2 particles in the melt produce a significant amount of AlP, which is a highly effective nucleating agent for Si. This encourages the nucleation of eutectic Al–Si grains during solidification, despite the depletion of AlP used in the Al_2Si_2Sr formation.

L. Lu et al. [24] stated that the interactions between Sr and Al1.5Ti1.5B on the Al–10Si–0.35Mg alloy become more noticeable as the amount of grain refiner added increases. These interactions have a greater effect on the eutectic than on the primary Al solidification. It involves the reaction between AlB_2 and Sr leading to the creation and settling of SrB_6 particles. As a result, the quantity of solute Sr in the molten alloy available for modification of eutectic Si decreases. Even after losing its modification, the combination of Sr and Al1.5Ti1.5B still demonstrates effective grain refining in the treated melt.

2.6. Role of Nb, Zr, Mg as grain refiners in Al alloys

In fact, previous research indicated that the Al–5Ti–B alloy is not very effective in refining Al–Si alloys with excessive Si. Thus, J.Xu et al. [39] investigated the nucleation and the growth of α–Al dendrites in Al–8Si–7Cu melts that were inoculated with Al–5Ti–1B and Al–1.67Ti–3.33Nb–0.5B. This study also focused on the evolution of grain number density and dendrite growth rate of α–Al, which led to an understanding of the significant difference in nucleation efficiency between $(Ti,Nb)B_2$ and NbB_2 in the Al–Si melt. The results revealed that the Al-1.67Ti-3.33Nb-0.5B alloy was more effective in refining the grain structure due to the presence of an ample amount of $(Ti,Nb)B_2$ particles. These particles exhibited strong potential for both epitaxial nucleation and unrestricted growth. Additionally, the Al-Nb-B alloy displayed remarkable resistance to Si-poisoning, which could be attributed to the high stability of $NbAl_3$ and the formation of $(Al,Nb)B_2$ on NbB_2 [40].

The work of M. Nowak et al. [41] demonstrates that the addition of Al–xNb–yB master alloys to aluminium and its alloys introduces effective Nb–B inoculants that facilate the enhancement of the grain structure by means of heterogeneous nucleation. It is found that the inoculation with Nb–based compounds (i.e. NbB_2 and Al_3Nb) leads to the grain refinement of near eutectic and hypereutectic Al–Si alloys [42].

F.Wang et al. [43] explored the detailed mechanism of the grain refinement of cast aluminium by zirconium. Due to the limited growth restriction effect of Zr in Al, it is proposed that the notable reduction in grain size of Al caused by Zr addition can be primarily attributed to the promotion of heterogeneous nucleation by the Al_3Zr particles formed in situ. In addition, D. Qiu et al. [44] studied the co–poisoning effect of Zr and Ti that occurs when a certain amount of Fe impurity is present in commercial grade aluminum alloys. The findings indicated that $TiAl_3$ is susceptible to poisoning because of the formation of a coating composed of Al_8Fe_4Zr on its surface. This is due to the fact that the Al_8Fe_4Zr phase has a strong crystallographic atom matching with $TiAl_3$, but not with the aluminum matrix. Also, the partial dissolution of Al_3Zr nucleant particles aggravates the poisoning effect.

Y. Zhang et al. [45] explored the grain refinement of cast Al–Si alloys through the application of an in situ integrated Al2.2Ti1B–Mg master alloy. The grain refinement performance of synthesized Al2.2Ti1B–Mg refiner was more effective than that of Al5Ti1B and Al3Ti3B refiners. The study revealed that the $MgAl_2O_4$ existed at the TiB_2 /Al interface. The TiB_2 is supposed to be the substrate to grow $MgAl_2O_4$ and the $MgAl_2O_4$ is for growth of aluminium phase. In another case, the TiB_2 is supposed to be the substrate of $MgAl_2O_4$ and the $MgAl_2O_4$ to be the substrate of $TiAl_3$ and the $TiAl_3$ to be the substrate of α–Al.

2.7. Role of rare earths in grain refining of Al alloys

Recently, to address the limitations of the Al–Ti–B grain refiner and enhance its performance, rare earth elements have been introduced. A significant interest in the impact of rare earth elements on the microstructures and properties of aluminum and its alloys is noticed [46]. Although extensive research has been conducted to understand the mechanism of grain refining and the effect of various parameters such as Ti content, Ti:B ratio, contact time, and

temperature on the refining efficiency, there is a lack of studies on the influence of Rare Earth content. Studies on the influence of Rare Earth content are profoundly lacking. Up to recently a new generation of master alloys based on RE have been developed. X. Wang et al. [47] investigated the effectiveness of Al–5Ti–1B–RE grain refiners for refining A357 alloy and analyzed the impact of different levels of grain refiner in detail. Rare earths (REs) used are Ce, La. Upon adding the Al–5Ti–lB–3.0RE grain refiner to the A357 alloy, the resulting reaction between $TiAl_3$ and RE produced multiple highly effective, smaller heterogeneous nuclei in the form of $Ti_2Al_{20}RE$ phase. This reaction occurred through the precipitation and interaction of RE with elements at the grain boundary, thus promoting the nucleation of α–Al grains. The presence of $Ti_2Al_{20}RE$ phase is advantageous as it has more crystal faces that match with Al, leading aluminum alloy to be more refined. It is noteworthy that the grain refinement efficiency achieved by introducing Ti, B, and rare earth elements is significantly superior to that of adding Ti and B alone. In general, the Ce and La elements have minimal solubility in the α–Al or eutectic silicon phases due to their large atomic radius compared to α–Al and silicon. W. Jiang et al. [48] confirmed the above finding of Wang et al. [47] the addition of 0.2% of RE, containing Ce and La elements, clearly reduced the sizes of the α–Al primary phase, eutectic silicon particles and SDAS value. Furthermore, it enhanced the overall morphology of the eutectic silicon particles. As result, the mechanical properties of A357 alloy are greatly improved.

H–L. Zhao et al. [49] analyzed the effect of Al–5Ti–0.25C–2RE master alloy on commercial A356 alloy. According to their observations, adding 3.0 wt% of Al–5Ti–0.25C–2RE to A356 can result in a better grain refining effect. This is because the master alloy introduces a greater amount of free Ti to the melt. In addition, $Ti_2Al_{20}Ce$ releases Ti and Al_4Ce to the melt, which serves as an effective nucleation phase for α–Al. Al_4Ce is also an effective nucleation phase for α–Al.

In the study of Q. Hongxu et al. [50], the impact of rare earth element Samarium addition on the microstructure of Al–7Si–0.7Mg alloys was investigated. It was found that the addition of 0.6% of Sm to the melt caused a significant decrease in the secondary dendrite arm spacing of the alloys. Also, it was observed to modify the eutectic silicon from a coarse plate–like morphology to a fine fibrous one.

Moreover, Yu Chen et al. [51] created a new type of grain refiner that includes both B and La elements to tackle the issue of refining B elements and preventing mutual poisoning between Sr and B elements. Their research displays the effectiveness of this new grain refiner in refining α–Al grains in Al–Si alloys with varying levels of Si content. They proposed that LaB_6 particles are effective heterogeneous nuclei for α–Al grains due to their crystallographic similarity and can effectively refine the grains. The addition of the La element helps prevent the negative interaction between Sr and B elements, which enhances the development of a completely modified eutectic silicon structure in the Al-Si alloys.

3. Mechanisms of grain refinement

In the casting process, grain refinement by adding master alloy containing inoculants particles into Al–Si alloys based on Titanium, Boron and Carbon have been standard practice in foundries. The formation of fine equiaxed structure morphology is the result of restraining the growth of columnar grains and by fractions of impurity particles acting as heterogeneous nucleation sites for α–Al dendrites [13].

Several theories, including the carbide–boride theory, peritectic theory, duplex nucleation mechanism, and peritectic hulk theory, have been proposed to explain the process of grain refinement achieved by using grain refiners. Figure 1 shows an illustration of the process of nucleation in various theories.
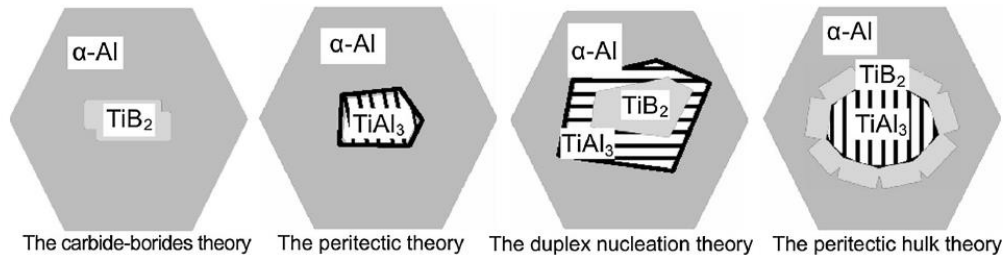
Figure. 1. *Illustration of the process of nucleation in various theories [52].*

Cibula was the first to suggest the carbide boride particle theory [53]. Noting that the heterogeneous nucleation of α–Al occurs on borides or carbides in solidification process of aluminum alloy. Borides are typically added through a master alloy, while carbides are created by reacting residual carbon with added titanium to form TiC. These particles (carbide particles, boride particles…) possessed qualities of being in small size and having a high melting point. They played a role as sites of nucleation for the formation of α–Al.

The theory of peritectic suggests that the process of refining grain by the refiner results from a peritectic reaction. The Al–Ti master alloy contains large $TiAl_3$ plates in an aluminium. In their research, Crossley et al. [54] put forward the idea of a binary peritectic reaction that is initiated by $TiAl_3$ as shown in figure 2.
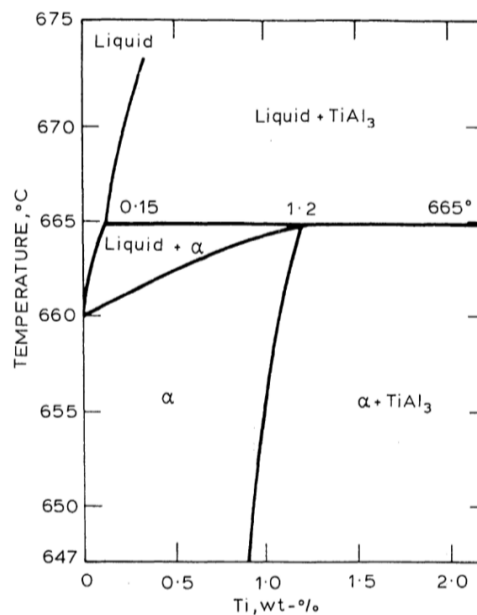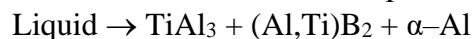
$$Liquid + TiAl_3 \rightarrow \alpha–Al$$

Figure. 2. *Al–Ti end of the binary equilibrium Diagram [18].*

Guzowski et al. [55] proposed a ternary peritectic reaction involving the addition of master alloy of Al–Ti–B.

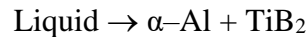$$Liquid + TiAl_3 + TiB_2 \rightarrow TiB_2 + \alpha–Al$$

However, Antonio et al. [56] suggested a ternary peritectic reaction for master alloy of Al–Ti–B at approximately 0.05 % Ti, 0.01 % B, and a temperature of 659.5 °C

$$Liquid \rightarrow TiAl_3 + (Al,Ti)B_2 + \alpha–Al$$

It is reported by Geoffrey [9] that the $(Al,Ti)B_2$ phase is not metastable, but will form at high B to Ti ratios.

The addition of an Al-B master alloy to the aluminum alloy melt was proposed by Murty et al. [14] to induce a binary eutectic reaction.

$$Liquid \rightarrow \alpha–Al + TiB_2$$

The exact mechanism of duplex nucleation in grain refinement is not fully understood. Yet, as stated by Mohanty and Gruzleski [18], it is believed that nucleation involved two distinct stages. Firstly, $TiAl_3$ particles would accumulate on the surface of TiB_2, and subsequently, α–Al nucleation would occur at the location where $TiAl_3$ and TiB_2 are present. This theory could only apply to hyperperitectic concentrations, as the rapid dissolution of aluminides is well established at hypoperitectic concentrations, as previously explained. $TiAl_3$ particles are not present as nucleation sites except at very short holding times.

The peritectic hulk theory accepts that $TiAl_3$ is a more powerful nucleant than TiB_2. L.Backerud and S.Yidong [57] suggested that the aluminide was encased by a hulk made of TiB_2. As a result, the dissolution rate of $TiAl_3$ was decreased by the hulk as diffusion must pass through the protective boride shell. After dissolving, the aluminide forms a liquid cell within the boride shell that has roughly the peritectic composition. As a result of the peritectic reaction, α–Al is formed and subsequent growth proceeds from there.

Additionally, a very small addition of Al–Ti–B master alloys makes the grain size refinement of aluminium. The hypernucluation theory was formulated by Jones [58] who explains hypernucleation through the segregation of solutes towards the interfaces of the substrate/ melt.

The Ti will segregate to the interface of TiB_2 and melt if the amount of dissolved Ti exceeds a certain level. This movement can result in the creation of a stabilized layer of atoms on the surface of TiB_2. This layer will continue to remain stable even at temperatures higher than the melting point of pure Al.

4. Evaluation of grain refining performance

A Both producers and consumers of master alloys have implemented assessment methods to guarantee the reliability of their product. The aim is to create an evaluation technique that can predict, with accuracy, the refining effectiveness of master alloys in certain casting situations, thereby enabling the determination of optimal addition levels. Regrettably, no straightforward, robust, and consistently replicable test has been formulated to achieve this level of accuracy.

Grain sizes can be measured on the ground and polished section taken from the cast using a linear intercept method. Metallographic analysis is a time consuming causing expensive activity in the foundry. Alternatively, chemical and thermal analysis of the melt are the indirect measurement used foundry techniques. Chemical analysis is an appealing technique for determining the quantity of grain refiner in the melt. However, the size of the grain is influenced not only by the chemical analysis but also by the cooling rate. The thermal analysis methods have been created in the shaped casting sector to predict the performance of the grain refiners in employed foundry alloys.

The thermal Analysis (TA) refers to the process of observing and understanding how the temperature of a material changes over time when it is heated or cooled. In the context of metal casting, TA involves recording and analyzing the cooling curve of a metal as it solidifies in a mold (CCA). This technique is based on the idea that the various events that take place during solidification are reflected in the shape of the cooling curve [59-63].

Thermal analysis curves can be used to forecast the ability of nucleation potential in relation to different proposed parameters. Several scholars have demonstrated a correlation between the shape of the trace below the alloy's liquidus temperature during the recalescence phase and the grain size in the sample. As a result, this shape can serve as a quantitative indicator of the effectiveness of the grain refiner. In fact, references [35] and [64] provide a

thorough explanation of thermal analysis technique that can be used as a quality control instrument in foundries worldwide. Solidification parameters are shown in Figures 3 and 4 and Table 2.

It is well known that the formation of grains in a casting is linked to the quantity of nucleation sites found within the melt when it reaches the liquidus temperature. A high number of nucleation sites means that numerous grains can be formed with minimal undercooling, leading to a fine grain structure. On the other hand, if only a few favorable sites are present at the liquidus temperature, substantial undercooling may occur.
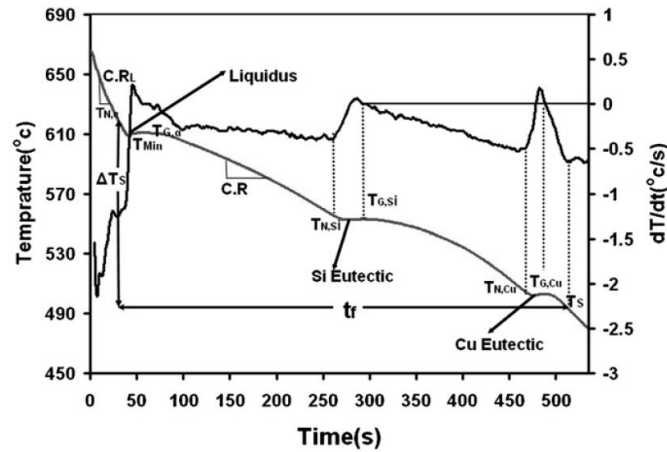

Figure. 3. *Representation of solidification characteristic parameters on a cooling curve of 319 alloy and its corresponding first derivative [35].*
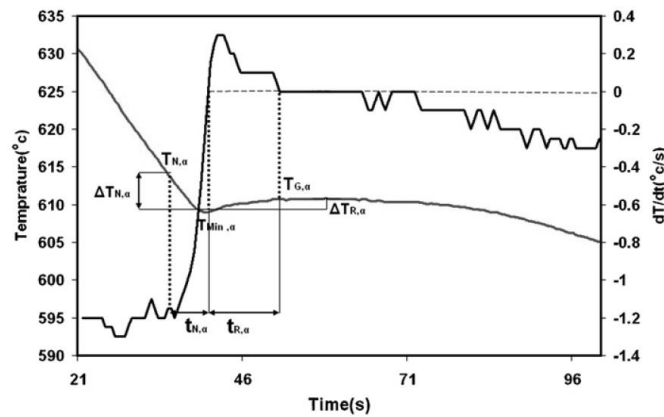

Figure. 4. *Representation of solidification characteristic parameters on a cooling curve of 319 alloy and its corresponding first derivative at the beginning of solidification (liquidus region) [35].*

Table 2. *The parameters that illustrate the characteristics of solidification observed in Figures 3 and 4 [35].*

Characteristic symbol	Characteristic description
$T_{N,\alpha}$	Nucleation temperature of α–Al dendrite (liquidus)
T_S	Temperature of solidus
ΔT_S	Solidification range ($\Delta T_S = T_{N,\alpha} - T_S$)
t_f	Total time of solidification
CR_L	Cooling rate in liquidus region
CR	Cooling rate in mushy zone
$T_{Min,\alpha}$	Minimum temperature of α–Al dendrite
$\Delta T_{N,\alpha}$	Nucleation undercooling temperature ($\Delta T_{N,\alpha} = T_{N,\alpha} - T_{Min,\alpha}$)
$t_{N,\alpha}$	Nucleation undercooling time
$T_{G,\alpha}$	Growth temperature of dendrite
$\Delta T_{R,\alpha}$	Temperature of Recalescence undercooling ($\Delta T_{R,\alpha} = T_{G,\alpha} - T_{Min,\alpha}$)
$t_{R,\alpha}$	Time of recalescence undercooling
$T_{N,Si}$	Nucleation temperature of Si eutectic
$T_{G,Si}$	Growth temperature of Si eutectic
$T_{N,Cu}$	Nucleation temperature of Cu–rich eutectic
$T_{G,Cu}$	Growth temperature of Cu–rich eutectic

To initiate reactions and progress in their evolution, a driving force is required. In the case of aluminum dendrite nucleation, this force is provided by lowering the temperature below the liquidus temperature, known as undercooling $\Delta T_{N,\alpha}$. When the melt is not supplemented with a grain refiner, a significant gap exists between the liquidus temperature $T_{N,\alpha}$ and the minimum temperature $T_{min,\alpha}$. This gap implies that there is an obstacle to nucleation, resulting in coarser grains in the cast. However, the addition of higher levels of nucleants to the melt can reduce the nucleation barrier, allowing for dendrite nucleation with less driving force. As a result, the undercooling temperature decreases considerably, leading to the formation of a fine grain structure.

It seems that several parameters associated with an undercooling and recalescence curve can be correlated with grain size. Obtaining thermal curves A356 alloy by using a cup moulds containing thermocouples, D.Casari et al. [65] assessed the efficiency of three Ti–B based grain refiners by thermal and microstructural analysis techniques. They report that a slight increase in liquidus temperature $T_{N,\alpha}$ is related to a decrease in grain size.

From observation on an Al–Si–Cu–Fe alloy, S. Farahany [64] concluded that $T_{N,\alpha}$ increased with increasing cooling rate but the growth temperature $T_{G,\alpha}$ decreased. The measured grain sizes was found to decrease as $T_{N,\alpha}$ increased. Maleken et al. [66] reports that by increasing master alloy content on 380.3 aluminum alloy, $T_{G,\alpha}$ and $\Delta T_{R,E}$ decreased and $T_{G,E}$ increased first and then decreased when the level of Al–10Sr–1Ti–2B is increased from 0 to 5 mass%.

5. Conclusion

In order to enhance and control the grain refiners effects on aluminium silicon alloys, it is crucial to understand the grain refinement mechanism in Al alloys. A single model that fully explains the phenomenon of grain refinement in various cast alloys has not yet been developed. Recently, hypernucleation hypothesis has been developed to explain some phenomena like the poisoning effect.

AlTi5B is the most grain refiner used in the foundry sector. Microscopic analysis indicated that the master alloy Al–Ti–B contains borides and aluminides AlB_2, TiB_2, and $(Al,Ti)B_2$, in addition to $TiAl_3$ could have significance in the refinement of grains. However, to improve the effectiveness of grain refiners and master alloys for both Al–free and Al–Si alloys, several parameters that affect the efficiency of grain refining have been proposed to be taken

into account. The performance of grain refiners is influenced by the composition of the Al-Si alloy. The effectiveness of grain refiners in aluminium is highly dependent on the type of alloying elements used. For example, the presence of small quantities of Nb, Mg or Zr, influences the performance of grain refiners. Furthermore, investigating the combined effects of modifier and grain refiner master alloys could have significant implications for the development of new materials and alloys, and could lead to improvements in the performance and reliability of a wide range of industrial applications. To assess the effectiveness of grain refinement, various techniques can be used, including microstructural analysis, chemical analysis, and thermal analysis.

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