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Control of Grain Refinement of Al-Si Alloys by Thermal Analysis

by

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A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment of the requirements of the degree of Doctor of Philosophy

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Abstract

Grain refinement of Al-Si casting alloys is commonly assessed by the presence of Ti and B in the melt, but in the last decade, thermal analysis has become an alternative control tool for the determination of the degree of refinement in the melt prior to casting. The objective of this work is to determine the best optimum method to predict the grain size in 319 and 356 Al-Si casting alloys by the use of the thermal analysis technique. Different time and temperature parameters from the cooling curve and its derivatives have been analyzed for a variety of grain refined samples. Four different master alloys (Al-6%Ti, Al-5%Ti-1%B, Al-2.5%Ti-2.5%B and Al-5%B) and two salt fluxes (AlTab-75%Ti and TiLite75BC-75%Ti-1.5%B) were used as grain refiners and samples were frozen at two different cooling rates (1.0 and 0.1 °C/s). The effect of type of refiner and cooling rate on the thermal analysis parameters has been analyzed.

A time parameter, t_1 , which is the duration of the recalescence period, and the maximum undercooling and recalescence temperatures, T_U and T_R respectively, yield the best correlation with grain size. These results are consistent irrespective of the type of grain refiner, for both 319 and 356 alloys, but only when the alloy solidifies at a cooling rate of 1.0 °C/s. Lower cooling rates produce scattering in the results.

Grain growth velocity, as calculated from the dendrite coherency point, correlates well with grain size for both alloys. A grain growth model is proposed to explain the effectiveness of these thermal parameters, where the duration of the recalescence period is related to a free growth period of the grains. Thermal analysis parameters related to the nucleation period seem to be sensitive to the type of grain refiner used and do not show good correlation with grain size.

Résumé

L'affinage des grains des alliages de fonderie d'Al-Si est habituellement évalué par la présence de Ti et de B dans la coulée. Lors de la dernière décennie, un nouvel outil de contrôle, l'analyse thermique, s'est imposé comme une alternative pour déterminer le degré d'affinage dans le bain avant de couler le métal. L'objectif de ce travail est de déterminer la meilleure méthode pour prédire la taille des grains dans les alliages de fonderie 356 et 319 en utilisant la technique de l'analyse thermique. Différents paramètres de temps et de température mesurés sur les courbes de refroidissement et leurs dérivatives ont été analysés pour une grande variété d'échantillons affinés. Quatre alliages mères différents (Al-6%Ti, Al-5%Ti-1%B, Al-2.5%Ti-2.5%B et Al-5%B) et deux sels sous forme de flux (AlTab-75%Ti et TiLite75BC-75%Ti-1.5%B) ont été utilisés comme affineurs de grains. Les échantillons ont été solidifiés à deux vitesses de refroidissement (1.0 et 0.1 °C/s). Les effets du type d'affineur et de la vitesse de refroidissement sur les paramètres thermiques ont été analysés.

Un paramètre de temps, t_l , qui correspond à la durée de la période de recalescence, et les températures maximales de surfusion et de recalescence, T_U et T_R respectivement, présentent les meilleures corrélations avec la taille des grains. Pour les deux alliages 356 et 319, ces résultats sont consistants indépendamment du type d'affineur de grains mais seulement lorsque l'alliage se solidifie à la vitesse de 1.0°C/s. Pour des vitesses de refroidissement plus basses, une dispersion dans les résultats est observée.

La vélocité de la croissance des grains, telle que calculée à partir du point de cohérence des dendrites, présente une bonne corrélation avec la taille des grains pour les deux alliages. Un modèle pour la croissance des grains, dans lequel la durée de la période de recalescence est liée à la période de croissance libre des grains, est proposé pour expliquer l'efficacité de ces paramètres thermiques. Les paramètres d'analyse thermique

reliés à la période de germination semblent être affectés par le type d'affineur utilisé et ne démontrent pas une bonne corrélation avec la taille des grains.

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Dedicated to you Papá,

You let me fly away when your wings were broken. You were always proud of me and you did not let your health cut my flight to new horizons. Wish you were here to see me fly... well, I bet you do, but from higher skies.

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Chapter 1 Introduction

The metal casting industry in the Western Hemisphere is expected to expand significantly in the following 10 years; and in particular, aluminum casting shipments are forecast to increase at an annual growth rate of 4%. In the present year (1999), the accelerated conversion of engine blocks and cylinder heads to aluminum will raise the shipments of sand and permanent mold castings. Automotive applications are the main reason for this growth, but aircraft and other sectors of the industry (photocopying, refrigeration and air conditioning) will also experience an average annual growth rate, estimated at 3%. Table 1.I shows the forecast for aluminum consumption in specific automotive parts.⁽¹⁾

Part	1998	2000	2006
Engine Block	25 %	35 %	55 %
Cylinder Head	72 %	90 %	94 %
Intake Manifold	70 %	60 %	40 %
Wheels	45 %	60 %	70 %
Transmission Case	92 %	95 %	95 %
Brakes,			
Suspension Parts	1 %	8 %	15 %

Table 1.I Percentage of light vehicles produced in the U.S.A.with various aluminum components.

In order to meet these growth expectations, aluminum casting producers rely on the technology that has been developing since about 1980 to manufacture quality aluminum alloys. Aluminum-silicon alloys comprise 90 % of the total cast aluminum production, due to their excellent castability and good corrosion resistance.⁽²⁾ Liquid metal treatment to control the melt chemistry, cleanliness and hydrogen content, as well as microstructural control, are critical in attaining optimum physical and mechanical properties in a casting.⁽³⁾ 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 α (Al) phase play a major role in the production of high quality aluminum castings.⁽²⁾

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 microstructural features leading to improved mechanical properties, and the reduction of macroporosity were the main reasons for the aluminum casting producers to adopt the technology of grain refinement.

Grain refinement in Al-Si casting alloys improves the mass feeding characteristics during solidification, resulting in reduced shrinkage porosity and the promotion of a smaller and improved porosity dispersion.^(3,4) 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.⁽³⁾ An incremental improvement in the ultimate tensile strength and the yield strength of A356 and Al-4%Mg-0.5%Mn cast alloys has been reported,^(5,6) whereas rigorous pressure-tests for leaks confirm the quality of grain-refined A356 aluminum alloy wheels.⁽⁷⁾ Porosity and cosmetics are also a major concern when wheels are polished and chrome-plated.⁽⁷⁾ Experimental results on fluidity show that a reduction in grain size increases the fluidity of the melt in spiral tests, with an increase in fraction solid at the dendrite coherency point for Al-7%Si-Mg and Al-11%Si-Mg.^(8,9) This property is related to the ability of the melt to feed a casting during solidification.

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 1.1 shows the combined effect of hydrogen content, silicon modification and grain refinement on microporosity of 356 alloy.⁽¹⁰⁾



Figure 1.1 Effect of hydrogen content, silicon modification and grain refinement on microporosity of 356 alloy.⁽¹⁰⁾

The process of solidification of Al-Si casting alloys begins with the nucleation and growth of the primary α (Al), followed by subsequent precipitation of various phases containing the alloying elements (Si, Cu, Mg, etc.). It is at this very first step (nucleation and growth) where the grain size of a casting is established. The solidification of a very clean liquid does pose a significant nucleation problem. As the temperature of the liquid drops, clustering of atoms produce crystalline regions due to a lowering in thermal agitation. For a spherical cluster of radius, r, the net energy to form the new phase is reduced in proportion to its volume, $4\pi r^3/3$, and the free energy per unit volume, ΔG_v . At the same time, new surface area is required involving extra energy because of the interfacial energy, γ_{SL} , per unit area of surface, Figure 1.2.⁽¹¹⁾ Therefore, the formation of a spherical solid particle results in a free energy change (Equation 1.1).



Figure 1.2 Free energy change associated with homogeneous nucleation of a sphere of radius r.⁽¹¹⁾

$$\Delta G = -4/3(\pi r^3 \Delta G_v) + 4\pi r^2 \gamma_{SL} \qquad (Equation 1.1)$$

where:

$$\Delta G_{\rm v} = L_{\rm v} \Delta T / T_{\rm m} \qquad (\text{Equation 1.2})$$

and

 L_v = Latent heat of fusion per unit volume

 $T_{\rm m}$ = Equilibrium solidification temperature

 ΔT = Undercooling below $T_{\rm m}$.

For a given undercooling, ΔT , there is a critical radius, r^* , associated with a maximum excess free energy. If $r < r^*$ the system lowers its free energy by dissolving the embryo, whereas when $r > r^*$ the free energy of the system decreases if the solid grows, overcoming the homogeneous nucleation problem (Figure 1.2).⁽¹¹⁾

By differentiating Equation 1.1 the critical, r^* , and, ΔG^* , can be calculated as

$$r^* = 2\gamma_{\rm SL} \,/\, \Delta G_{\rm v} \tag{Equation 1.3}$$

and

$$\Delta G^* = 16\pi\gamma_{\rm SL}^3 / 3(\Delta G_{\rm v})^2 \qquad (Equation 1.4)$$

and by substituting Equation 1.2 for ΔG_v the following is obtained:

$$r^* = (2\gamma_{\rm SL}T_{\rm m} / L_{\rm v}) (1/\Delta T) \qquad (Equation 1.5)$$

and

$$\Delta G^* = (16\pi\gamma_{\rm SL}^3 T_{\rm m}^2 / 3L_{\rm v}^2) (1/\Delta T^2)$$
 (Equation 1.6)

where it is clear that the critical radius, r^* , and the total energy, ΔG^* , can be decreased by increasing the undercooling, ΔT .⁽¹¹⁾

Most of the time, however, the liquid contains other solid particles in suspension, or as part of the walls of its container, on which crystals can form. In this case the interfacial energy component of Equation 1.1 can be reduced or even eliminated. Foreign nuclei in a melt can lead to a range of heterogeneous nucleation temperatures, making nucleation easier at progressively smaller undercoolings, ΔT , of the liquid for more effective nuclei. In the presence of very favorable nuclei, the solidification of the liquid can start at practically zero undercooling.^(11,12)

When a solid embryo is in contact with a flat surface, i.e. the mold wall, and assuming γ_{SL} is isotropic, a spherical cap of radius, *r*, with a wetting angle, θ , is formed as the equilibrium shape, reducing the total interfacial energy, Figure 1.3.⁽¹¹⁾



Figure 1.3 Heterogeneous nucleation of spherical cap on a flat mold wall.⁽¹¹⁾

The equilibrium pertains when

$$\gamma_{SL} \cos \theta = \gamma_{ML} - \gamma_{SM}$$
 (Equation 1.7)

The formation of the embryo is now associated with two additional interfacial energies, thus

$$\Delta G_{het} = -V_{S}\Delta G_{V} + A_{SL}\gamma_{SL} + A_{SM}\gamma_{SM} - A_{SM}\gamma_{ML} \qquad (Equation 1.8)$$

where:

 $\Delta G_{\rm V}$ = Volume free energy change in transforming liquid to solid

 $V_{S} = Volume of spherical cap$

 A_{SL} = Area of solid/liquid interface

 A_{SM} = Area of solid/mold interface

 γ_{SL} = free energy of solid/liquid interface

 γ_{SM} = free energy of solid/mold interface

 γ_{ML} = free energy of mold/liquid interface.

The first two interfacial energies in Equation 1.8 are positive as the interfaces are created during the nucleation process, but the third one is negative since it represents the

destruction of the mold/liquid interface under the spherical cap. Equation 1.8 can be written in terms of the wetting angle, θ , and the cap radius, r, for which

$$\Delta G_{\text{het}} = \{ -4/3(\pi r^3 \Delta G_v) + 4\pi r^2 \gamma_{\text{SL}} \} \mathbf{S}(\theta) \qquad (\text{Equation 1.9})^{(11)}$$

where:

$$S(\theta) = (2 + COS \theta) (1 - COS \theta)^2 / 4$$
 (Equation 1.10)⁽¹¹⁾

Equation 1.9 is equal to the equation for homogenous nucleation (Equation 1.1), except for the factor $S(\theta)$, which has a value of ≤ 1 , and is referred to as the shape factor.⁽¹¹⁾ When the interfacial energy between the embryo and the substrate becomes minimal, $S(\theta) \rightarrow 0$ and the total free energy for nucleation is reduced. This reduction of the interfacial energy occurs if similarities between crystal structure exist at least in one atomic plane of the embryo and one of the substrate.⁽²⁾

It has been experienced that the grain size of a casting is inversely related to the number of foreign nuclei in the melt, which are able to act during the solidification process. Then, if each grain is nucleated by one foreign particle, a greater number of nuclei will allow more grains to form, resulting in a smaller grain size. Not all foreign particles are good nuclei for the formation of solid. In liquid aluminum foundry alloys, different particles can be found, ranging from oxides and spinels, to the wall of the mold itself. At a given undercooling, ΔT , any particle may or may not be effective as a nucleant, and the particles with the best crystallographic similarity to aluminum (which promote lower surface energy) will become effective nucleants at temperatures close to the equilibrium freezing point of the liquid, T_m .⁽²⁾

In the rapid freezing of a casting, the rate of heat extraction can exceed by far the latent heat of solidification generated, producing a significant undercooling that allows many heterogeneous nuclei to become active and results in a fine grain size. Although this procedure provides finer grain sizes than any other technique, it is usually impractical as a large amount of latent heat has to be removed from a large casting in order to generate the required undercoolings.⁽²⁾

Other techniques to induce grain refinement include crystal fragmentation, where growing dendrites can be damaged to create seeds of new grains. The application of ultrasonic vibration to solidifying alloys, the use of volatile mold coatings, or the mechanical stirring of the melt are examples of dendrite fragmentation techniques.⁽¹³⁾

Among the various mechanisms of grain refinement, chemical grain refinement proves to be the most effective. A substrate with a very low interfacial energy is placed into the melt, either by adding a nucleus, or generating the nucleus in the melt by some type of phase reaction. Heterogeneous nucleation takes place on the substrates, and coupled with growth restriction by constitutional factors, leads to grain refinement. Titanium and boron have been used as the main elements for grain refinement of aluminum alloys, and since their introduction as grain refiners there has been considerably controversy about the mechanism by which these elements promote grain size reduction in wrought and cast aluminum alloys.⁽²⁾

Chemical grain refiners are added to the melt as salt fluxes or master alloys. Salt fluxes contain K_2TiF_6 and KBF₄ salts as the active ingredients, which react with the molten aluminum releasing titanium and boron. Aluminides (TiAl₃) and borides (TiB₂) are formed in the melt, acting as heterogeneous nuclei for the formation of crystals. Despite their good refining power, salts are prone to generate gas in the melt and to produce corrosive fumes. Salts can also react with elements like strontium and reduce the modification of the eutectic silicon structure.⁽¹³⁾

More effective are the master alloys produced by reacting salts with aluminum under controlled conditions. Aluminides and borides are embedded in an aluminum matrix, containing typically 100 million or more intermetallic particles per cubic centimeter, each particle being a potential nucleant when released into the melt. Master alloys are commonly produced as waffle ingots or extruded rods, containing titanium (in the order of 2 to 10 wt. %) or boron (up to 5 wt. %), or a combination of both elements in aluminum. Master alloys having a Ti/B ratio of unity (Al-3%Ti-3%B), have been found to be the most effective for the grain refinement of Al-Si casting alloys.^(13.14)

Although effective, chemical grain refinement has to be carefully monitored, since longer contact times (time of residence of the nucleant particles in the melt) result in dissolution or settling of the refining particles and some loss of the refining effect. Commonly, a sample is taken from the melt and solidified, and either a microscopic or chemical analysis is performed on the sample in order to assess the degree of refinement of the liquid aluminum.⁽¹³⁾ If a fine grain size is achieved, or if the titanium or boron content is increased in the chemical composition of the sample, the molten aluminum is ready to be poured into a mold. If not, proper refinement must be done.

Sample preparation for these techniques are time consuming and the results do not always reflect the true refining condition of the melt. Special tests have been designed to obtain samples for grain size measurement in wrought aluminum alloys, and although good correlation has been found between these tests, most of the time the true solidification condition of the real casting is not well simulated. Sample preparation for revealing grain size in aluminum casting alloys requires complicated anodizing techniques, and usually the assessment of refinement is done by a less accurate comparative visual technique.⁽¹³⁾

Spectrochemical analysis also has its own drawbacks. Considered as a comparison technique, it compares the element intensity ratios in the sample, to the intensity ratios of a calibration curve in order to extrapolate a concentration value from the curve. The results are only as good as the calibration curve itself.⁽¹⁵⁾ Sample preparation also plays an important role in the quality of the analysis, as impurities from the melt and varying chill rates of the sample can affect the matrix of the metal.⁽¹⁶⁾ In addition, the presence of titanium or boron does not guarantee the presence of effective substrates in the melt if the refiner has had a long contact time with the melt.

An alternative for grain size measurement of aluminum casting alloys is the thermal analysis technique. This technique monitors the temperature changes in a sample as it solidifies, and the resulting plot is a curve of temperature versus time, Figure 1.4.

From this curve, thermal arrests related to latent heat evolution from phase transformations can be detected and related to the microstructure of the solidified sample.



Figure 1.4 Cooling curve and the $\Delta T_{\text{R-U}}$ parameter.⁽¹⁷⁾

The grain size of castings has been related to differences in temperature between a minimum. $T_{\rm U}$, occurring immediately after the beginning of solidification and the maximum temperature, $T_{\rm R}$, reached due to recalescence of the sample. This quantity has been called the recalescence undercooling, $\Delta T_{\rm R-U}$.⁽¹⁷⁾ Figure 1.5⁽⁵⁾ presents the correlation between the grain size of A319 alloy and the so called $\Delta T_{\rm R-U}$ parameter. Although considerable scattering is observed, this parameter has been used commercially to monitor the grain refinement of castings.

The thermal analysis technique estimates the nucleation potential of the melt during solidification but only for a specific cooling rate, and the characteristic cooling curve parameters must be correlated with the actual state of nucleation of the melt.⁽¹⁷⁾

The advantage of the thermal analysis technique is that it can be used as an online control tool. Faster results can be obtained with the certainty that the results reflect the nucleation potential of the melt. The objective of the present investigation is to analyze various parameters of the cooling curve, in order to obtain a better and more reproducible parameter for the control of the grain refinement in aluminum casting alloys. Although temperature parameters are commonly used, time parameters are explored, since calibration errors in the thermocouples used can give misleading results when temperature parameters alone are analyzed.



Figure 1.5 Grain size versus undercooling, $\Delta T_{\text{R-U}}$, for A319 aluminum alloy.⁽⁵⁾

Two major Al-Si casting alloys, 319 Al-Si-Cu and 356 Al-Si-Mg, are used as the base material. Different chemical grain refiners are added in the form of master alloys or salt fluxes, with varying Ti/B ratios and at different addition levels. Cooling rates are also varied in order to observe their effect on the results produced. The overall aim of the study is to produce a better thermal analysis technique for use on the shop floor.

Chapter 2 Mechanisms of Grain Refinement in Aluminum

Historically, titanium and boron were introduced to the melt by the addition of salt fluxes in early grain refining experimentation. Usually, the active ingredients in these refiners were K_2TiF_6 and KBF₄, which reacted with molten aluminum to release titanium and boron.⁽¹³⁾ Despite their efficiency as refiners, they offered several disadvantages. Salt fluxes tend to increase the hydrogen content of the melt, produce corrosive fumes, yield low recovery of the refining elements, and raise the level of inclusions in the melt.^(13,18)

Ever since, chemical refinement by controlled heterogeneous nucleation has been accomplished in the aluminum industry by the addition of Al-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 technique.

2.1 Grain refinement by titanium addition

Among the various theories presented by several authors, the *Peritectic Theory* proposed by Crossley and Mondolfo⁽¹⁹⁾ has been taken as a base mechanism in the explanation of grain refinement of aluminum alloys by titanium addition. The Al-Ti phase diagram⁽²⁰⁾ (Figure 2.1), exhibits a peritectic reaction at 1.2 wt.% titanium and 665 °C, with the limit of the peritectic horizontal placed at 0.15% Ti. According to Crossley and Mondolfo,⁽¹⁹⁾ the grain refinement of aluminum is associated with this reaction.

Titanium, when present in sufficient amounts (>0.15%), forms primary crystals of TiAl₃ which react peritectically with the liquid forming α (Al). Compositions are usually in the hypoperitectic range and the transformation takes place according to Reaction 2.1.

Liquid + TiAl₃
$$\rightarrow \alpha$$
 (Al) + Liquid (Reaction 2.1)

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 2.2). Al-Ti master alloys contain TiAl₃ particles in an aluminum 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.⁽²⁾ 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 TiAl₃ particles.⁽²⁰⁾



Figure 2.1 Al-Ti phase diagram.⁽²⁰⁾

The *Peritectic Theory* has been confirmed by other authors^(21,22) who have found particles of TiAl₃ at the center of aluminum grains and observed orientation relationships between this compound (TiAl₃) and the surrounding aluminum. Despite the agreement with this peritectic theory, Davies et al.⁽²²⁾ assumed an error in the phase diagram due to the fact that the nucleating particles were found even at very low titanium contents (0.01 wt.% Ti). Along this same line, earlier studies by Cibula⁽²³⁾ established that TiC particles were responsible for the reduction in grain size of aluminum alloys at low concentrations of titanium (0.01 wt.%), but later experiments^(24,25) yielded very little success in trying to increase the carbon content in alloys containing titanium due to the lack of wettability of carbon or TiC by molten aluminum. Cibula's so called Carbide Theory was based mainly on the fact that at very low concentrations, titanium could not form aluminides, but the carbon present in the melt from the crucibles and tools (no intentional addition of carbon was made) could react with titanium to form TiC. Recent studies by Mohanty et al.⁽²⁵⁾ have demonstrated that TiC is not an effective nucleant due to its thermodynamic instability in the melt. In recent years, only a few authors⁽²⁶⁾ have supported Cibula's *Carbide Theory*, and there has been little attempt to develop it commercially.



Figure 2.2 Nucleation of α (Al) by the peritectic reaction in the Al-Ti system.⁽²⁾

For Al-Ti master alloys, it has been found that at titanium levels below the peritectic, the refining effect fades due to dissolution of the TiAl₃ particles in the melt.⁽²⁰⁾ Also, the morphology of the TiAl₃ particles has been found to affect the refining effectiveness of the master alloy. For plate-like structures the refining effect lasts longer. although it takes time to become effective in the melt from the moment of addition. At high titanium concentrations, titanium aluminide crystals act as nucleants for primary aluminum, and at the same time, further growth becomes limited by the diffusion of titanium from TiAl₃ through the shell of solid aluminum⁽²⁷⁾.

2.2 Grain refinement by titanium and boron addition

It is well known that boron addition to Al-Ti master alloys greatly improves the effectiveness of grain refinement in aluminum alloys, but the exact mechanism by which it takes place has not been clearly established. Several studies have been done in this respect, and the literature is abundant with thermodynamic studies (sometimes contradictory) and experimental findings. McCartney⁽²⁸⁾ and Guzowski and co-authors⁽²⁷⁾ have made critical reviews of this work which can be summarized in three main theories that are reviewed here. For a more in-depth study of the different mechanisms, references 27 and 28 are suggested.

Boride Theory

Cibula⁽²⁴⁾ postulated that when boron was added to aluminum alloys refined with titanium, insoluble particles of TiB₂ (or perhaps (Al,Ti)B₂) were directly responsible for the reduction in grain size at very low titanium concentrations, and that fading occurred due to boride particle agglomeration and settling. Contrary to this idea, Marcantonio and Mondolfo⁽²⁹⁾ proposed that the boron addition reduced the solubility of titanium in molten aluminum, and expanded the peritectic reaction of the Al-Ti system towards the Al-rich end, allowing TiAl₃ crystals to exist even at very low titanium concentrations. Other researchers⁽²²⁾ have also contradicted the *Boride Theory* of Cibula by noting that boron containing particles are found at grain boundaries, and not at grain centers.

Several authors^(27,29-32) have found what has been called a metastable phase of $(Al,Ti)B_2$ which is formed by a range of solid solutions of AlB_2 and TiB_2 . Sigworth⁽³¹⁾ claims that the $(Al,Ti)B_2$ phase acts as a direct nucleant for aluminum in Al-Si alloys, while Cornish⁽³⁰⁾ established that the formation of this series of solid solutions does not play an important role in the grain refining of aluminum alloys. Kuisalaas and Bäckerud⁽³²⁾ observed during the production of Al-Ti-B master alloys that this metastable phase transformed into TiB₂, during holding in the liquid state. By making variations in the preparation technique, a whole range of boride phases, between AlB₂ and TiB₂, may be produced. Guzowski and co-authors⁽²⁷⁾ observed that boron allows TiB₂ and (Al.Ti)B₂ to form "duplex" particles with TiAl₃, which in turn become nucleation sites for aluminum. This observation contradicts the theory suggested by Marcantonio and Mondolfo⁽²⁹⁾ where boron shifts the Al-Ti peritectic reaction to lower titanium contents.

Despite these contradictions, these authors have definitely established the presence of the following particles in the grain refined metal: $TiAl_3$, TiB_2 , AlB_2 and a mixture of (Al,Ti)B_2. From these observations two theories have emerged. Neither of these, which are described below, has been proven conclusively.

Peritectic Hulk Theory

In this theory, proposed by Bäckerud,⁽³³⁾ small (Al,Ti)B₂ particles dissolve completely in the melt and TiAl₃ particles dissolve partially, establishing a titanium diffusion profile around them. This increases the titanium concentration in this region (around the aluminides), and the solubility product for TiB₂ is exceeded. The boride then precipitates on the surface of the aluminide phase forming a protective shell against dissolution of the TiAl₃ particles. With time, a simultaneous diffusion of titanium (outwards) and aluminum (inwards) takes place through the shell, creating pools of liquid aluminum saturated with titanium. These peritectic cells trigger the heterogeneous nucleation when the temperature reaches the peritectic temperature (665 °C). When this occurs, α (Al) nucleates inside the shell, breaks it and continues to grow into the surrounding liquid. A schematic diagram of this theory is shown in Figure 2.3. It has been observed⁽³²⁾ 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 TiAl₃. The grain refining effect of these duplex particles seems to fade with time due to the complete dissolution of the aluminide,^(32,33) but other authors⁽³⁴⁾ 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.⁽³⁰⁾



Figure 2.3 Model for the Peritectic Hulk Theory.⁽³³⁾

- (a) Partial dissolution of TiAl₃ and diffusion of B towards TiAl₃,
- (b) Solubility product of TiB_2 is exceeded,
- (c) Protective shell of TiB₂ on TiAl₃ is formed,
- (d) Simultaneous diffusion of Al and Ti through protective shell,
- (e) Nucleation and growth of α (Al).

Hypernucleation Theory

Jones and Pearson^(35,36) have established that when there is excess titanium (above the ratio Ti/B = 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 2.4. Fading, according to this mechanism, is due to the agglomeration and settling of boride particles. Experimental evidence^(20,34) supports this theory based on fading recovery, but the thermodynamics of this theory have yet to be precisely established.⁽³⁶⁾



Figure 2.4 Model for the Hypernucleation Theory.⁽³⁶⁾

- (a) Excess Ti (Ti/B > 2.21) in solution,
- (b) Ti segregated to the TiB_2 -melt interface,
- (c) Formation of TiAl₃ layer on TiB₂,
- (d) Nucleation of α (Al) by peritectic reaction.

2.3 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 shown the importance of boron in Al-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 AlB₂ as a nucleant for aluminum. According to Cibula,⁽²⁴⁾ AlB₂ particles are able to nucleate aluminum, but Maxwell and Hellawell⁽³⁷⁾ contend that AlB₂ is not an effective nucleant for pure aluminum. AlB₂ and TiB₂ have nearly identical structures,⁽¹⁴⁾ and similar 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 AlB₂ will become a site for heterogeneous nucleation of primary aluminum.

In general, three 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 TiB_2 stoichiometry (Ti/B=2.21).⁽³⁸⁾

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.^(14,39)

Al-Ti refiners, originally used in the wrought aluminum 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 titanium.⁽¹⁸⁾ 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 2.2.⁽⁴⁰⁾

Liquid + Ti_xSi_yAl_{1-(x+y)}
$$\rightarrow \alpha$$
 (Al) + Liquid (Reaction 2.2)

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 2.2 occurs at approximately 600 $^{\circ}C$,⁽⁴⁰⁾ just below the liquidus temperature of 356 and 319 Al-Si casting alloys.

Sigworth and Guzowski⁽¹⁴⁾ 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 AlB₂). Other authors⁽³⁸⁾ have proposed that excess boron forms a layer on TiB₂ particles and nucleates α (Al) by a eutectic reaction at 659.7 °C (Reaction 2.3).

Liquid
$$\rightarrow \alpha$$
 (Al) + AlB₂ (Reaction 2.3)

Also, in Al-Si alloys, Mohanty and Gruzleski⁽³⁸⁾ found that an Al-Ti-Si phase forms on TiB_2 when titanium is in excess. This Al-Ti-Si phase subsequently nucleates primary aluminum by means of the peritectic reaction.

2.4 Grain refinement by boron addition

In early experiments,^(21,24) AlB₂ was believed to nucleate pure aluminum, based on X-ray diffraction results of centrifuged samples. Also, Sigworth et al.⁽¹⁴⁾ reported superior grain refinement obtained by the addition of boron alone (as Al-4% B master alloy) over the conventional Al-Ti and Al-Ti-B additions (Figure 2.5). It has been proposed⁽³⁸⁾ that the effect of boron alone in the grain refinement of pure aluminum is virtually nil, but for Al-Si alloys, it becomes very significant due to the eutectic reaction at 0.02 wt.% B (Reaction 2.3). 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 2.2 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.

Tøndel et al.⁽⁴¹⁾ 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 produce good refinement in Al-Si alloys, and the presence of AlB₂, rather than AlB₁₂ ensures a degree of grain refinement similar or superior to the titanium containing master alloys.



Figure 2.5 Grain refining of 356 Al-Si alloy with Al-Ti, Al-Ti-B and Al-B.⁽¹⁴⁾

2.5 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.⁽³⁵⁾ the effect of Zn, Mg and Si in aluminum alloys, is to restrict grain growth by constitutional undercooling. Bäckerud and co-authors^(42,43) 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.

StJohn et al.⁽⁴⁴⁾ 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, decreases 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 2.6), followed by an increase associated with a change in the growth mode of the interface, as reported by Bäckerud et al.⁽⁴³⁾

To conclude this review, Table 2.I 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.



Figure 2.6 Effect of Si addition on grain refinement of aluminum.⁽⁴⁴⁾

	Pure AI and Wrought Alloys		Al-Si Casting Alloys	
Master Alloy	Effectiveness	Mechanism	Effectiveness	Mechanism
				Drop in peritectic
		Peritectic		formation temp.
Al-Ti	Good	formation of	Poor	of Ti _x Si _y Al _{t-(x+y)} to
	lf Ti > 0.15%	$\alpha(AI)$ on TiAl ₃		below liquidus of
				alloy
				α(Al) nucleates
Al-Ti-B	Good	Formation of	Reasonable	of Ti _x Si _y Al _{1-(x+y)}
Ti/B > 2.2		TiAl ₃ layer on		which forms
		TiB₂ particle		peritectically on
		surface		TiB ₂ *
				Eutectic
AI-B	Not Effective	AIB₂ not wetted	Excellent	formation of $\alpha(AI)$
		by α(Al)		$L \rightarrow \alpha(AI) + AIB_2$
		Solute Ti		Eutectic
Al-Ti-B	Not Effective	necessary for	Good,	formation of $\alpha(AI)$
Ti/B < 2.2		formation of TiAl ₃	better than	at TiB ₂ interface
		on TiB ₂	if Ti/B > 2.2	due to solute B

*Refinement limited by drop in peritectic temperature with Si.

Table 2.I Summary of grain refinement mechanism in aluminum.⁽⁴⁰⁾
Chapter 3 Thermal Analysis of Aluminum Alloys

Among the various techniques used in the industry for process control of aluminum casting manufacturing, thermal analysis has proved to be an excellent tool in the production of quality molten metal. This on-line process control technology, was first used by nonferrous foundries in the early 80's, and since then, dramatic reductions in scrap rates have been obtained.⁽⁴⁵⁾

Traditionally, microstructural features of castings have been assessed by time consuming metallographic techniques. These procedures may require up to eight to ten hours per casting starting with the melting of the metal, addition of the refiners and modifiers, pouring, cooling, grinding and polishing specimens, and concluding with a detailed microscopic analysis.^(13,45) Another option has been spectrochemical analysis, which also requires specimen preparation, and can be so time consuming that changes in melt chemistry may take place while the analysis is being done.^(15,45,46)

Thermal analysis has the advantage of speed when compared to these other techniques. Thermal analysis has been considered as the metallurgical fingerprint of the solidification process, and its output, the cooling curve, has been correlated to microstructural features of castings with excellent productivity results.^(45,46) Specimens can be taken from the melt, and results are generated within five minutes without destroying samples. Corrective measures can then be taken to achieve the desired melt quality before the molten metal is poured.^(45,46)

The development of relatively inexpensive microprocessor technology has permitted thermal analysis equipment that can be used in a shop-floor environment with minimum errors in the data acquisition due to noise from the plant. Other techniques, such as the Differential Thermal Analysis (DTA) and Differential Scanning Calorimetry (DSC) are also used in order to detect thermal events that take place in solidifying (or melting) samples, but these are more sophisticated and require laboratory conditions for their application.⁽⁴⁷⁾

Conventional thermal analysis was first developed in the cast iron industry for the detection of the carbon equivalent,⁽⁴⁸⁾ but over the last 20 years, this practice has become a part of the technological developments in the aluminum industry. Grain size, eutectic silicon modification and more recently iron-bearing intermetallics in aluminum casting alloys have all been analyzed by thermal analysis providing reasonable qualitative and quantitative results.^(5,49,50) Nevertheless, the technique as presently developed is far from perfect, and much remains to be done in relating the results of the thermal analysis to quantitative aspects of the microstructure.

3.1 Principles of thermal analysis

The principle of thermal analysis, which was initially used for the determination of phase diagrams, is to pour a molten specimen into a cup, measure its temperature as it solidifies, and plot a corresponding curve of temperature versus time, called the cooling curve.⁽¹⁷⁾ Once this data has been obtained, a mathematical treatment follows, in order to interpret the cooling curve. During freezing, a liquid metal reduces its temperature at a certain cooling rate determined by the surroundings. When solidification begins, the cooling rate of the metal is reduced by the evolution of latent heat (latent heat of solidification). This produces thermal arrests, which change the slope of the cooling curve, allowing for the detection of the liquidus temperature and other subsequent reactions in the alloy, until the sample is totally solidified.⁽⁵¹⁾

The cooling curve represents the difference between the heat extracted from the sample and the evolution of latent heat in the sample. If internal temperature gradients in

a sample are negligible, that is assuming Newtonian cooling, the heat balance equation for a cooling specimen is given by Equation 3.1.⁽⁵²⁾

$$- V\rho C_p dT/dt = hA (T-T_o)$$
 (Equation 3.1)

- [heat lost by metal] = [heat transferred to surroundings]

where:

$$dT/dt = -hA (T-T_0) / V\rho C_p \qquad (Equation 3.2)$$

and

V = volume of specimen

 ρ = density of metal

 C_p = specific heat of metal

T = temperature of specimen

 $T_o =$ temperature of surroundings

t = time

h = heat transfer coefficient

A = surface area

dT/dt = cooling rate of specimen.

For the case when a phase transformation occurs.⁽⁵³⁾

$$dQ_{L}/dt - V\rho C_{p} dT/dt = hA (T-T_{o})$$
 (Equation 3.3)

[heat from phase transformation]-[heat lost by metal] = [heat transferred to surroundings]

where:

$$dT/dt = [dQ_L/dt - hA (T-T_o)] / V\rho C_p$$
 (Equation 3.4)

and

 Q_L = latent heat of solidification.

For pure metals and eutectic alloys, the solidification process is achieved at a constant temperature, leading to only one thermal arrest, characterized by a plateau in the cooling curve, Figure 3.1 (a).⁽¹⁷⁾ The latent heat of solidification evolved is balanced by the rate of heat extraction from the sample, maintaining a constant temperature (dT/dt =

0) in the sample during solidification. For solid solution alloys, the solidification takes place over a range of temperatures, and the transformation is shown as a change in slope of the cooling curve at the beginning and end of solidification, Figure 3.1 (b).⁽¹⁷⁾ At T_L , latent heat is given off, reducing the slope of the curve (reducing the cooling rate of the sample). At T_S , when all the latent heat is given off, the cooling rate of the sample increases, being now only a function of the heat transfer between the sample and the surroundings (Equation 3.2).

For binary hypoeutectic Al-Si casting alloys (5 to 7 wt.% Si), the characteristic cooling curve is a combination of these two types of cooling curves (Figures 3.1 (a) and (b)).⁽¹⁷⁾ As can be seen from the phase diagram in Figure 3.2,⁽²⁾ these alloys first solidify as the α (Al) phase over a range of temperature from T_L, down to the eutectic composition which is reached at (577 °C). At that point, the Al-Si eutectic is solidified at constant temperature until no further latent heat is given off.



Figure 3.1 Ideal cooling curve of (a) pure metal and (b) solid solution alloy.⁽¹⁷⁾



Figure 3.2 Phase diagram of the Al-Si system.⁽²⁾

In more complex Al-Si alloys such as 319 Al-Si-Cu and 356 Al-Si-Mg alloys, the end of solidification does not occur at the Al-Si eutectic temperature (T_E), but at lower temperatures determined by secondary eutectic reactions, such as those in which the phases Al₂Cu and Mg₂Si are formed. The cooling curve then becomes complex, presenting several thermal arrests due to the different reactions taking place in the melt as it solidifies.⁽⁵⁴⁾ Some of these arrests may be very difficult to detect due to their small associated heat effect. A typical cooling curve for 319 Al-Si-Cu alloy shows the primary aluminum solidification, as well as the Al-Si and Al-Al₂Cu eutectic precipitation, Figure 3.3.

Temperature and time parameters from the cooling curve may be used as fingerprints to indicate the extent of grain refinement and eutectic modification of an alloy. The primary arrest undercooling (at the primary aluminum solidification, Figure 3.3) has been used to determine the degree of grain refinement, while depression of the eutectic temperature (at the Al-Si eutectic precipitation, Figure 3.3) is used to monitor the extent of modification of the Al-Si eutectic structure.⁽¹⁷⁾ Time parameters have also been

correlated with the degree of eutectic modification in 319, 355, 356, 357, 380 and 413 alloys, where the total length of the eutectic plateau increases with increasing strontium content.⁽⁴⁹⁾



Figure 3.3 Cooling curve of 319 Al-Si-Cu casting alloy.

3.2 Grain refinement and the first thermal arrest

In solidifying molten aluminum, the state of nucleation may be assessed from the cooling curve. Early experiments^(19,21,23) on grain refinement of aluminum have related the degree of grain refinement of the metal by the addition of inoculants to the degree of undercooling at the primary arrest. When a melt contains few, or no, favorable heterogeneous nucleation sites, the metal cools until a certain degree of undercooling, (ΔT) , is reached (at a temperature below T_m). This undercooling is necessary in order to activate other impurities in the melt or generate homogeneous nucleation. On the other hand, when an alloy has sufficient favorable sites for nucleation, solidification starts at low or no undercooling ($\Delta T \rightarrow 0$), and the alloy has a fine grain size.⁽¹¹⁾

In Figure 3.4 (a), the liquidus undercooling observed at the first thermal arrest has usually been taken as the ideal reference to assess the degree of grain refinement in aluminum foundry alloys.^(5,55) Figure 3.4 (a) shows some of the different possible temperature parameters obtained from this thermal arrest for hypoeutectic aluminum-silicon alloys.⁽¹⁷⁾ The difference between the maximum recalescence temperature (T_R) and the maximum undercooling temperature (T_U). Equation 3.5, has been related to the degree of grain refinement with relative success. Figure 1.5.^(5,56-59)

$$\Delta T_{\rm R-U} = T_{\rm R} - T_{\rm U} \qquad (Equation 3.5)$$

Different time parameters have also been suggested, Figure 3.4 (b), and although these have been shown to work in the laboratory, no commercial applications have yet been made with these parameters.⁽¹⁷⁾ Charbonnier⁽⁵⁵⁾ and Tenekedjiev and Gruzleski⁽⁴⁹⁾ have established that the liquidus undercooling time, t₁ in Figure 3.4 (b), relates better to the degree of grain refinement than does the undercooling. Charbonnier⁽⁵⁵⁾ presents a correlation between grain size and the ΔT_{R-U} and the liquidus undercooling duration, t₁, for hypoeutectic Al-Si alloys, and although no experimental data is presented, the time parameter appears to provide a good correlation with grain size. Figure 3.5.



Figure 3.4 Temperature and time parameters.⁽¹⁷⁾

It is important to note at this point that the liquidus undercooling indicated on Figure 3.4 (a), $\Delta T_{\text{R-U}}$, does not represent the undercooling, ΔT , required for the nucleation of solid. $\Delta T_{\text{R-U}}$ is only the point at which heat loss from the sample becomes less than the rate of heat generation from latent heat evolution. The actual nucleation point occurs before T_{U} , as explained in section 3.4. The term, $\Delta T_{\text{R-U}}$, has been misused by many authors, and although the tendency of $\Delta T_{\text{R-U}}$ to reduce correlates well with fine grain size of castings, this phenomenon has also been associated with coarser grain structures, Figure 3.5.



Figure 3.5 Changes in liquidus undercooling, ΔT_{R-U} , and liquidus undercooling time. t₁, related to grain size of hypoeutectic Al-Si alloys.⁽⁵⁵⁾

3.3 First derivative parameters

The cooling curve does not always indicate in a very obvious way all the reactions occurring during solidification of a casting, due to the small amounts of heat evolved by certain phase transformations. More sensitive techniques have to be developed. It has been found⁽⁶⁰⁾ that the first derivative of the cooling curve can be employed to emphasize small heat effects not resolved on the cooling curve itself. It is clear from Figure 3.6 that peaks on the first derivative accentuate the effects of heat evolution during solidification, allowing for the analysis of more sensitive and meaningful parameters.



Figure 3.6 First derivative of the cooling curve.⁽⁶⁰⁾

The first derivative of the cooling curve has been used in the determination of the starting solidification time.^(53,60-62) and also to relate the magnitude of the liquidus undercooling peak to the ease of nucleation of primary grains.⁽⁶³⁾ By using the first derivative (the cooling rate) and higher order derivatives, weak arrests can be picked up from the curve and related to phase reactions occurring in the melt due to the presence of small quantities of alloy elements. The first peak generated on the cooling curve first derivative represents the magnified effect of the latent heat evolution from the nucleation of primary aluminum, Figure 3.7. The beginning of solidification can be established as the point where a sharp increase in the derivative occurs. Initially, the liquid cools at a certain rate, and when grains form from heterogeneous nucleation sites, latent heat of fusion is evolved, reducing the cooling rate and producing recalescence.⁽⁶⁴⁾

Researchers⁽⁶⁵⁾ have integrated the first derivative curve, on Figure 3.7, and obtained reasonable correlation with the nominal grain size, Figure 3.8, by measuring the area below the positive segment of the derivative curve, called the liquidus peak parameter.



Figure 3.7 Primary arrest and the first derivative of the cooling curve.



Figure 3.8 Nominal grain size vs. liquidus peak parameter for a commercial SAE 331 Al-Si-Cu alloy.⁽⁶⁵⁾

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Many researchers^(53,60,66,67) have calculated the evolution of latent heat from a solidifying metal by integrating the area below the first derivative, in a similar way to the integration of peaks in the DTA and DSC. In these techniques, the heat evolved or absorbed, due to a phase transformation, can be calculated by taking the difference between the thermal events observed in a sample and in a neutral reference, which undergoes no physical transformation involving absorption or release of heat, within the temperature range investigated.⁽⁴⁷⁾

Using the first derivative, the neutral reference can be simulated, by using the portions of the derivative curve not affected by transformation and interpolating them into the region of the transformation. This is procedure is known as Computer-Aided Cooling Curve Analysis (CA-CCA).

Equation 3.2 gives the derivative of the cooling curve when no phase transformation occurs. This equation can be considered as the neutral reference, $(dT/dt)_{NR}$. Equation 3.4 is the derivative of the cooling curve when a phase transformation occurs. $(dT/dt)_{CC}$. Figure 3.9.⁽⁶⁴⁾ shows both of these functions as well as the cooling curve for a 319 alloy. By subtracting Equation 3.2 from 3.4, in the time interval of a phase transformation, the latent heat released during that transformation can be calculated as follows.

$$(dT/dt)_{CC} - (dT/dt)_{NR} = (dQ_L/dt) / V\rho C_p$$
 (Equation 3.6)

rearranging terms

$$dQ_{L} / dt = V\rho C_{p} [(dT/dt)_{CC} - (dT/dt)_{NR}]$$
 (Equation 3.7)

and integrating

$$Q_{L} = V\rho C_{p} \int [(dT/dt)_{CC} - (dT/dt)_{NR}]dt \qquad (Equation 3.8)$$

where

$$Q_L = V\rho C_p$$
 [area under $(dT/dt)_{CC}$ – area under $(dT/dt)_{NR}$].



Figure 3.9 First derivative and neutral reference derivative for 319 alloy.⁽⁶⁴⁾



Figure 3.10 Area below (dT/dt)_{CC} related to the latent heat evolution of primary aluminum formation.

Figure 3.10 shows the area under the first derivative, $(dT/dt)_{CC}$, related to the latent heat evolution from the nucleation of primary aluminum to the end of the recalescence. Although the first derivative of the cooling curve has a theoretical basis, the commercial use of derivative parameters has hardly been explored, and only limited experimental data and information on the interpretation of derivative parameters are found in the literature.⁽⁶⁵⁾

3.4 Additional thermal analysis parameters

Higher order derivatives of the cooling curve have been explored, in order to obtain a more sensitive parameter to correlate with microstructural features in castings.^(68,69) It has been found that the second derivative can be used as a precise indicator of the nucleation temperature, T_N , of metals, and that higher derivatives become meaningless and prone to electrical noise alteration.⁽⁶⁹⁾ A minimum peak in the second derivative shows the precise moment when the cooling rate, $(dT/dt)_{CC}$, shifts upwards, indicating the start of latent heat evolution. Figure 3.11.



Figure 3.11 Second derivative of the cooling curve indicating the nucleation temperature, T_N , of $\alpha(Al)$ in 319 alloy.

The second derivative has also found use in the detection of minor reactions, such as the formation of iron-rich intermetallics in aluminum foundry alloys. A minimum on the second derivative can be used to identify the initial formation time and temperatures of the Al_5FeSi intermetallic, the aluminum-silicon eutectic and the Mg₂Si-Al eutectic and Al₂Cu-Al eutectics.⁽⁵⁰⁾

These higher order parameters have not been used to any great extent in commercial applications. In general, the grain refinement of aluminum alloys is still measured from the conventional cooling curve using simple undercooling. Nevertheless, it is quite possible that by use of more complex parameters, a better understanding of the state of the melt may be obtained and a better control of the final product can be achieved. The development of such parameters is one of the main aims of this thesis.

3.5 Factors to control in thermal analysis

Several practical factors must be controlled in order to obtain reliable thermal analysis results. The first of these is the pouring temperature of the melt. A high superheat is known to weaken the effect of grain refiners⁽¹⁷⁾ as does prolonged holding of the refiner in the melt,^(17,70) while lower temperatures might produce rapid freezing and give incorrect results.^(55,71) A minimum sampling temperature should be established, bearing in mind the thermal equilibrium of the sample in the cup before nucleation occurs. Several molds (commercial sand cups, graphite molds and preheated steel cups) have been used in the study of thermal analysis in order to assure a uniform temperature distribution across the sample at the beginning of solidification, and to yield high reproducibility and sensitivity in the results.^(17,55,56,60,62,71) Physical stability of the thermal analysis equipment is also important as vibration is believed to cause scattering in the results.⁽⁵⁾

Once the melt has attained equilibrium (thermal and physical) with the sampling cup, the cooling rate of the thermal analysis sample becomes the critical factor to control. It is well known that a fast cooling rate produces refinement of the microstructure, but slower cooling rates yield sharper cooling curves with more obvious arrests.^(58,62) Due to the strong effect of the cooling rate on the microstructure of the sample, measurements taken from a thermal analysis are valid only for that particular cooling rate.⁽⁵⁸⁾

Nucleation and growth of primary aluminum begins at the specimen edge and progresses towards the center of the sample. The accuracy and position of the thermocouple in the test mold are also important factors to control since the thermal conditions vary from one location to another.^(55 62 72) Bäckerud and Sigworth⁽⁶⁰⁾ have introduced the concept of adding two thermocouples to the sampling cup, in order to measure the difference between the temperature at the wall (*Tw*) and at the center of the cup (*Tc*). With this parameter (*Tw*–*Tc*), they have been able to detect metallic phases that have a very low latent heat of transformation.

Chapter 4 Experimentation

4.1 Methodology

The objective of this work was to determine the relationship between the different parameters of the cooling curve and the degree of grain refinement in Al-Si casting alloys, in order to establish a more reliable control parameter in the assessment of quality control of the melt prior to casting. The general methodology used was to produce different degrees of grain refinement in samples of Al-Si foundry alloys using a variety of grain refiners at different levels of addition. Conventional thermal analysis was carried out during the solidification of the samples, at different cooling rates, to study the effect of both degree of refinement and cooling rate on the parameters of the cooling curve and its derivatives.

4.2 Base alloys

For the purpose of this investigation, 319 Al-Si-Cu and 356 Al-Si-Mg alloys were selected due to their excellent castability, mechanical and physical properties, and their importance in the manufacture of automotive castings. In the aluminum-silicon alloy system, shown in Figure 3.2, these alloys are located in the hypoeutectic part of the diagram.⁽²⁾ The standard composition,⁽⁷³⁾ as well as the initial composition of the alloys actually used in this study, are given in Table 4.I. Figures 4.1 (a) and (b) show the typical microstructure of these alloys as received in ingot form.

Chemical Composition of 319 and 356 Alloys					
	*Standard Com	position (Wt. %)	Initial Composition Used (Wt. %)		
Element	319	356	319	356	
Si	5.5 to 6.5	6.5 to 7.5	6.25	7.05	
Cu	3.0 to 4.0	0.25 max.	3.35	0.01	
Mg	0.10 max.	0.20 to 0.45	0.10	0.38	
Fe	1.0 max.	0.6 max.	0.37	0.08	
Mn	0.50 max	0.35 max.	0.10	0.002	
Zn	1.0 max.	0.35 max	0.05	0.01	
Ni	0.35 max.		0.007	0.001	
Ti	0.25 max.	0.25 max.	0.12	0.07	
B			0.0003	0.0003	
AI	Balance	Balance	Balance	Balance	

*Reference 73.

 Table 4.I Chemical composition of 319 and 356 alloys.



(a). 319 alloy.



(b). 356 alloy. Figure 4.1 Microstructure of 319 and 356 alloys.

Both 319 and 356 alloys exhibit a lamellar eutectic silicon structure within the primary aluminum matrix. 319 alloy also contains eutectic Al₂Cu, complex eutectics of Al-Cu-Mg-Si,⁽⁶⁴⁾ and iron intermetallics (Al₅FeSi) in the form of needles. The 356 alloy contains a small amount of the Mg₂Si- α (Al) eutectic.

4.3 Grain refiners

In order to generate different degrees of grain refinement in the samples, four different master alloys were used, as well as two refining salts containing metallic titanium and KBF₄. It was not the main intention of this work to evaluate and establish a comparison between the different refiners, but during the course of the experimentation various observations were made on the effectiveness of each type of grain refiner.

Master alloys were supplied by KBAlloys in the form of waffle ingots. The master alloys selected were Al-6%Ti, Al-5%Ti-1%B, Al-2.5%Ti-2.5%B and Al-5%B. Two salt fluxes in the form of tablets were also used as refining agents. Ti-B, TiLite75BC, produced by Foseco, Inc., and Al-Ti, AlTab, produced by Shieldalloy Metallurgical Corp. were the salt fluxes used. This wide selection of grain refiners covered most of the mechanisms of grain refinement that are supposed to take effect in 319 and 356 alloys. It can be seen from Table 4.II that titanium and boron are the main secondary elements in the master alloys, suggesting the presence of suitable substrates for the heterogeneous nucleation of primary aluminum. The chemical composition of the salt fluxes is also given in Table 4.II.

According to the different theories of grain refinement, the type and morphology of the refining substrates is a factor in the effectiveness of a grain refiner. In order to identify the type of substrates to be released into the melt, the refiners were characterized by scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDS -JEOL JSM-840A), electron microprobe analysis with wave length dispersive spectroscopy (EPMA/WDS - CAMEBEX) and by X-ray diffraction analysis (X-RD Phillips APD 1700).

Chemical Composition of Aluminum Master Alloys (wt.%)								
Grain Refiner	Ti	В	Fe	Si	ĸ	Na	Mg	Al
Al-6%Ti	6.10	0.001	0.20	0.04			0.01	Balance
Ai-5%Ti-1%B	4.90	1.1	0.15	0.06				Balance
AI-2.5%Ti-2.5%B	2.80	2.6	0.17	0.14				Balance
AI-5%B	0.02	5.1	0.12	0.12	0.54	0.16		Balance
			·	1	L	r		
	Chemi	cal Com	positio	n of Sal	t Fluxes	(wt.%)		
Product		Ti			8		Bala	ince
*TiLite75BC		75% Metallic Ti		1.5% B as KBF.			KCI	
**AlTab		75% Metallic Ti					KAIF	

*Distributed by FOSECO.

**Distributed by Shieldalloy Metallurgical Corp.

 Table 4.II Chemical composition of grain refiners.

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4.4 Sample preparation

Grain refined samples were produced for the two Al-Si alloys by melting 3 kg of metal in a 10-kg graphite crucible using a gas furnace at 730 °C. To achieve different degrees of grain refinement, master alloys and fluxes were added to the melt to raise the titanium and/or boron content in the alloy. The target titanium and boron addition levels for each case are indicated in Table 4.III.

Ti and B Addition Levels for 319 and 356 Alloys				
		319 Alloy	356 Alloy	
Sample Identification	Grain Refiner	Ti target (Wt.%)	Ti target (Wt.%)	
1	AI-6%Ti	0.14	0.09	
2	68 66	0.16	0.12	
3	66 66	0.20	0.16	
4	AI-5%Ti-1%B	0.14	0.09	
5	66 68	0.16	0.12	
6	66 66	0.22	0.17	
7	AI-2.5%Ti-2.5%B	0.14	0.09	
8	66 66	0.16	0.12	
9	68 68	0.22	0.17	
10	TiLite75BC	0.16	0.12	
11	66 66	0.22	0.17	
12	86 68	0.32	0.25	
13	AlTab	0.14	0.09	
14	66 66	0.16	0.12	
15	66 66	0.22	0.17	
		B target (Wt.%)	B target (Wt.%)	
16	AI-5%B	0.015	0.015	
17	66 66	0.023	0.023	
18	68 66	0.038	0.038	

Table 4.III Target Ti and B addition levels for 319 and 356 alloys.

A specific amount of grain refiner, wrapped in aluminum foil, was added to the melt by immersion using a graphite plunger. The exact amount of refiner was calculated from the weight of the base alloy melted and the residual titanium content in the alloy. The time allowed for dissolution of the refiner in the melt was 5 minutes at 730 °C. Prior to casting the samples, mechanical stirring of the melt was done for 20 seconds to reduce fading of the refiner due to settling of the substrates released in the melt. It is known that as little as 5 minutes is enough time for a refiner to dissolve in the melt and become effective.⁽³⁹⁾ Stirring of the melt prior to casting is known to recover the effectiveness of the refiners due to redistribution of the substrates in the melt.⁽³⁴⁾ Figure 4.2 shows a schematic of the mechanism of refiner addition to the melt.



Figure 4.2 Refiner addition to the melt using a graphite plunger.

Once the melt was inoculated, six cylindrical samples were produced for each addition level of titanium or boron: three for fast cooling rate experiments and three for low cooling rate experiments. In this way, the repeatability of the results could be monitored. A sample for spectrochemical analysis was also obtained for each case, to determine the actual amount of the refining elements present in the thermal analysis samples. Spectrochemical analysis of the samples was performed at Nemak, S.A. with an optical emission spectrometer (Spectrolab X-7 by SPECTRO) with elemental range of 0 to 0.5 wt.% for titanium and 0 to 0.04 wt.% for boron.

The samples were cast in graphite crucibles coated with boron nitride, Figure 4.3. These crucibles were later used for remelting of the samples in an induction furnace, for the thermal analysis experiments.



Figure 4.3 Graphite crucible for sample production.

4.5 Solidification and data acquisition

For the generation of thermal analysis results, samples in the as-received condition and grain refined condition were remelted in graphite crucibles, Figure 4.3, using an induction furnace (Inductotherm 150-30R). The time for remelting the samples was between 5 to 10 minutes before the temperature reached 730 °C. The induction stirring generated by the furnace, allowed proper mixing of the melt to avoid settlement of the refining particles. Once the samples reached 730 °C, the crucibles were placed over an insulating material (Fiberfrax). The liquid samples were not poured into different

molds to avoid the chill effect of colder walls and loss of temperature during the transfer. Rather, the samples were solidified inside the graphite crucibles themselves at two different cooling rates. Cooling rates of approximately 1 °C/s were achieved by solidifying the sample in the graphite mold at room temperature (fast cooling rate). Cooling rates of approximately 0.1 °C/s (low cooling rate) were obtained by placing an insulating cover (Fiberfrax) around and on top of the graphite crucible, Figure 4.4.



Figure 4.4 Methods to obtain two different cooling rates using graphite crucibles.

Chromel-alumel (K-type) thermocouples with a 0.81 mm sheath diameter were introduced in the wall and in center of the crucibles, at 20 mm from the bottom to register the temperature during solidification. This technique was developed by Bäckerud,⁽⁶⁴⁾ who used it to register the beginning of nucleation and the coherency point of the dendritic structure.

The thermocouples were covered with a stainless steel sheath to be recovered after each experiment. The same two-thermocouple set was used for all of the experiments of a particular alloy and cooling rate, to ensure the same temperature accuracy in that set of experiments. Thermocouples were calibrated at two reference temperatures, the equilibrium freezing temperature of pure aluminum (660.3 °C), and the eutectic temperature of the pure binary Al-Si system (577 °C). The accuracy of the thermocouples used for each set of experiments is reported in Chapter 6. The temperature of the samples was measured until just after the final liquid present in the alloy had solidified (below 480 °C), for both 319 and 356 alloys.

A DS-16-8-TC DATA*shuttle*TM 16 bit data acquisition system was connected to the thermocouples by shielded extension grade thermocouple wire to digitalize the analog signal and to store it in a 75 MHz Pentium processor personal computer. The data acquisition system allowed for high noise rejection and accurate cold junction compensation. An interface software (QuickLog PCTM) allowed modification of the rate of data acquisition, which was registered at 10 Hz (every 0.1 sec.) for the fast cooling rate and at 2 Hz (every 0.5 sec.) for the low cooling rate experiments. Data were stored in the hard drive of the computer, to be analyzed later by a thermal analysis software. Figure 4.5 shows a schematic diagram of the system used for thermal analysis data acquisition and analysis.

The importance of the rate at which data is registered has been poorly addressed in previous conventional thermal analysis experiments,⁽⁷⁴⁾ and some practical advice is necessary in order to retrieve valuable and more precise information from a thermal analysis experiment. Experiments were run to observe the effect that different data acquisition rates had on the thermal analysis parameters. 356 alloy specimens (0.08wt.% Ti) from the same melt were solidified, following the procedure mentioned before, at 1.1 and 0.15 °C/s. The freezing temperature was registered at 2, 5 and 10 Hz and the respective cooling curves and derivatives were analyzed. Results are reported in Chapter 6.



Figure 4.5 System for data acquisition and thermal analysis.

4.6 Thermal analysis

Data from the thermal analysis experiments were given in situ as cooling curves by the interface software, and stored as temperature and time columns in ASCII format in the PC. A Pascal program, developed at the Universidad Autónoma de Nuevo León, México by Prof. R. Colás, calculated the first and second derivatives of the cooling curve and allowed detailed analysis of the curves. The program uses an algorithm that adjusts a parabolic curve of the type ($T = a + bt + ct^2$) by the least squares method, to an odd number of temperature-time (T-t) values. The values of a, b, and c are the coefficients of the parabola that best fits the (T-t) values. By selecting a higher odd-number of (T-t) values, a smoothing of the curves is produced, reducing the noise which occurs mainly in the derivative curves. The effect of smoothing on the thermal analysis parameters was analyzed and will be discussed in Chapter 6.

The parameters analyzed from the cooling curve are shown in Figure 4.6 and explained in Table 4.IV.



Figure 4.6 Cooling curve parameters.

Parameter	Represents		
T _N	Nucleation temperature (°C)		
Τ _υ	Maximum undercooling temperature (°C)		
T _R	Maximum recalescence temperature (°C)		
ΔT_{R-U}	Difference between $T_R - T_U$ (°C)		
ΔT_{N-U}	Difference between $T_N - T_U$ (°C)		
ΔT_{N-R}	Difference between $T_N - T_R$ (°C)		
t _N	Nucleation time (sec.)		
tu	Time of beginning of recalescence (sec.)		
t _R	Time of end of recalescence (sec.)		
t ₁	Duration of recalescence (sec.)		
t ₂	Time elapsed between nucleation and		
	beginning of recalescence (sec.)		
t ₃	Time elapsed between nucleation and end of		
	recalescence (sec.)		

 Table 4.IV Parameters of the cooling curve.

The parameters related to the beginning and end of recalescence could be determined directly from the cooling curve, but for the parameters related to the nucleation temperature, the first and second derivatives of the cooling curve had to be used. In most of the cases, the time parameters were obtained from the derivatives and the temperature parameters were taken from the cooling curve using the appropriate time values.

Since the first derivative is the change in slope of the cooling curve, the times of beginning and end of recalescence (minimum and maximum on the cooling curve) are detected as zeros on the first derivative curve (dT/dt = 0), Figure 3.7. The nucleation time was defined as indicated in section 3.4, from a minimum peak on the second derivative, Figure 3.11.

Even though two thermocouples were used, all the parameters were determined from the thermocouple placed at the center of the sample. The reason for this was the different accuracy of the commercial thermocouples used, which varied as much as -2 °C. Figure 4.7 shows the registered temperatures from three commercial K-type thermocouples for the freezing temperature of pure aluminum.



Figure 4.7 Liquidus temperature of pure aluminum as registered by commercial thermocouples.

Good comparisons between wall and center temperatures require that both thermocouples should have a similar accuracy. This was not possible to achieve with the commercial thermocouples used, but some analysis using the differences in temperature between the wall and the center was performed and will be discussed in Chapters 6 and 7.

The area below the first derivative curve was analyzed by CA-CCA (section 3.3) and a correlation between grain size and latent heat evolution from 319 samples solidified at $1.0 \,^{\circ}$ C/s was made. These results will be discussed in Chapters 6 and 7.

For the calculation of latent heat evolved from the phase transformation.⁽⁶⁸⁾ the first derivative of the cooling curve of the neutral reference. Equation 3.2, had to be obtained. Integrating Equation 3.2 from the maximum initial temperature, T_1 , to a certain temperature, T, the following was obtained,

$$\int_{T_{1}}^{T} dT / (T - T_{0}) = \int_{0}^{t} (-hA / V\rho C_{p}) dt$$
 (Equation 4.1)

$$(T - T_{o}) / (T_{i} - T_{o}) = \exp(-hA / V\rho C_{p}) t$$
 (Equation 4.2)

Thus, the cooling curve of the neutral reference is given by:

$$T_{\rm NR} = C_1 \exp\left(-C_2 t\right) + T_0 \qquad (Equation 4.3)$$

and the respective derivative is given by:

$$(dT/dt)_{NR} = -C_1C_2exp(-C_2t)$$
 (Equation 4.4)

where:

$$C_1 = T_i - T_o$$
$$C_2 = hA / V\rho C_p.$$

The values for the calculation of C_1 and C_2 were obtained from experimental data and reported values in the literature.⁽⁷³⁾ For the 319 alloy these values are as follows:

 $\rho = 2.79 \text{ g/cm}^3$ $C_p = 963 \text{ J/kgK}$ $V = 50.265 \text{ cm}^3$ $A = 50.265 \text{ cm}^2$

The value for the apparent heat transfer coefficient. h. was calculated from Equation 3.2 using experimental data from the cooling curve of the specimens in the liquid state, just before the nucleation temperature. $T_{\rm N}$.⁽⁶⁷⁾ The latent heat was calculated using Equation 3.8, and the solid fraction evolved during solidification was calculated according to Equation 4.5.⁽⁶⁸⁾

fs =
$$(C_p / L) \int_{0}^{t} [(dT/dt)_{CC} - (dT/dt)_{NR}] dt$$
 (Equation 4.5)

where:

 $L = Q_L / V \rho$.

4.7 Grain size measurement

Conventional techniques for grain size measurement, developed mainly for wrought aluminum alloys, consist of the grinding and fine polishing of a sample, an often difficult to achieve anodizing step, and an examination under crossed polarizers. Such techniques give good results, but are long and difficult to accomplish. A more simple technique, which is less time consuming, easier to achieve, and relatively inexpensive was developed for grain size measurement in this investigation.⁽⁷⁵⁾

Samples were cut 20 mm from the bottom transversally, at the point where temperatures were measured and ground on 120, 240, 400 and 600 grit paper. The rotation speed of the grinding wheel used was 300 rpm, and it was often found possible to eliminate the 600 grit grinding step. It was also found that there was no need to polish the surface, since results obtained after etching polished surfaces were not better than those produced on as-ground samples. The choice of the chemical etchant for the different Al-Si alloys (319 and 356) depended on the alloy composition. Table 4.V lists the chemical solutions used and the etching procedure for the two alloys. Ultrasonic cleaning was done as a final step after etching, if the samples were to be stored for some time.

Once the surface was etched and the grains were revealed, the samples were viewed with a stereoscopic microscope, or with a camera with an appropriate macrozoom lens. To better highlight the grain structure, filtered lights at different incident angles were used. Absorption filters were employed to produce nearly monochromatic light. A combination of red, green, blue and yellow light gave an enhanced contrast to the grain structure. This examination was better carried out in a dark room.

ALLOY	ETCH COMPOSITION	PROCEDURE	
		Immerse sample for 20	
	As used by Barker (76)	seconds or until desired	
319	10 ml HF	contrast is obtained. Swab	
	15 ml HCl	with HNO_3 to desmut, and	
	25 ml HNO₃	rinse in running water for 1	
	50 ml H₂O	minute.	
		Swab surface until contrast in	
	FeCl ₃ aqueous solution ^(77,78)	revealed grains is high	
356	35 g FeCl₃	enough. Swab with HNO ₃ to	
	200 ml H2O	desmut, and rinse in running	
		water for 1 minute.	



Four 110 volt, 75 watt opal lamps were used, and the distance from the light source to the sample surface, as well as the incident angle, had to be adjusted according to the contrast desired. The distance and the incident angle were a direct function of the intensity of the light used. It was necessary to homogeneously illuminate the sample surface with each of the colored lights to avoid patches that reduced the contrast between grains in certain regions of the surface. As many colors as desired could be used, and each lamp could be set in order to obtain the best surface illumination. Figure 4.8 presents the set-up used for viewing. The four lamps face the sample, and a 35-mm camera is fixed above the sample.



Figure 4.8 Set-up for macroscopic analysis.

The output image obtained by this method was photographed on 35-mm negative film using a camera equipped with a 55-mm zoom lens and a 2X tele-converter. A scale was also photographed to assess the final magnification of the printed photographs. The grain size of the samples was measured by the intercept method,⁽⁷⁹⁾ using an array of 5 parallel lines with a total length of 250 mm, placed over the photographs, which had the

appropriate magnification to allow a proper statistical analysis of the grain size, Figure 4.9. Counts were done in ten fields of each sample, and the standard deviation of the counts was calculated.



Figure 4.9 Macrograph of 356 alloy and parallel-line array for grain counting.

Chapter 5

Experimental Results on Grain Refinement

5.1 Grain refiner characterization

Al-6%Ti Master Alloy

The microstructure of the Al-6%Ti master alloy shows needle-like precipitates with an average length of 200 μ m, embedded in an aluminum matrix. The SEM/EDS analysis characterized these precipitates as TiAl₃ by calculating the atomic and weight percent of titanium and aluminum in these particles. X-ray diffraction analysis also identified the TiAl₃ particles by the presence of high intensity peaks of this phase. The microstructure of the master alloy as well as the X-RD and SEM/EDS analysis are presented on page A-1 of appendix A. Appendix A also summarizes the characterization information for the other grain refiners.

Al-5%Ti-1%B Master Alloy

The Al-5%Ti-1%B master alloy also contained the TiAl₃ phase, but with a blocky morphology of approximately 50 μ m average diameter. This phase was also identified by SEM/EDS and X-RD analysis (page A-2). Clusters of another precipitate were also observed and identified as TiB₂ (and probably (Al,Ti)B₂), segregated to the grain boundaries of the aluminum matrix. X-RD analysis and X-ray mapping using EPMA/WDS allowed the identification of the TiB₂ phase. Page A-3 in appendix A shows a secondary electron image of the microstructure of the Al-5%Ti-1%B master alloy, as well as the X-ray maps for titanium and boron present in the master alloy.

Al-2.5% Ti-2.5% B Master Alloy

In this master alloy, the identification of the refining particles was a little more difficult, because the particles were agglomerated in globular clusters of approximately 50 µm average diameter. X-ray mapping showed a high concentration of Ti and B in these clusters, and X-ray diffraction analysis showed peaks of TiAl₃, and TiB₂, suggesting the presence of a mixture of substrates within these globular-like precipitates. Page A-4 shows the microstructure of this alloy, the spectrum of the X-RD analysis and the X-ray maps for titanium and boron.

Al-5%B Master Alloy

The Al-5%B master alloy contained blocky AlB₂ particles clustered around cavities containing Na, K and F, presumably from the salts used to produce the master alloy. AlB₂ was identified by X-ray diffraction analysis, and no AlB₁₂ was found. The AlB₁₂ phase is not considered an appropriate substrate for the nucleation of primary aluminum.⁽¹⁴⁾ Page A-5 shows the microstructure and the X-RD pattern of this master alloy, as well as the EPMA/WDS analysis for the AlB₂ phase. Page A-6 shows a cavity in the microstructure of the master alloy, and the spectrum of the EDS analysis showing the presence of Na, K and F.

Salt Fluxes

Both TiLite75BC and AlTab were analyzed by X-ray diffraction. The analysis showed the presence of metallic titanium and KAlF₄ for the AlTab salt flux, and KBF₄ and KCl for the TiLite75BC salt flux, as indicated by the chemical composition provided by the distributors. The presence of metallic titanium in the TiLite75BC salt flux was not corroborated in the analysis, possibly due to titanium segregation during sample preparation. Page A-7 shows the X-RD patterns for both AlTab salt flux and TiLite75BC salt flux.

5.2 Ti and B recovery in grain refined samples

Once the base metal was refined with the different master alloys, the chemical composition of each of the samples was analyzed in order to determine the exact composition, and consequently the recovery of titanium and boron. Table 5.I presents the results of the titanium and boron content in the samples refined for the 319 and 356 alloys. The target values for each element can be found in Table 4.III (page 43).

Ti and B Concentration in Refined Samples				
for 319 and 356 Alloys				
		319 Alloy	356 Alloy	
Sample	Grain Refiner			
Identification		Ti obtained (Wt.%)	Ti obtained (Wt.%)	
1	AI-6%Ti	0.136	0.096	
2	56 LS	0.146	0.119	
3	66 66	0.178	0.143	
4	Al-5%Ti-1%B	0.139	0.091	
5	16 51	0.161	0.106	
6	66 66	0.231	0.140	
7	Al-2.5%Ti-2.5%B	0.132	0.078	
8	66 66	0.140	0.065	
9	64 66	0.119	0.120	
10	TiLite75BC	0.117	0.078	
11	46 66	0.122	0.080	
12		0.135	0.095	
13	AlTab	0.115	0.074	
14	68 46	0.123	0.078	
15	66 66	0.126	0.075	
		B obtained (Wt.%)	B obtained (Wt.%)	
16	AI-5%B	0.0030	0.0046	
17	66 66	0.0077	0.0076	
18	66 66	0.0161	0.0106	

Table 5.I Ti and B concentration in refined samples of 319 and 356 alloys.

Figures 5.1 (a) through (f) show the titanium (or boron) recovery from each of the grain refiners for 319 and 356 alloys. Because the starting material always contained a certain amount of either titanium or boron, the recovery is defined by Equation 5.1.

Recovery = Obtained Concentration – Initial Concentration X 100% (Equation 5.1) Target Concentration – Initial Concentration.



ſ	а	١
Ľ	α	,



(b)


(c)



(d)

60



Figures 5.1 (a-f) Titanium and boron (for Al-5%B master alloy) recovery from the grain refiners for 319 and 356 alloys.

5.3 Grain size measurement

Grain size of the grain refined samples was measured by the line intercept method.⁽⁷⁹⁾ A pattern (array of 5 parallel lines, measuring 50 mm each) was placed over the photographs and counts of grains intercepting the lines were made in 12 randomly chosen fields. Each grain, totally crossed by a line, counted as one intercept, and when grains were partially crossed (at the tip of the lines) a value of half an intercept was considered. The fields with the highest and lowest counts were eliminated and the counts of the other ten fields were considered for grain size measurement.

For statistical assessment of the results, the following values were obtained:

N_{i} ,	number of total intercepts per field.
Σ,	number of total intercepts per sample.
$\tilde{N} = \Sigma / 10.$	average value of intercepts per field.
$\Delta N_{\rm i} = N_{\rm i} - \tilde{N}.$	deviation from the average per field.
ΔN_i^2 .	squared value of ΔN_i per field,
$\Sigma \Delta N_i^2$,	sum of ΔN_i^2 per sample.
$V_0 = \left[\left(\Delta N_1 \right)^2 + \right]$	$(\Delta N_2)^2 + (\Delta N_i)^2] / (i-1) =$ variance of the observed counts (i = 10)
$s_0 = \sqrt{V_0},$	standard deviation of the counts
$\mathbf{C}.\mathbf{V}.=s_0/\tilde{N},$	coefficient of variation of the counts
\sqrt{N}	squared root of average value of intercepts per field.

Table 5.II shows a typical worksheet for the grain size measurement of a 356 sample refined with Al-5%Ti-1%B master alloy. Usually, two or three photographs per sample had to be taken to obtain measurements from all the sample. The magnification of the photographs used for each particular sample is also given in Table 5.II. The results for grain size measurement of all the samples are given in Appendix B, and include the most significant statistical values obtained, that is \sqrt{N} , s_0 and C.V., as well as the magnification used in the photographs.

Sample				Line			5	al	
356 alloy		1	2	3	4	5			
	Field			1		<u>. </u>	Sum	$\Delta N_{\rm i}$	ΔN_{i}^{2}
			11	ntercept	S				
Master Alloy	1	15.5	15.5	13 5	12	14	70.5		
AI-5%Ti-1%B	2	11	11.5	12.5	14	13	62	-3.25	10.56
Wt.% Ti	3	15	14	15	14	12	70	4.75	22.56
0.14	4	13	12	14	12	12	63	-2.25	5.06
Magnification	5	16.5	11.5	12	13	15.5	68.5	3.25	10.56
8.4 X	6	16	13	14.5	10.5	14	68	2.75	7.56
Notes	7	14.5	13	13	13.5	14	68	2.75	7.56
	8	13	15.5	11	11	10.5	61	-4.25	18.06
	9	14.5	16	12	11	10	63.5	-1.75	3.06
	10	11.5	13	15	12	13	64.5	-0.75	0.56
	11	14	12	12	12	14	64	-1.25	1.56
	12	9	85	13	10	135	54		
Total Length = 250mm x 10 fields = 2500r				= 2500m	m	Σ	652.5	$\Sigma \Delta N_i^2$	87.13
Real Length = 2500mm / 8.4 = 297.62mn				1	Ñ	65.25	V ₀	9.68	
						\sqrt{N}	8.07	<i>S</i> ₀	3.11
Grain Size = (Real Length x Σ) x 1000 [=] μ m				[=] μ m	Grair	Size	456 μm	C.V.	0.047

Table 5.II Worksheet for the grain size measurement of a 356 alloy sample.

Figure 5.2 shows macrographs of 356 alloy samples solidified at ~1.0 °C/s with different grain sizes. In general, primary dendrite arms become shorter as grain size is reduced, until a globular-like grain morphology is obtained, as seen when the grain size became 316 μ m. The repeatability of grain size results in the triplicate samples improved as the grain size was reduced. Figure 5.3 shows the difference from the average grain size for 319 alloy samples solidified at ~1.0 °C/s. Secondary dendrite arm spacing (DAS) is not affected by grain refinement, but does vary with differences in cooling rate. The

cooling rate was measured from the first derivative of the cooling curve, at the point just before nucleation of primary aluminum.

Figure 5.4 shows DAS measurements for 4 different grain sizes in 319 and 356 samples solidified at ~1.0 and ~0.1 °C/s. Micrographs of 319 samples (Figures 5.5 a-c) with different grain sizes solidified at ~1.0 °C/s show how the secondary dendrite arm spacing remains constant while the primary dendrites become shorter. The tree-like structure (Figs. 5.5 a and b) degrades down to a rosette-like structure (Fig. 5.5 c), with only a few of the secondary arms attached to primary stems.



Figure 5.2 Macrographs of 356 samples solidified at ~1.0 °C/s with differences in average grain size.



Figure 5.3 Difference from the average grain size for 319 alloy samples solidified at ~1.0 °C/s.

Effect of Grain Size on DAS



Figure 5.4 Effect of grain size and cooling rate on secondary dendrite arm spacing (DAS) for 319 and 356 alloys, solidified at ~1.0 and ~0.1 °C/s.





b) Grain Size = $654 \mu m$.



c) Grain Size = $332 \mu m$.

Figures 5.5 (a-c) 319 samples with different grain size solidified at ~1.0 °C/s.

5.4 Grain refiner effectiveness

Differences in grain refining effectiveness were observed between the different master alloys and salt fluxes used in this investigation. Results are shown in graphical form in Figures 5.6 (a-f). The average grain size is plotted versus the analyzed titanium content for the Al-6%Ti and Al-5%Ti-1%B master alloys and the AlTab salt flux. For the Tilite75BC salt flux and the Al-2.5%Ti-2.5%B and Al-5%B master alloys, the average grain size is plotted versus the analyzed boron content since the effect of boron seems to correlate better with grain size of the samples.



a) Al-6%Ti master alloy.



b) Al-5%Ti-1%B master alloy.

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c) AlTab salt flux.

TiLite75BC Salt flux



d) TiLite75BC salt flux.



e) Al-2.5%Ti-2.5%B master alloy.



f) Al-5%B master alloy.

Figures 5.6 (a-f) Refining effectiveness of master alloys and fluxes on 319 and 356 alloys.

Chapter 6 Experimental Results on Thermal Analysis

In this chapter, different parameters of the cooling curve are correlated to grain size of 319 and 356 alloy samples, in order to obtain a reliable control parameter for the assessment of grain refinement of Al-Si casting alloys by thermal analysis. First, an analysis of temperature measurement accuracy and data acquisition rate is presented to stress the importance of these factors in the application of the thermal analysis technique.

6.1 Temperature measurement accuracy

In total, eight thermocouples were used during this investigation. Two commercial Ktype thermocouples per experimental condition were used, and the accuracy of the readings was monitored by melting pure aluminum and a pure binary Al-Si alloy and registering the equilibrium freezing temperature and the eutectic temperature, respectively, at the center of samples. Several readings were done at different intervals during a set of experiments. Appendix C shows in a graphical form the accuracy measurements for the eight thermocouples used. The thermocouple life, on the horizontal axis of the graphs, represents the number of times each thermocouple was previously used. From these measurements, the following observations can be summarized:

- Actual temperature measurements were always lower than the calibration temperatures, in some cases 2 to 3 °C below the expected temperatures, Figure C.1 (a).
- 2. In most of the cases, the temperature differences between the two thermocouples used for each set of experiments were nil for the initial experiments, but after some use, a

difference in measurements was detected, but this difference remained more or less constant, Figure C.2 (a).

- A slightly better accuracy was observed at the lower calibration temperature (577 °C), Figures C.3 (a-b).
- 4. In most cases the accuracy of the thermocouples was maintained. Figures C.4 (a-b), but that was not always the case.

Table 6.1 shows the average accuracy of two thermocouples used for 319 alloy samples solidified at ~ 1.0 °C/s. Thermocouple # 3 was used to measure the wall temperature of the samples and thermocouple # 4 measured the center temperature of the sample while solidifying.

	Calibration Temp.			Calibration Temp	
	660.3 °C			577.	0°C
Thermocouple Life	Thermocouple		Thermocouple Life	Thermocouple	
(Previous	# 3	#4	(Previous	# 3	#4
Measurements)	T (°C)	T (°C)	Measurements)	T (°C)	T (°C)
0	657.99	658.07	5	575.83	576.02
1	658.21	658.16	6	575.66	575.76
2	658.17	658.15	7	575.76	575.83
3	658.09	658.17	8	575.81	575.78
4	658.16	658.18	9	575.55	575.68
22	658.56	658.15	23	575.68	575.50
33	658.65	658.28	34	575.50	575.38
44	658.57	658.17	45	575.28	575.10
55	658.73	658.23	56	575.52	575.20
66	658.59	657.90	67	575.27	574.66
77	658.48	657.32	78	575.15	574.52
Avg. Temp. (°C)	658.38	658.07	Avg. Temp. (°C)	575.55	575.40
Avg. Accuracy (°C)	-1.94	-2.25	Avg. Accuracy (°C)	-1.45	-1.60

Table 6.I Accuracy of thermocouples used for 319 alloy solidified at ~ 1.0 °C/s.

Thermocouple Response Time

Another aspect of temperature measurement is the response time of the thermocouples used, particularly in systems involving fluids undergoing phase changes. No instrument responds instantaneously to changes in the environment, thus the response of a temperature sensor is characterized by a first order thermal response time, τ , which is defined by Equation 6.1.⁽⁸⁰⁾

$$\tau = \rho V C_{o} / hA \qquad (Equation 6.1)^{(80)}$$

where:

 τ = response time of thermocouple

 ρ = density of thermocouple

V = volume of thermocouple

 C_p = specific heat of thermocouple

h = heat transfer coefficient of the liquid

A = area of the liquid in contact with the thermocouple.



Figure 6.1 Graphical representation of a temperature ramp change.⁽⁸⁰⁾

In cases where lineal changes in temperature occur (known as ramp changes), for temperature sensors immersed in an environment whose temperature is rising (or falling) at a constant rate, dT/dt, τ is the interval between the time when the environment reaches a given temperature and the time when the sensor indicates this temperature. Figure 6.1 shows this in a graphical form. For practical purposes, the sensor will reach the new temperature at approximately 5τ after the beginning of the ramp change.⁽⁸⁰⁾ Conventionally, the response time is defined as the time required to reach 63.2% of an instantaneous temperature change.



Figure 6.2 Response time study, in water, of metal sheathed thermocouples.⁽⁸¹⁾

For the commercial thermocouples used, the manufacturer (OMEGA Engineering Inc.)⁽⁸¹⁾ indicates a response time of approximately 0.25 seconds for 0.81 mm sheath diameter probes immersed in water. Figure 6.2. Since an additional stainless steel sheath was used for recovering the thermocouples, the response time was calculated from Figure 6.1 and from experimental data. Figure 6.3 shows results of an experiment where the melt temperature was detected in approximately 2 seconds after immersion of a thermocouple at room temperature. If this time lag (2 sec.) is considered as 4τ from Figure 6.1, the response time, τ , for the thermocouple used would be 0.5 seconds, twice the value indicated by the manufacturer. Nevertheless, once the thermocouples were immersed in the melt, approximately 50 seconds (for the fast cooling rate) and 200 seconds (for the slow cooling rate) elapsed from the maximum temperature measured, T_1 , to the nucleation temperature, T_N (at around 610 °C). Figure 6.4. This relatively long time permitted thermal equilibrium to be reached between the melt and the thermocouples prior to the onset of solidification.



Figure 6.3 Detection of melt temperature after 2 seconds. Thermocouple immersion was done at approximately 20.5 seconds on the time scale.



Figure 6.4 Time elapsed from maximum temperature measured to nucleation temperature, T_N (at approximately 610 °C).

6.2 Data acquisition and curve smoothing

A set of experiments was performed to analyze the effect of data acquisition rate and curve smoothing on the thermal analysis parameters. Figures 6.5 and 6.6 show the first derivative of the cooling curve at the onset of nucleation, where the first derivative (or cooling rate) is more or less constant when the liquid is cooling, and then sharply deviates upwards when latent heat is evolved from solidification. Results indicate that when a larger number of data points is acquired per second (10 Hz), the cooling curve becomes smooth, but the first derivative becomes noisy, hiding possible reactions that could be occurring during solidification. The graphs in the left portion of Figure 6.5 show the noise reduction in the first derivative as fewer data points are acquired per second (5 Hz and then 2 Hz), at a cooling rate of $1.1 \,^{\circ}$ C/s). It is observed that at lower cooling rates (0.15 $^{\circ}$ C/s), the effect of the data acquisition rate is more pronounced, that is, higher data acquisition rates (5 Hz) produce much higher noise levels on the derivative curve.



Figure 6.5 Effect of data acquisition rate and curve smoothing on the first derivative for a cooling rate of 1.1 °C/s. 356 alloy (0.08wt.% Ti).

A mathematical smoothing function can be used to reduce the noise in the derivative curves, by increasing the number of (T-t) values fitting in the parabola ($T = a + bt + ct^2$) by the least squares method. The effect of choosing a 10 step smoothing (step = odd-number of (T-t) values + 1) over a no-smoothed curve (2 step smoothing) can be seen by comparing the left and right hand graphs presented in Figures 6.5 and 6.6.



Figure 6.6 Effect of data acquisition rate and curve smoothing on the first derivative for a cooling rate of 0.15 °C/s, 356 alloy (0.08wt.% Ti).

It is evident that the smoothing in the derivatives is improved with lower data acquisition rates, and that smoother curves are obtained at higher cooling rates. In order to obtain reliable parameters from the thermal analysis technique, data should be collected and analyzed in the proper way. Thus, it is important to know the effect of data acquisition rate and smoothing on the thermal analysis parameters, for a particular cooling rate.

It must always be kept in mind that although enough data per second are necessary to detect certain minor reactions during solidification (usually on the first derivative curve), the amount of noise, brought on by the derivation of the cooling curve itself, may hide these reactions. Critical points on the derivative curve such as the onset of nucleation are not clear when a noisy curve is analyzed.



Figure 6.7 Effect of data acquisition rate and curve smoothing on the second derivative for a cooling rate of 1.1 °C/s, 356 alloy (0.08wt.% Ti).

When analyzing the second derivative of the cooling curve, the effect of higher data acquisition rates is also evident, as well as the effect of the mathematical smoothing. A second derivative peak related to the nucleation of primary aluminum is not detected with the raw second derivative (smooth 2) acquired at 10 Hz (top left corner of Figure 6.7). But when mathematical smoothing is used (smooth 10), the peak is noticed (encircled at top right corner of Figure 6.7). At lower data acquisition rates (2 Hz), the peak is observable from the raw data (bottom left corner of Figure 6.7), but is more

evident on the smoothed curve (smooth 10, bottom right corner of Figure 6.7). This peak may appear difficult to distinguish from all the noise in the second derivative, but if one refers to Figure 3.11 (page 36), it is evident that the sharp deviation of the first derivative coincides with the minimum peak (or valley) observed on the second derivative. In this way, a reference time for the location of this peak is obtained from the first derivative.

Derivation (first and second) of the cooling curve brings valuable information along with noise. When higher data acquisition rates are necessary, mathematical smoothing of the curves (cooling curve and derivative) is used to reduce this output noise, but since mathematical noise reduction involves alteration of the raw data, this may in some way affect the values of the thermal analysis parameters.



Figure 6.8 Deviation of $\Delta T_{\text{R-U}}$ due to smoothing for a 356 alloy (0.08%Ti) solidified at ~ 1.0 °C/s.

The effect of curve smoothing on two parameters was analyzed. First, the change in $\Delta T_{\text{R-U}}$ with degree of smoothing is presented in Figure 6.8. The black circles represent the $\Delta T_{\text{R-U}}$ value when the cooling curve is smoothed progressively in intervals of 10 steps up to 100 steps. A slight deviation from the value obtained from the raw data (0 steps) is noted as the number of smoothing steps increases. However, when the cooling curve is smoothed in a straight operation (with 10, 20, 30...or 100 steps) the $\Delta T_{\text{R-U}}$ deviates much more from the original value (open triangles).

The time parameter t_1 , was the other parameter analyzed, for which, raw and smoothed cooling curves (*sc* on Figure 6.9) were used. In a similar way to Figure 6.8, Figure 6.9 exhibits the effect of smoothing the derivative curve at progressive intervals (circles) and in a straight way (triangles). Again, interval smoothing tends to keep the time parameter close to the original t_1 value, whereas straight smoothing shifts the values downward. It is also observed that results obtained from an initial raw cooling curve (open symbols), do not vary from the results obtained using a previously smoothed cooling curve (*sc*, black symbols), Figure 6.9.

This discussion indicates that whenever graphical data are smoothed, valuable results can be obtained if smoothing is done in a proper way. Smoothing of the initial cooling curve can improve the output of the first and second derivative curves, without affecting the original values of certain thermal analysis parameters.



Figure 6.9 Deviation of t_1 due to smoothing for a 356 alloy (0.08%Ti) solidified at ~ 1.0 °C/s.

6.3 Correlation between thermal analysis parameters and grain size

The thermal analysis parameters studied include most of the parameters indicated in Table 4.IV. The results of all the values obtained from the thermal analysis experiments are given in Appendix D. Triplicate samples were taken for each experimental condition to assess the repeatability of the measurements. To analyze the repeatability, the average value of the three replicas was obtained for each thermal analysis parameter, and the difference of each measurement from the average was calculated. The differences of all the experiments were averaged for each base alloy (319 and 356). Table 6.II shows the average of these differences, where it can be seen that the ΔT_{R-U} parameter shows the least average variability (+/- 0.11 °C or less). The parameter with the most variability is t₃ (from +/- 0.77 to +/- 1.43 sec.)

	Reproducibility of Thermal Analysis Parameters								
		(Taken	from A	verage	of Triplic	ate Sarr	nples)		
Alloy	Τ _U	T _R	T _N	$\Delta T_{\rm R-U}$	$\Delta T_{\rm N-U}$	$\Delta T_{\rm N-R}$	t ₁	t ₂	t ₃
ę c	(°C)	(°C)	(°C)	(°C)	(°C)	(°C)	(sec.)	(sec.)	(sec.)
319	+/-	+/-	+/-	+/-	+/-	+/-	+/-	+/-	+/-
(1.0 °C/s)	0.21	0.18	0.55	0.11	0.53	0.51	0.50	0.49	0.77
319	+/-	+/-	+/-	+/-	+/-	+/-	+/-	+/-	+/-
(0.1 °C/s)	0.08	0.09	0.28	0.05	0.26	0.27	0.49	1.31	1.43
356	+/-	+/-	+/-	+/-	+/-	+/-	+/-	+/-	+/-
(1.0 °C/s)	0.24	0.22	0.58	0.09	0.45	0.49	0.48	0.59	0.81
356	+/-	+/-	+/-	+/-	+/-	+/-	+/-	+/-	+/-
(0.1 °C/s)	0.19	0.18	0.28	0.05	0.19	0.18	0.90	1.21	1.39

Table 6.II Difference from the average of triplicate measurements to assess reproducibility of the thermal analysis parameters.

From a control viewpoint, linear behavior is the simplest, and thus, linear correlation coefficients, R^2 , are given in Tables 6.III and 6.IV for each of the thermal analysis parameters studied. These coefficients can be used as a guide to the effectiveness of each parameter as an indicator of grain size, for the 319 and 356 alloys solidified at the two different cooling rates and for a particular grain refiner used.

It can be seen from Table 6.III that the highest correlation obtained was for the $T_{\rm U}$, $T_{\rm R}$, and $t_{\rm I}$ parameters in the case of the 319 alloy, and it remained more or less constant for all the different types of refiners used and different cooling rates. The t_3 parameter also showed a high correlation with grain size, but only for the fast cooling rate condition. The nucleation temperature, $T_{\rm N}$, showed a relatively high correlation for the 319 alloy at fast cooling rate conditions, similar to that of the $t_{\rm I}$ parameter at slow cooling rates.

Table 6.IV shows that for the 356 alloy the best correlation values were obtained for the $T_{\rm U}$, $T_{\rm R}$ and $\Delta T_{\rm R-U}$ parameters at fast cooling rates. In this case, not all the refiners gave a similar value, particularly the AlTab salt flux, which had the lowest correlation value. The time parameter, t₁, yielded a high correlation but only when using Al-5%B and Al-2.5%Ti-2.5%B master alloys at fast cooling rates. At slow cooling rates the correlation values are low, but again, the best correlation could be obtained with the temperature parameters $T_{\rm U}$ and $T_{\rm R}$ for most of the refiners used.

Table 6.V shows linear correlation coefficients for each of the thermal analysis parameters, irrespective of the grain refiner used. From this table, it can be seen that at low cooling rates (~0.1 °C/s), the correlation coefficient values are lower than those at the higher rate. When higher cooling rates are used to solidify the specimens, the correlation between grain size-thermal analysis parameters is improved. It is evident that in some cases (319 alloy) the undercooling and recalescence temperatures (T_U and T_R , respectively) give the best correlation with grain size. Figure 6.10 shows the correlation between grain size and the undercooling temperature, T_U , for the 319 alloy solidified at the fast cooling rate.

Linear Correlation Coefficients with Grain Size									
319 Alloy Fast Cooling Rate									
Refiner ↓	τυ	T _R	T _N	∆ 7 _{R-U}	∆ <i>T</i> _{N-U}	ΔT_{N-R}	t ₁	t ₂	t3
A !- 6%Ti	0.97	0.98	0.87	0.22	0.42	0.56	0.93	0.70	0.93
Al- 5%Ti- 1%B	0.97	0.98	0.88	0.76	0.35	0.09	0.96	0.47	0.95
Al 2.5%Ti- 2.5%B	0.92	0.94	0.86	0.18	0.44	0.55	0.95	0.80	0.95
AI- 5%B	0.94	0.97	0.52	0.42	0.44	0.47	0.92	0.63	0.90
TiLite 75BC	0.97	0.97	0.84	0.56	0.53	0.11	0.95	0.22	0.95
AlTab	0.77	0.76	0.00	0.56	0.42	0.58	0.37	0.45	0.51
	<u> </u>	31	19 Alloy	y Slow C	ooling R	ate			
Refiner ↓	Τυ	T _R	T _N	∆T _{R-U}	∆ <i>T</i> _{N-U}	∆ 7 _{N-R}	t ₁	t ₂	t ₃
Al- 6%Ti	0.95	0.94	0.38	0.42	0.68	0.75	0.62	0.50	0.10
Al- 5%Ti- 1%B	0.95	0.96	0.80	0.59	0.79	0.82	0.82	0.64	0.23
Al 2.5%Ti- 2.5%B	0.68	0.73	0.00	0.82	0.68	0.73	0.82	0.46	0.05
Al- 5%B	0.97	0.96	0.26	0.78	0.76	0.79	0.83	0.66	0.11
TiLite 75BC	0.97	0.96	0.43	0.32	0.74	0.78	0.91	0.51	0.00
AlTab	0.82	0.86	0.17	0.80	0.38	0.49	0.78	0.30	0.01

Table 6.III Linear correlation coefficients of the thermal analysis parameterswith grain size for 319 alloy.

Linear Correlation Coefficients with Grain Size									
356 Alloy Fast Cooling Rate									
Refiner ↓	Τυ	T _R	T _N	∆ 7 _{R-U}	∆7 _{N-U}	∆T _{N-R}	t ₁	t ₂	t3
Al- 6%Ti	0.63	0.46	0.07	0.73	0.15	0.03	0.19	0.10	0.28
Al- 5%Ti- 1%B	0.84	0.80	0.15	0.77	0.14	0.00	0.52	0.05	0.36
Al 2.5%Ti- 2.5%B	0.77	0.31	0.20	0.94	0.05	0.08	0.78	0.02	0.28
AI- 5%B	0.93	0.69	0.43	0.97	0.04	0.25	0.90	0.14	0.76
TiLite 75BC	0.63	0.39	0.04	0.78	0.23	0.01	0.35	0.11	0.36
AlTab	0.07	0.03	0.04	0.05	0.01	0.02	0.11	0.00	0.06
	<u> </u>	35	56 Alloy	y Slow C	ooling R	ate			
Refiner ↓	τυ	T _R	T _N	∆ <i>T</i> _{R-U}	∆7 _{N-U}	∆ <i>T</i> _{N-R}	t ₁	t ₂	t ₃
Al- 6%Ti	0.42	0.44	0.56	0.15	0.31	0.37	0.04	0.26	0.24
Al- 5%Ti- 1%B	0.53	0.54	0.53	0.00	0.04	0.03	0.33	0.04	0.33
Al 2.5%Ti- 2.5%B	0.72	0.74	0.56	0.04	0.00	0.00	0.34	0.03	0.04
Al- 5%B	0.11	0.03	0.13	0.67	0.03	0.18	0.06	0.07	0.02
TiLite 75BC	0.76	0.79	0.55	0.03	0.38	0.34	0.32	0.21	0.01
AlTab	0.21	0.32	0.07	0.21	0.07	0.21	0.18	0.25	0.06

Table 6.IV Linear correlation coefficients of the thermal analysis parameterswith grain size for 356 alloy.

	Coolin	g Rate	Coolin	g Rate	
Thermal	1.0	°C/s	0.1 °C/s		
Analysis					
Parameter	319 Alloy	356 Alloy	319 Alloy	356 Alloy	
τ _υ	0.88	0.66	0.68	0.01	
T _R	0.88	0.21	0.71	0.00	
T _N	0.51	0.44	0.17	0.03	
Δ 7 _{R-U}	0.28	0.89	0.09	0.22	
Δ <i>T</i> _{N-U}	0.26	0.02	0.37	0.08	
ΔT _{N-R}	0.05	0.32	0.40	0.17	
t ₁	0.69	0.72	0.41	0.00	
t ₂	0.28	0.14	0.40	0.12	
t ₃	0.80	0.47	0.10	0.11	

Table 6.V Linear correlation coefficients between grain size and thermal analysisparameters for 319 and 356 alloys solidified at two cooling rates.



Figure 6.10 Grain size vs. undercooling temperature, $T_{\rm U}$, for a 319 alloy solidified at ~ 1.0 °C/s.

Temperature parameters, such as T_U , T_R and T_N , are believed to vary according to the refining potency of the master alloy added to the melt. Calibration errors in commercial thermocouples (usually +/- 2 °C) are almost certainly the main cause of scattering in temperature parameter results.

Thermal analysis parameters involving the calculation of the nucleation time and temperature (T_N , t_2 , t_3 , ΔT_{N-U} and ΔT_{N-R}) gave a low correlation with grain size (Table 6.V), possibly due to imprecision in the procedure to determine the nucleation point.

The most used parameter for assessing the grain size in aluminum casting alloys has been the $\Delta T_{\text{R-U}}$ parameter. Figure 6.11 show the use of $\Delta T_{\text{R-U}}$ as an indicator of grain size for 356 alloy solidified at two cooling rates. The effect of the low cooling rate can be observed in this figure, where scattering and lower $\Delta T_{\text{R-U}}$ values are obtained when the alloy is solidified at ~ 0.1 °C/s.



Figure 6.11 Grain size vs. ΔT_{R-U} , for a 356 alloy solidified at two cooling rates.

Time parameters have also been correlated to grain size of aluminum castings. Figure 6.12 shows the correlation between the time parameter, t_1 , and grain size for a 319 alloy solidified at fast cooling rate. This parameter, t_1 , is the duration of recalescence in the solidification process, and can be related to the growth of grains during this period. A small value of t_1 signifies that the grains do not have a long growth period. Longer values of t_1 are related to longer grain growth times.



Figure 6.12 Grain size vs. t₁, for a 319 alloy solidified at 1.0 °C/s.

6.4 Dendrite coherency point and latent heat evolution

As indicated previously, two thermocouples (at the wall and center of the samples) were used to measure the temperature of the samples during solidification. Using this technique, a valley on the T_W - T_C curve (wall temperature – center temperature) indicates the point of coherency of the dendritic structure, where the dendrite growth is no longer frontal, but lateral, and a final grain size is established.⁶⁴ Figure 6.13 shows the cooling curve for the central and wall thermocouples for a non-refined 319 alloy sample,

as well as the T_W-T_C curve. The valley is indicated by a circle, and the respective coherency point temperature is indicated by an arrow on the left vertical axis.



Figure 6.13 Determination of the dendrite coherency point from the difference of wall and center temperatures for a 319 alloy sample solidified at 1.0 °C/s.

The use of this particular technique was only possible for the fast cooling rate condition, since at low cooling rates, the temperature difference, T_{W} - T_{C} is very small (almost zero), and the valley indistinct, as shown in Figure 6.14.

The dendrite coherency point is useful for the practical determination of the average linear growth velocity of dendrite tips.⁸² This is accomplished by dividing the average grain radius by the time elapsed between the nucleation point and the coherency point. Experimental results show that there is a linear relationship between the grain size of both 319 and 356 alloy samples and the velocity of the growth front, for the experimental conditions used for solidification (cooling rate of ~1.0 °C/s), Figures 6.15 and 6.16.



Figure 6.14 T_W - T_C curve for refined 319 alloy solidified at 0.1 °C/s with no apparent indication of the dendrite coherency point.



Figure 6.15 Linear behavior between grain size and velocity of the growth front for 319 alloy samples solidified at 1.0 °C/s.



Figure 6.16 Linear behavior between grain size and velocity of the growth front for 356 alloy samples solidified at 1.0 °C/s.

The experimental results also show that the time elapsed between the nucleation and the coherency point is not very different for all the grain sizes obtained. averaging 37 seconds for the 319 alloy and 39 seconds for the 356 alloy. Detailed results are given in Appendix E. It should be mentioned that not all the T_W-T_C graphs showed such a sharp valley as in Figure 6.13, and for this reason the location in time of the coherency point was sometimes difficult, but not impossible, as for the low cooling rate samples.

Latent heat and fraction solid calculations for the fast cooling rate samples show that at the coherency point, the fraction solid is similar for all the different grain sizes, averaging a value of 0.24 for the 319 alloy and 0.20 for the 356 alloy, Figures 6.17 and 6.18 respectively. The results of these calculations, as well as the calculations for the low cooling rate samples, are summarized in Appendix F. The fraction solid measured at different stages of the solidification process yields an interesting behavior when correlated with grain size. Table 6.VI presents the linear correlation coefficients of the grain size plotted against the fraction solid measured at different stages of the solidification process using the different grain refiners for both 319 and 356 alloys solidified at fast and slow cooling rates.



Figure 6.17 Grain size vs. fraction solid at dendrite coherency point for 319 alloy solidified at 1.0 °C/s.





	Linear Correlation Coefficients, R ²						
between Grain Size and Fraction Solid							
319 Alloy	Fa	ast Cooling	Rate	Low Cooling Rate			
	R ² at	R ² at	R ² at	R ² at	R ² at		
Refiner	Τ _υ	T _R	Coherency	Τ _U	T _R		
			Point				
Al-6%Ti	0.77	0.93	0.02	0.63	0.47		
Al-5%Ti-1%B	0.29	0.96	0.01	0.79	0.61		
Al-2.5%Ti-2.5%B	0.76	0.96	0.19	0.58	0.78		
AlTab	0.24	0.38	0.18	0.65	0.70		
TiLite75BC	0.01	0.96	0.01	0.50	0.75		
AI-5%B	0.77	0.93	0.37	0.81	0.68		
		······································	d.e.	3	<u></u>		
356 Alloy	F	ast Cooling	Rate	Low Cooling Rate			
	R ² at	R ² at	R ² at	R ² at	R ² at		
Refiner	Τ _υ	T _R	Coherency	τ _u	Τ _R		
			Point				
AI-6%Ti	0.00	0.54	0.36	0.11	0.01		
AI-5%Ti-1%B	0.21	0.72	0.06	0.00	0.21		
Al-2.5%Ti-2.5%B	0.24	0.76	0.41	0.03	0.27		
AlTab	0.03	0.02	0.00	0.00	0.17		
TiLite75BC	0.20	0.51	0.00	0.09	0.12		
Al-5%B	0.34	0.93	0.16	0.31	0.01		

Table 6.VI Linear correlation coefficients, R ² , between grain size and fraction solid a
different stages of solidification for 319 and 356 alloys, solidified
at fast (1.0 °C/s) and low (0.1 °C/s) cooling rates.

It is clear from Table 6.VI that at the point of maximum recalescence temperature, T_R , the best correlation is obtained, mainly for the fast cooling rate conditions. When the results are plotted irrespective of the grain refiner used, a linear relationship between fraction solid at T_R and grain size, is also observed for both 319 and 356 alloys solidified at the fast cooling rate, Figures 6.19 and 6.20 respectively.







Figure 6.20 Grain size vs. fraction solid at T_R for 356 alloy solidified at 1.0 °C/s.

Chapter 7 Discussion

7.1 Grain size determination by thermal analysis parameters

Good linear correlation with grain size was obtained for several thermal analysis parameters, and in general it was observed that faster cooling rates yielded better correlations in this experimental work. A time parameter, t_1 , which is the duration of the recalescence period, as well as the maximum undercooling temperature, T_U and maximum recalescence temperature, T_R , yielded the best correlations. On the other hand, thermal analysis parameters involving the calculation of the nucleation time. t_N , and temperature, T_N , were the ones with lower correlation values.

For the analysis of the results, it was considered that during the nucleation stage, there may be more than one group of substrates that are effective at different undercoolings, due to differences in size, morphology, orientation relationship with primary aluminum, etc. Thevoz⁽⁸³⁾ presented an analysis of the heterogeneous nucleation rate, n, as a function of the undercooling, ΔT , given by Equation 7.1.

$$\dot{\mathbf{n}}(\Delta T) = (No-\mathbf{n}(t)) K_1 \exp(-K_2/T\Delta T^2)$$
 (Equation 7.1)

where

 $n(\Delta T)$ = heterogeneous nucleation rate

No = maximum density of heterogeneous nucleation sites available

n(t) = heterogeneous nucleation sites active at time, t

 $K_1, K_2 =$ experimental constants
The values of K_1 and K_2 are characteristic of specific nucleation sites at specific undercoolings, for which a saturation occurs (when $n(t) = N_0$) for a particular melt condition at the maximum undercooling, T_{U} , just before recalescence.

The discussion which follows groups the thermal analysis parameters studied, into the two stages that determine the grain size of aluminum castings during solidification: nucleation and growth.

Parameters Related to the Nucleation Stage

Nucleation temperature, T_N

Since the grain density is directly related to the number of nuclei present in the melt, the nucleation temperature, T_N , would also be supposed to correlate well with grain size. But as suggested by Thevoz,⁽⁸³⁾ there may be different "families" of nucleation sites that are effective at different undercoolings for a particular melt condition. So, the nucleation temperature, T_N , as registered from the experiments may just be the beginning of a series of nucleation events, and not necessarily an instantaneous nucleation temperature for all the sites available in the melt.

In certain cases, a high correlation with grain size is observed for the T_N parameter, particularly for the 319 alloy solidified at high cooling rate (Table 6.III). This is likely due to homogeneity in the properties of the refining particles. That is, most of the refining particles in the melt could be part of a "family" of nucleation sites and have the same suitable conditions for nucleation (similar size, morphology, orientation relationships with α (Al), etc.), and thus, similar T_N . In this same context, samples treated with AlTab salt flux may have a negligible correlation between T_N and grain size, again due to the lack of effective nucleation sites with similar properties.

The nucleation time, t_N , and temperature, T_N , are parameters which are difficult to measure, and any other parameters derived from these may have the same correlation problems with grain size. It was shown that the maximum undercooling and recalescence temperatures, T_U and T_R respectively, have good correlation with grain size, but the

difference between T_N and T_U (ΔT_{N-U}) and the difference between T_N and T_R (ΔT_{N-R}) do not yield that same good correlation. Again, different undercoolings (values of ΔT), for different families of nucleation sites, may not allow a unique and precise T_N parameter to be obtained.

Duration of nucleation, t₂

If it is considered that all the nucleation events end when the maximum undercooling temperature, T_U , is reached,⁽⁸³⁾ then the time parameter, t_2 (t_U - t_N) would be considered as the duration of nucleation. This parameter could also have correlation problems with grain size due to the difficulty of calculating the nucleation time, and as for the nucleation temperature, this time, t_N , may just indicate the beginning of several nucleation events occurring until t_U is reached (when n(t) = No, see Equation 7.1). Then, the time parameter, t_2 , will only be meaningful if all the nucleation sites in the melt activate at the same time.

Also, during the nucleation period, t_2 , the nucleation rate, $n(\Delta T)$, is entirely a function of the amount and type of refining particles that reduce the undercooling, ΔT , required for nucleation, and not a function of the time elapsed after the first nucleation event is registered.

For the fast cooling rate condition, the value of t_2 is small for both 319 and 356 alloys (averaging 5.2 sec.), and the fraction solid evolved up to this time, is almost negligible (Appendix F). At low cooling rates, this time increases up to 13.4 seconds on average, but the fraction solid evolved remains negligible.

Time period between nucleation and end of recalescence, t₃

As with the other parameters relating nucleation time and temperature calculations, the time duration between nucleation and end of recalescence, t_3 , did not exhibit a good correlation with grain size. Even though this parameter is determined by the duration of recalescence, t_1 ($t_3 = t_1 + t_2$), which has a good correlation with grain size at fast cooling rates (Table 6.V), there may be a strong influence of the duration of

nucleation, t_2 , on the repeatability of the results. Only the 319 alloy solidified at fast cooling rate showed a good correlation between the grain size and t_3 , and this was possibly because the T_N parameter also showed good correlation values.

Maximum undercooling temperature, T_{U}

This temperature parameter, T_U , yielded one of the best correlations with grain size (Tables 6.III and 6.IV) and could be used as a reliable indicator of the grain size of Al-Si casting alloys, that is if a good thermocouple calibration system is used. At this temperature, T_U , it is considered that the maximum density of heterogeneous nucleation sites is reached, and that now the grain growth mechanism will also become important in the final grain size determination. Thus, this parameter can be considered as a link between the nucleation and growth stages.

When the melt contains a high density of effective substrates, and assuming that most of them belong to one "family" of nucleation sites, a lower undercooling, ΔT , is necessary to activate all of the nucleation sites, thus increasing the value of T_U (Figure 6.10) at which n(t) = No (see Equation 7.1), and reducing the grain size. When recalescence takes place, at T_U , no more nucleation sites become active due to the local increase of temperature in the melt, generated by the latent heat evolved.

If a grain refiner supplies a high number of effective nucleation sites with homogeneous properties (morphology, size, orientation relationships, etc.), the nucleation sites become active at lower ΔT 's, thus reaching the maximum density of heterogeneous nucleation sites available at higher T_U 's. On the other hand, when a grain refiner supplies only a few, or ineffective nuclei (with different properties), higher undercoolings, (ΔT 's), are necessary to activate all of the nucleation sites and reach the maximum density of heterogeneous nucleation sites, at lower T_U 's. These effects are illustrated in Figure 7.1, which shows the cooling curves of a well refined and poorly refined 319 alloy, where the T_N and T_U temperatures are also indicated.



Figure 7.1 Cooling curves of well and poorly refined 319 alloy. solidified at fast cooling rate.

Parameters Related to the Grain Growth Stage

Maximum recalescence temperature, T_R

The recalescence temperature is another parameter that yielded a high linear correlation with grain size, particularly for the 319 alloy. This temperature, T_R , is also known as the growth temperature, at which the frontal growth of grains takes place before the dendrite coherency point is reached, where primary dendrites impinge on each other and the final grain size is established.

The parameter, T_R , as well as T_U , is readily determined from the first derivative, and represents the temperature at which recalescence finishes and the melt begins to cool again. Results indicate that this temperature may be determined by the maximum undercooling experienced by the melt, since a linear relationship can be established between these two temperature parameters, T_R and T_U , Figure 7.2.



Figure 7.2 Relationship between T_U and T_R for 319 alloy solidified at 0.1°C/s

Calculations of latent heat and fraction solid evolution showed that at T_R , the amount of solid evolved can be related to the grain size of the samples solidified at the fast cooling rate, Figures 6.19 and 6.20. At the slow cooling rate, only the 319 alloy yielded good linear correlation values for both T_U and T_R with grain size (Table 6.III).

Difference between $T_{\rm R}$ and $T_{\rm U}$, $\Delta T_{\rm R-U}$

This parameter has usually been used for the assessment of grain size in Al-Si casting alloys, and has been considered as the "undercooling" necessary for nucleation. The results found in this thesis showed that only the 356 alloy solidified at the fast cooling rate gave good correlation between ΔT_{R-U} and grain size, Table 6.V. Appendix D shows that this parameter has very low values, particularly for the low cooling rate condition (less than 0.5 °C), with the result that the minimal temperature fluctuation or thermocouple accuracy error can affect this parameter greatly. In addition, the linear relationship between T_U and T_R indicates that the difference between them will be more

or less constant for any grain size, since the slope of the curve in Figure 7.2 is approximately 45 °.

Duration of recalescence, t₁

This time parameter also yielded a good correlation with grain size, as shown in Figure 6.12 for the 319 alloy solidified at the fast cooling rate. This parameter can be related to the grain growth, since a linear relationship was found between t_1 and the fraction solid evolved during this time. Figure 7.3. That is, the shorter the recalescence period, t_1 , the smaller the grain size and the smaller the amount of solid produced at T_R . An advantage of using this parameter over the temperature parameters, T_R and T_U , is that thermocouple calibration is not a factor to obtain precise and accurate measurements of time, thus making the t_1 parameter a valuable one in the prediction of grain size.





Figure 7.3 Relationship between fraction solid evolved during recalescence and the duration of the recalescence, t_1 , for 319 alloy solidified at 1 °C/s.

7.2 Dendrite coherency point and fraction solid evolution

The technique used to measure the dendrite coherency point appears to be applicable only for certain solidification conditions (cooling rates of ~ 1.0 °C/s). At lower cooling rates (~0.1 °C/s), the valley on the T_W - T_C curve that indicates the location of the coherency point, flattens with time, and there is no particular indication of the coherency point.

No good correlation could be found between the time elapsed from the nucleation temperature, t_N , to the time of the coherency point and the grain size of the samples. Instead, relationships between the fraction solid evolved at different times (or temperatures) and grain size were obtained. It has been reported that grain refinement increases the fraction solid at the time of dendrite coherency.⁽⁸²⁾ However, it was found in the present work that a similar value of fraction solid at the dendrite coherency point is obtained, irrespective of the grain size of the specimens, an average of 0.24 for the 319 alloy and 0.20 for the 356 alloy. This is shown in Figures 6.17 and 6.18 respectively, for samples solidified at the fast cooling rate.

From the dendrite coherency point, the linear growth velocity of the primary dendrite tips was calculated for the samples solidified at fast cooling rate, and the results indicate that there is a linear relationship between the grain size and the growth velocity, for both 319 and 356 alloys. If the graphs of the dendrite tip linear growth velocity versus grain size for the 319 and 356 alloys are superimposed (Figures 6.15 and 6.16), the values appear to be part of a single graph. That is, the grain size increases as the growth velocity becomes faster, irrespective of the base alloy and refiner used.

According to the results obtained here, the thermal analysis parameters that are best related to the grain size of Al-Si casting alloys are the duration of recalescence, t_1 , the maximum undercooling temperature, T_U , and the maximum recalescence temperature, T_R . Growth velocity obtained from the coherency point determination and fraction solid calculations suggest that:

- 1. When few nucleation sites are active at $T_{\rm U}$, the average growth velocity of the grains reaches a value of approximately 27 μ m/s, Figure 6.15.
- 2. When a high density of effective nucleation sites are present at $T_{\rm U}$, the average growth velocity of the grains is reduced to approximately 4 μ m/s, Figure 6.16.
- 3. At $T_{\rm U}$, the fraction solid evolved is not as relevant as when the maximum recalescence temperature, $T_{\rm R}$, is reached.

It is suggested that the grain size is strongly influenced by the effectiveness and number of nucleation particles added to the melt, and that the growth of grains during the recalescence period plays an important role in the final grain size of the samples. It is proposed that after T_U (at time t_U), the grains nucleated grow individually in the undercooled melt until thermal fields around them interact with each other, reducing the growth velocity. When a high density of grains is present, the thermal fields will interact sooner, leaving a shorter time for the grains to grow freely into the melt. When the density of grains in the melt is low, the interaction of these fields comes later in time, allowing for the grains to increase their size, Figure 7.4.

It is proposed that the maximum growth velocity is reached at T_R (at time t_R), due to the high correlation of this parameter with grain size, as well as the high correlation of the fraction solid evolved at this temperature with grain size. Then, the duration of the recalescence, t_1 , would represent the time available for the grains to grow freely in the melt before their thermal fields interact with each other, reducing the growth velocity until the dendrite coherency point is reached.





7.3 Accuracy and repeatability of temperature data

Thermocouple accuracy has been tested and results indicate that commercial thermocouple measurements may deviate by as much as 3 °C from the calibration temperatures. In some cases, this accuracy was maintained throughout the experiments, but that was not always the case, Figure C.1 (a). It is worth noting in Appendix C that the accuracy of the two thermocouples in each accuracy test varied in a similar way, except after a long period of use. This may indicate that changes in accuracy in the tests arose from a variation in the melt temperature and not from thermocouple inaccuracy. If this is the case, the temperature values obtained for correlation with grain size, T_U , T_R , etc., are

reliable for grain size assessment, as well as the T_W - T_C values obtained to calculate the dendrite coherency point.

As shown in Table 6.II, the most variable parameters from the triplicate measurements, were those related to the nucleation temperature and time, T_N , ΔT_{N-U} , ΔT_N , R, t₂ and t₃. As has been said, the nucleation temperature, T_N , is a particularly difficult parameter to measure since different sites may trigger the nucleation of primary aluminum at different undercoolings.⁽⁸³⁾ The nucleation temperature, T_N , and time, t_N, as calculated in this work, are defined as the moment when the first latent heat evolution is detectable from the first derivative (and from a minimum peak on the second derivative), Figures 3.10 and 3.11, but that does not imply that this is the exact moment at which nucleation occurs.

The other parameters, T_U , T_R , ΔT_{R-U} and t_1 , show a better accuracy since they are defined with more precision from the first derivative. When dT/dt = 0, the time at which either the maximum undercooling temperature, T_U , or the maximum recalescence temperature, T_R , occur, can be determined. Once these times, t_U and t_R , are located on the first derivative curve, the time parameter, t_1 , and the temperature parameters, T_U , T_R and ΔT_{R-U} , can be determined from the cooling curve.

From the analysis made on data acquisition rate it can be said that higher data acquisition rates produce an increased amount of noise in the derivative curves, particularly when low cooling rates are used. This happens because when more data points are acquired, more slope changes occur, varying the value of the derivative more frequently and generating more noise in the dT/dt curve than when fewer data points are acquired per second.

Most of the time this noise makes the accurate observation of the time parameters impossible in the first derivative, as shown in the top left corner of Figure 6.5. Also, this noise can hide peaks related to important events occurring during the solidification process, and thus, small acquisition rates are recommended when no subsequent mathematical smoothing steps of the first derivative curve are used.

In order to reduce the noise from the data acquisition, a smoothing of the cooling curve and the derivatives is done. When smoothing the curves by fitting the values on a curve by the least squares method, the values of some thermal analysis parameters may be changed. If the smoothing is done at short intervals (taking just a few *T*-t values to fit the curve), the values of ΔT_{R-U} and t_1 are close to the original value obtained from the raw data. If long intervals are used (many T-t values are used to fit the curve in one step), there is considerable shift from the original ΔT_{R-U} and t_1 values, and this shift increases as the *T*-t values used increase. Figures 6.8 and 6.9. So, in order to guarantee the accuracy and repeatability of the data when smoothing is performed on the curves, the same smoothing procedure, involving short interval smoothing steps, should be used for all the experiments.

7.4 Grain refinement results and grain size repeatability

From the grain size results, Figures 5.6 (a-f), an evident conclusion is that the grain size of the initial 356 samples is smaller than the 319 alloy samples, considering that the residual titanium content in the 319 alloy is higher (0.12wt.%) than in the 356 alloy (0.07wt.%). Nevertheless, after the first grain refinement addition, the grain size of the 319 alloy is reduced at a faster rate than that of the 356 alloy. When the amount of refiner addition is increased, the grain size of both 356 and 319 alloys is similar, particularly at fast cooling rates (except for AlTab salt flux and Al-5%B master alloy additions).

It was not determined if the base alloys were in a pre-refined condition (due to the presence of residual Ti and B, see table 4.1). What is clear from the results is that a minimum grain size can be reached at certain addition levels, after which, the grain size remains constant. For example, Figure 5.6 f shows that after an addition of 0.005wt.%

boron, the grain size of the 319 alloy remains constant at approximately 700 μ m, and in the 356 alloy it remains constant at approximately 400 μ m.

It is known that silicon, copper and zinc hinder titanium grain refinement,⁽²⁾ but the results obtained here indicate that the presence of copper does not affect. to a great extent, the grain size of the 319 alloy samples (Figures 5.6 a, b and d) compared with the grain size of the 356 alloy (with no copper) when boron is also present. Still, if boron is the only refining element present, larger grain size values are obtained in 319 alloy (Figure 5.6 f).

A particular case is the use of AlTab salt flux as a refiner. As can be seen from Figure 5.6 c, AlTAb salt flux does not perform well as a grain refiner, since titanium is added in a metallic form and not as a substrate (such as TiAl₃ or TiB₂). Also, the growth restriction effect that titanium may have on the grain structure is not very pronounced since the recovery of titanium from this product in 319 and 356 alloys is very low (Figure 5.1 e).

Differences in grain size for the fast and low cooling rate conditions may be due to the fact that at the fast cooling rate the liquid is more undercooled than at the low cooling rate (see T_U values for 319 alloy at fast and low cooling rates. Appendix D). This will generate more active nucleation sites. Additionally, settling of refining particles could have occurred due to the long time elapsed (~200 sec.) before nucleation occurred in the melt solidified at the low cooling rate.

The repeatability of the grain size measurements is shown in Figure 5.3, where the vertical axis represents the difference between the average grain size value of the three experimental replicas and the value of an individual experiment. An improvement in repeatability is observed as the grain size becomes smaller, and this can be explained by considering that initially (at higher grain size values), the grains are semi-equiaxed and tend to elongate due to growth of primary arms in specific crystallographic directions. When the growth is restricted, either by thermal or constitutional factors or by physical crowding, the grains become more equiaxed (Figure 5.2).

Another way of observing this effect is presented in Figure 5.5, where the degradation of the primary dendrite arms into a rosette-like grain structure is evident. Secondary dendrite arm spacing is only affected by the freezing rate of the sample⁽¹²⁾ and not by differences in grain size of the samples, as seen in Figure 5.4. Also from Figure 5.4, it can be observed that the secondary dendrite arm spacing is smaller than the grain size, and that the variability of the grain size measurements (Figure 5.3) for the medium and large grain size results falls within one dendrite arm spacing (50 to 100 μ m). This indicates that at very small grain sizes, each grain is composed, more or less, of a single dendrite arm, with no more than three or four secondary arms.

The coefficient of variation (C.V.) of the number of total intercepts measured for an ideal specimen with 300 to 500 intersections counted, falls within a value of 0.060 to 0.045 respectively.⁽⁷⁹⁾ In this investigation, the C.V. values obtained for the majority of the samples fell within this range, and only 356 samples solidified at ~0.1 °C/s gave slightly higher values, see Appendix B. It may be that these samples contained increased porosity, which could have altered the measurements in some way. Nevertheless, an apparent standard deviation value (s_0), markedly higher than \sqrt{N} indicates probable nonuniformity in the samples, which was not the case for the measurements of grain size in the 356 low cooling rate samples, nor for the rest of the samples, which always showed \sqrt{N} values higher than the s_0 (Appendix B).

7.5 Recovery of grain refiners

It is clear from the characterization of the master alloys that there are differences in the type of substrates added to the melt. These differences in type and also in morphology are responsible for the effectiveness of the grain refiners, and it was expected that differences in grain size would be predicted from the thermal analysis experiments, in which the solidification conditions were also varied. One way in which the effectiveness of a grain refiner might be assessed is to plot the grain size of a casting versus the amount of titanium and boron added to the melt (or the weight of master alloy added per ton of aluminum). Thus, the amount of titanium or boron in the final casting could be an indicator of the degree of refinement. It is a common practice on the foundry floor to obtain a chemical analysis of a sample and relate it to the degree of refinement of a casting. It is also true that the recovery from a master alloy addition will not always be 100%. Factors such as agglomeration and settling of the refining particles can lead to a poor recovery of titanium and boron in the final chemical analysis.

From the results of the chemical analysis of the refined samples, it can be seen that the recovery of titanium is always lower for the salt fluxes (< 20 %, Figures 5.1 d-e). That is probably due to the reactivity of the fluxes in the melt at the moment of introduction. The addition procedure for the salt fluxes was to wrap the refiner in aluminum foil and place it on top of the liquid metal in order to avoid gas production inside the melt.

From the plots of titanium and boron recovery of the master alloys, it can be seen that when the refining substrates are present as $TiAI_3$, the recovery is greater (> 60 %, Figures 5.1 a-b) than when TiB_2 , AlB_2 and/or $(Al,Ti)B_2$ particles are present (< 60 %, Figures 5.1 c and f). The dissolution of $TiAI_3$ particles might produce a more even dispersion of titanium in the melt, whereas the less soluble boride particles may sink in the crucible and produce low titanium and boron readings in the chemical analysis. Another possible factor for the reduced recovery in the Ti-B alloy might be that the master alloys are produced as ingots and they may have some heterogeneity in chemical composition due to settling of particles during ingot solidification. When cutting sections of the refiner ingot, this heterogeneity might be passed onto the refined material, particularly if the amount needed is only a few grams (in some cases not even 10 grams for Al-5%B master alloy). In the case of salt fluxes, the amount added can also be a strong factor in the low recovery, since the highest amount needed for refinement weighed less than 10 grams, and in some cases there were flux additions below 1 gram.

Chapter 8 General Conclusions

- 1. A time parameter, t_1 , defined as the duration of recalescence, correlates well with grain size, irrespective of the base alloy or type of refiner used. This parameter is obtained accurately from the first derivative of the cooling curve, when dT/dt = 0, at the beginning and end of the recalescence period, and it is not affected by thermocouple calibration errors.
- 2. The maximum undercooling temperature, $T_{\rm U}$, as well as the maximum recalescence temperature, $T_{\rm R}$, do have good correlation with grain size. These two temperatures vary more or less in the same order with grain size, indicating that the values of $T_{\rm R}$ are a consequence of the change in $T_{\rm U}$.
- 3. The nucleation time, t_N , and temperature, T_N , are parameters difficult to measure and do not correlate well with grain size. The thermal analysis parameters derived from them present similar correlation problems with grain size due to the imprecision in determining a unique nucleation time.
- 4. Change in the values of the time parameter, t_1 , and the temperature parameter, ΔT_{R-U} , are observed when smoothing of the derivative curve is done by fitting a large number of T-t values in the curve T= a + bt + ct² by the least squares method in a single step. This is avoided by fitting fewer T-t values in the curve progressively (interval smoothing).
- 5. Thermal analysis can be a valuable on-line tool for the determination of grain size in Al-Si casting alloys if appropriate solidification conditions are used, since the cooling rate has an effect on the thermal analysis parameters. At a cooling rate of 1.0 °C/s, a

good correlation with grain size can be obtained for several thermal analysis parameters. At lower cooling rates, the thermal analysis parameters may lose their correlation with grain size.

- 6. The two thermocouple technique used to measure the dendrite coherency point is only applicable for cooling rates approximated to 1.0 °C/s. At lower cooling rates (0.1 °C/s), the T_W - T_C curve flattens with time with no particular indication of the coherency point.
- 7. The dendrite tip linear growth velocity, obtained from dendrite coherency point measurements for the fast cooling rate condition, correlates well with grain size for both 319 and 356 alloys. Large grain sizes correspond to faster growth velocities and small grain sizes correspond to slower growth velocities.
- 8. The fraction solid evolved at the coherency point does not change with grain size in the ranges analyzed (300 to 2000 μ m), for both 319 and 356 alloys solidified at the fast cooling rate.
- 9. The fraction solid evolved during the recalescence period has a linear correlation with the duration of this period, t₁.
- 10. When grain size is to be assessed by measuring the content of titanium (or boron) in the melt, the results are valid only for a particular type of refiner used, due to differences in recovery from one refiner to another. As a result, it is not possible to establish a correlation between the weight percent of the refining elements and grain size.

Statement of Originality

The following aspects of the present work are considered to be original contributions to knowledge:

- 1) This work presents the use of the duration of recalescence, t_{I} , as a reliable parameter for the assessment of grain size in Al-Si casting alloys. It is demonstrated for the first time that this parameter can be used irrespective of the grain refiner added to the melt, and irrespective of the base alloy (either 319 or 356 alloy). In addition, this parameter is free from thermocouple accuracy errors, which affect other thermal analysis parameters such as T_U and T_R .
- 2) It is shown that the average grain growth velocity, obtained from dendrite coherency point calculations, is lineally related to the grain size of 319 and 356 alloys, solidified at 1.0 °C/s. This velocity is slower for small grains than for large grain sizes.
- 3) A physical model for the growth of grains during the recalescence period is proposed in order to validate the use of the time parameter, t₁, as an accurate indicator of the grain size in Al-Si casting alloys. The values of the grain growth velocity obtained for the 319 and 356 alloys fall in the same range, suggesting that this model may be valid for both alloys. This is reasonable since the growing phase in each case is primary aluminum.

In the initial stage of grain formation (nucleation), the effectiveness of the refining particles defines the number of grains to be formed until T_U is reached. After that, the grains grow to a certain velocity until thermal fields surrounding them interact with each other, at T_R . This elapsed time of free growth in the melt is the t_l parameter. After T_R the grain growth velocity is reduced until the dendrite coherency point is reached and the final grain size is established. Thus, if a high density of nucleation sites is active after T_U , their thermal fields will interact sooner with each other and will reduce the growth velocity. When fewer nucleation sites are active, there will be more time for growth, longer t_1 , and larger grains will be formed.

List of Symbols

Symbol	Meaning	Units
α(Al)	primary aluminum alpha phase	
ΔG	total free energy	J/mol
ΔG^*	critical free energy	J/mol
$\Delta G_{\rm het}$	heterogeneous nucleation free energy	J/mol
ΔG_{V}	free energy per unit volume	J/m ³
ΔN_i	$N_{\rm i} - \tilde{N}$, deviation from the average per field	
ΔN_i^2	squared value of ΔN_i per field	
ΔT	undercooling below T _m	°C
$\Delta T_{\rm N-R}$	difference between $T_{\rm N}$ - $T_{\rm R}$	°C
$\Delta T_{\text{N-U}}$	difference between $T_{\rm N}$ - $T_{\rm U}$	°C
$\Delta T_{\text{R-U}}$	difference between $T_{\rm R}$ - $T_{\rm U}$	°C
ŶML	free energy of mold/liquid interface	N/m
γsl	free energy of solid/liquid interface	N/m
үѕм	free energy of solid/mold interface	N/m
ρ	density	kg/m ³
Σ	number of total intercepts per sample	
$\Sigma \Delta N_i^2$	sum of ΔN_i^2 per sample	
τ	response time	S
θ	wetting angle	0
A	surface of cross-sectional area	m²
A _{SL}	area of solid/liquid interface	m²
A _{SM}	area of solid/mold interface	m²
C ₁	T_i - T_o , constant for the calculation of T_{NR}	°C
C ₂	hA/V ρ C _p , constant for the calculation of T_{NR}	s
Cp	specific heat	J/kg°C

Symbol	Meaning	Units
C.V.	s_0 / \tilde{N} , coefficient of variation of the counts	
dQ _L /dt	rate of heat released during phase transformation	J/s
dT/dt	cooling rate	°C/s
(dT/dt) _{CC}	cooling rate (first derivative of cooling curve)	°C/s
(dT/dt) _{NR}	cooling rate of neutral reference	°C/s
$(d^2T/dt^2)_{CC}$	second derivative of cooling curve	°C/s ²
fs	solid fraction	
h	heat transfer coefficient	W/m ² °C
<i>K</i> ₁	experimental constant for nucleation	s ⁻¹
<i>K</i> ₂	experimental constant for nucleation	°C3
Lv	latent heat of fusion per unit volume	J/m ³
'n	rate of heterogeneous nucleation	m ⁻³ s ⁻¹
Ni	number of total intercepts per field	
No	maximum density of heterogeneous nucleation sites	m ⁻³
n(t)	heterogeneous nucleation sites active at time t	m ⁻³
Ň	$\Sigma/10$, average value of intercepts per field	
$\sqrt{\tilde{N}}$	squared root of average value of intercepts per field	
QL	latent heat of solidification	J
r	radius of spherical cluster	m
r*	critical radius of spherical cluster	m
R^2	linear correlation coefficient	
s ₀	$\sqrt{V_0}$, standard deviation of the counts	
S(θ)	$(2+\cos\theta)(1-\cos\theta)^2/4$, shape factor	
T	temperature	°C
t	time	s
T _C	center temperature	°C
T _E	eutectic temperature	°C
T _i	maximum initial temperature	°C
TL	liquidus temperature	°C

Symbol	Meaning	Units
T _m	equilibrium solidification temperature	°C
T _N	nucleation temperature	°C
t _N	nucleation time	S
T _{NR}	temperature of neutral reference	°C
To	room temperature	°C
T _R	maximum recalescence temperature	°C
t _R	time of end of recalescence	S
Ts	solidus temperature	°C
T _U	maximum undercooling temperature	°C
tu	time of beginning of recalescence	S
Tw	inner mold wall temperature	°C
to	initial time	S
tı	t _R -t _U , duration of recalescence	S
t ₂	t _U -t _N , duration of nucleation stage	S
t3	t_1+t_2 , time between nucleation and end of recalescence	S
V	volume	m³
Vs	volume of spherical cap	m ³
Vo	$[(\Delta N_1)^2 + (\Delta N_2)^2 + \dots (\Delta N_i)^2]/(i-1) = \text{variance of the}$	
	observed counts (<i>i</i> =10)	

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Appendix A

Grain Refiner Characterization

AI-6%Ti Master Alloy



Micrograph



[×] 100 α (Al) 64 α (Al) α (Al) TiAl₃ 36 16 α (AI) TiAl₃ TiAl₃ 4.0 TiAl, TiAl, 0.0 20 60 [727 100 40 go

X-Ray Diffraction Pattern

AI-5%Ti-1%B Master Alloy



EDS Analysis



Micrograph



AI-5%Ti-1%B Master Alloy (Cont'd)



Secondary electron image



X-ray map for titanium



X-ray map for boron

Al-2.5%Ti-2.5%B Master Alloy



Micrograph



X-ray map for titanium



X-ray map for boron



AI-5%B Master Alloy



EPMA/WDS Analysis	<u>At. %</u>	
on AIB ₂ Particle	AI	33.43
10 KeV	В	66.25

Micrograph



AI-5%B Master Alloy (Cont'd)



Micrograph of cavity on AI-5%B master alloy



AITab Salt Flux



TiLite75BC Salt Flux


Appendix B Grain Size Results

							Grain
Refiner	Sample	Ti	лŇ	<i>S</i> 0	C.V.	Mag.	Size
	I.D.	(wt.%)				(X)	(μm)
			7.22	3.48	0.066	2.65	1808
N/A	0	0.12	6.90	3.46	0.072	2.65	1979
			7.03	3.52	0.071	2.65	1908
		0.420	7.98	3.89	0.061	3.95	993
	1	0.136	7.99	3.93	0.061	3.95	990
			<u> </u>	4.40	0.069	3.95	332
Al-6%Ti	2	0 146	6.00	J.24 3 13	0.072	0.10 9.10	702
		0.140	6.67	2.04	0.071	8 10	692
			7.00	3 30	0.067	8 10	629
	3	0.178	7.22	3.24	0.062	8.10	592
			6.88	2.87	0.060	8.10	651
			7.32	3.59	0.066	8.10	576
	4	0.139	7.09	4.16	0.082	8.10	613
			7.25	3.52	0.066	8.10	586
			8.91	3.24	0.040	8.10	388
AI-5%TI-1%B	5	0.161	8.65	3.42	0.045	8.10	412
			8.92	2.52	0.031	8.10	388
			9.56	3.77	0.041	8.10	337
	6	0.231	9.63	2.98	0.032	8.10	332
			9.67	3.86	0.041	8.10	330
	-	0.432	7.57	3.42	0.059	8.10	537
	(0.132	7.54	3.77	0.066	8.10	541
			7.45	3.79	0.068	8.10	550
AI-2 5%Ti-2 5%B	ß	0 140	7.72	3.07	0.031	8.10	517
7.1 2.07011 2.0700	0	0.140	7.67	3.94	0.000	8.10	525
			7.00	2.62	0.073	8 10	561
	9	0.119	7.36	2.60	0.047	8 10	569
			7.19	4.06	0.078	8.10	597
		<u> </u>	8.35	1.30	0.018	3.95	907
	10	0.117	8.12	3.38	0.051	3.95	959
			7.99	3.74	0.058	3.95	991
			9.00	1.79	0.022	8.10	380
TiLite75BC	11	0.122	8.79	2.92	0.037	8.10	399
			8.80	2.36	0.030	8.10	398
		0.405	9.18	4.44	0.052	8.10	365
	12	0.135	9.00	3.14	0.038	8.10	381
	<u></u>		8.88		0.046	8.10	391
	12	0 1 1 5	7.60	4.37	0.071	2.00	1349
	13	0.115	7.00	2.14	0.034	2.00	1530
			7 77	2.50	0.007	2.05	1559
AlTab	14	0.123	7.61	2.35	0.042	2.65	1625
}	14	0.120	7.40	2.20	0.037	2.65	1719
			7.62	2.67	0.045	3.95	1089
	15	0.126	7.36	3.04	0.056	3.95	1166
			7.61	4.07	0.070	3.95	1090
				T			Grain
Definition	Sample	В	Ŵ	So	C.V.	Mag.	Size
Refiner	I.D.	(wt.%)				(X)	(µm)
	1	·	9.00	4.67	0.057	3.95	781
	16	0.0030	8.98	5.28	0.065	3.95	784
1			8.63	2.38	0.031	3.95	850
			6.85	3.68	0.078	8.10	657
AI-5%B	17	0.0077	6.55	3.29	0.076	8.10	718
			6.65	3.19	0.071	8.10	696
			6.87	2.08	0.044	8.10	654
	18	0.0161	6.72	3.17	0.070	8.10	682
			6.93	2.57	0.053	8.10	642

	Samole	Ti	√ N	S٥	C.V.	Mag.	Grain Size
Refiner	I.D.	(wt.%)				(X)	(μ m)
			5.32	1.18	0.041	4.91	1796
N/A	0	0.12	5.88	1.75	0.050	4.91	1469
		···- •	5.92	2.65	0.075	4.91	1453
	1	0.136	6.93	4,36	0.029	4.91	1060
			6.74	2.71	0.059	4.91	1119
A1 CO/ T			7.30	3.58	0.067	4.91	954
AI-6%11	2	0.146	7.14	4.32	0.084	4.91	998
			6.18	1.54	0.035	4.91	989
	3	0.178	6.41	3.11	0.075	7.56	805
			6.44	2.40	0.057	7.56	796
			6.61	1.81	0.041	7.56	755
	4	0.139	6.79	2.26	0.048	7.56	716
			6.59	3.38	0.077	7.56	761
Al-5%Ti-1%B	5	0 161	0.49	2.34	0.055	7.50	/ 84 757
	5	0.101	6.66	2.59	0.058	7.56	745
			6.29	4.62	0.116	7.56	834
	6	0.231	6.54	2.79	0.065	7.56	771
			6.87	1.64	0.034	7.56	699
	-	0.400	6.34	1.95	0.048	7.56	822
	(Ų.1 32	6.18	1.95	0.050	7.55	863
			6.24	2.11	0.054	4 91	1060
Al-2.5%Ti-2.5%B	8	0.140	6.86	1.54	0.032	4.91	1081
		l	6.86	1.81	0.038	4.91	1080
			6.58	3.13	0.072	4.91	1175
	9	0.119	6.73	1.70	0.037	4.91	1123
	<u> </u>		6.56	1.81	0.041	4.91	1181
	10	0 117	6.12	2 29	0.045	7.56	828
		•••••	6.32	2.26	0.056	7.56	827
			6.53	2.11	0.049	7.56	775
TiLite75BC	11	0.122	6.37	2.09	0.051	7.56	815
			6.25	2.60	0.066	7.56	846
	42	0.125	6.14	2.19	0.058	7.56	877
	12	0.135	6.20	2.70	0.070	7.50	802
			7.12	2.72	0.053	4.91	1004
ł	13	0.115	7.25	1.63	0.030	4.91	967
			7.16	2.03	0.039	4.91	993
Altab		0.000	6.40	3.19	0.077	4.91	1240
Airao	14	0.123	6.60	1.71	0.039	4.91	1168
			5.30	3.08	0.093	4.91	1201
	15	0.126	6.25	2.64	0.067	4.91	1301
			6.28	2.44	0.061	4.91	1291
							Grain
Pofiner	Sample	B	Ä	S ₀	C.V.	Mag.	Size
	<u> </u>	(wt.%)		<u> </u>		(X)	<u>(μm)</u>
		0.0000	6.47	1.73	0.041	7.56	789
	16	0.0030	6.14	3.03	0.080	1.55	877 774
		<u> </u>	663	1.97	0.040	7.56	752
AI-5%B	17	0.0077	6.65	1.42	0.032	7.56	746
			6.70	2.22	0.049	7.56	736
			6.80	2.36	0.051	7.56	715
	18	0.0161	6.84	2.00	0.042	7.56	706
	I	l	6.71	2.36	0.052	7.56	732

	Sample	Ti	147	\$a	сv	Mag	Grain
Refiner	I.D.	(wt.%)	YIT	30	0.1.	(X)	(µm)
			6.43	2.11	0.050	8.40	718
N/A	0	0.070	6.65	1.81	0.040	8.40	673
			6.43	0.98	0.023	8.40	718
	1	0 096	6.95	2.35	0.047	8.40	507
			6.87	1.89	0.039	8.40	629
			7.43	2.21	0.040	8.40	539
Al-6%Ti	2	0.119	7.68	2.78	0.047	8.40	504
	 		7.00	2.46	0.050	8.40	607
	3	0 143	7.91	4.45	0.071	8.40	4/5
	5	0.140	8.26	2.72	0.040	8 40	436
		· · · · · · · · · · · · · · · · · · ·	6.71	2.20	0.048	8.40	661
	4	0.091	6.71	2.63	0.058	8.40	659
			6.79	1.89	0.040	8.40	644
	_		7.00	2.83	0.057	8.40	606
AI-37011-170D	5	0.106	6.75	1.93	0.042	8.40	652
			0.08	2.49	0.052	8.40	628
	6	0 140	8.07	3 11	0.000	8.40	444
		0.110	7,90	5.09	0.081	8.40	476
		· · · · · · · · · · · · · · · · · · ·	8.52	3.00	0.041	8.40	409
	7	0.078	8.46	4.78	0.066	8.40	416
			8.47	4.53	0.063	8.40	414
			8.57	6.28	0.085	8.40	405
AI-2.3% [I-2.3%D	8	0.065	8.72	3.22	0.042	8.40	391
			8.84	3.40	0.043	8.40	381
	٩	0 120	8 11	2.02	0.045	0.40 8.40	450
	Ū	0	7.88	4.76	0.076	8.40	478
			6.96	3.07	0.063	8.40	625
	10	0.078	6.62	2.29	0.052	8.40	679
			6.71	1.96	0.043	8.40	661
Til Ho75BC		0.000	7.42	3.74	0.067	8.40	539
i incherooo		0.080	7.50	2.89	0.050	8.40	520
			8.00	3.69	0.045	8.40	465
	12	0.095	8.05	2.49	0.038	8.40	459
			8.09	3.41	0.052	8.40	454
			6.39	1.90	0.046	8.40	728
	13	0.074	6.68	2.63	0.058	8.40	666
			6.67	2.49	0.055	8.40	681
AlTab	14	0.078	6.60	∠.8∠ 1.80	0.000	0.40 8.40	60A
	17	0.070	6.48	2.20	0.052	8.40	720
			6.34	2.12	0.052	8.40	752
	15	0.075	6.78	2.33	0.050	8.40	659
			6.81	2.75	0.059	8.40	652
			_				Grain
Refiner	Sample	B	↓ vN	S0	C.V.	Mag.	Size
	I.D.	(wt.%)		[1	(X)	<u>(μm)</u>
	40	0.0040	9.71	2.75	0.029	8.40	316
	סו	0.0046	9.03	3.82 2.54	0.041	0.4U 8.40	327 34 <i>4</i>
			9.73	<u> </u>	0.020	8 40	338
AI-5%B	17	0.0076	9.39	2.77	0.031	8.40	337
			9.39	3.27	0.037	8.40	337
			9.27	3.69	0.042	8.40	346
	18	0.0106	9.46	2.07	0.023	8.40	332
	L		9.41	2.91	0.032	8.40	336

	Sample	Ti	J A I	50	сv	Мал	Grain
Refiner	I.D.	(wt.%)	***		0.1.	(X)	(um)
			5.93	5.11	0.145	8.40	846
N/A	0	0.07	6.12	2.69	0.071	8.40	794
			6.16	2.42	0.063	8.40	783
	1	0.096	5.45	5.27	0.126	8.40	714
	I	0.050	5.85	3.71	0.110	8.40 8.40	869
			6.37	2.80	0.068	8.40	732
AI-6%Ti	2	0.119	6.66	2.18	0.049	8.40	610
			6.52	3.32	0.078	8.40	699
		• • •	6.76	7.03	0.153	8.40	651
	3	0.143	6.30	6.16	0.154	8.40	749
			5.09	3.49	0.138	8.40	<u>/29</u> 921
	4	0.091	5.50	2.45	0.097	8.40 8.40	896
		0.001	5.80	3.20	0.094	8.40	882
			5.90	3.29	0.094	8.40	853
AI-5%Ti-1%B	5	0.106	6.31	4.53	0.113	8.40	747
			6.37	3.74	0.092	8.40	733
			6.56	4.99	0.115	8.40	691
	6	0.140	6.68	5.13	0.114	8.40	666
			6.69	3.58	0.079	8.40	664
	7	0.078	7.00	7.91	0.130	8.40	492
		0.073	7.05	5.00	0.102	8.40	502
	<u> </u>		7.80	3 79	0.033	8 40	488
AI-2.5%Ti-2.5%B	8	0.065	7.83	4.00	0.065	8.40	485
			7.34	6.08	0.110	8.40	551
			7.05	3.85	0.077	8.40	598
	9	0.120	7.39	6.33	0.115	8.40	544
			7.29	2.53	0.047	8.40	559
			6.21	1.85	0.047	8.40	770
	10	0.079	6.16	3.11	0.081	8.40	783
	<u> </u>		6.35	1.99	0.049	8.40	<u> </u>
TiLite75BC	11	0.080	7.08	4.29 4.79	0.090	8.40	592
	1	0.000	6.78	4.96	0.033	8 40	646
			7.39	5.58	0.101	8.40	544
	12	0.095	7.35	4.18	0.077	8.40	551
			7.24	4.71	0.089	8.40	566
			6.16	4.11	0.108	8.40	782
	13	0.074	6.20	3.91	0.101	8.40	773
			6.27	4.85	0.123	8.40	755
AlTab	14	0.078	6.40	2.UD 4 33	0.050	0.4U 8.40	620
		0.070	6.01	4.33	0.090	8.40	762
1		<u> </u>	6.33	2,91	0.072	8,40	741
	15	0.075	6.40	4.65	0.113	8.40	726
			6.19	4.98	0.12 9	8.40	776
						1	Grain
Definer	Sample	B	Ŵ	So	C.V.	Mag.	Size
Kefiner	I.D.	(wt.%)			[(X)	(µm)
			8.63	4.50	0.060	8.40	399
	16	0.0046	8.52	3.15	0.043	8.40	410
]	ļ		8.54	4.87	0.066	8.40	408
AL 59/ D	4-	0.0070	8.41	5.96	0.084	8.40	421
A-3%D	1/	0.0076	8.42	0./1	0.094	5.4U 9.40	420
			8 36	0.00 	0.097	<u> </u>	425
	18	0.0106	8 29	3 69	0.001	8 40	433
			8.42	6.82	0.096	8.40	420

356 Alloy, Slow Cooling Rate (~0.1 °C/s)

Appendix C Temperature Measurement Accuracy

















(a) Accuracy at 660.3 °C.











Appendix D Measurements of Thermal Analysis Parameters

Grain	Sample	Tu	T _R	$T_{\rm N}$	$\Delta T_{\rm R-U}$	$\Delta T_{\rm N-H}$	ΔTN-R	t ₁	t ₂	ta
Refiner	I.D.	(°Č)	(°Ĉ)	(°Ĉ)	(°င်)	(°C)	(°C)	(sec.)	(sec.)	(sec.)
		603.12	604.08	608.88	0.96	5.76	4.79	14 31	8 16	22 47
	0	603.50	604.51	608.53	1.01	5.02	4.01	12.78	7.04	19.82
	0	603.46	604.39	608.84	0.93	5.38	4.45	15.43	6.92	22.35
		606.37	607.52	611.80	1.15	5.43	4.28	8.02	6.84	14.86
	1	606.78	607.89	610.71	1.11	3.93	2.82	7.12	5.64	12.76
	•	606.67	608.09	611.14	1.42	4.47	3.05	8.45	5.76	14.21
		607.42	608.69	610.90	1.27	3.48	2.21	7.34	4.72	12.06
AI-6% I I	2	607.48	608.88	612.64	1.40	5.16	3.76	6.76	5.79	12.55
	-	607.68	609.03	612.71	1.35	5.03	3.68	6.75	5.95	12.70
		608.51	609.52	611.70	1.01	3.19	2.18	6.56	4.72	11.28
	3	608.81	609.65	611.96	0.84	3.15	2.31	6.00	4.15	10.15
		607.94	609.29	611.94	1.35	4.00	2.65	5.38	4.57	9.95
		608.08	608.46	612.36	0.38	4.28	3.90	5.18	6.11	11.29
	4	607.92	608.67	612.83	0.75	4.91	4.16	5.46	6.20	11.66
		607.89	608.58	612.01	0.69	4.12	3.43	5.17	5.17	10.34
AL 50/ T;		609.56	609.66	614.00	0.10	4.44	4.34	2.57	6.23	8.80
AI-3 % H-	5	608.96	609.26	612.48	0.30	3.51	3.22	3.79	4.94	8.73
1%B		609.02	_609.11	614.35	0.09	5.33	5.24	2.83	7.11	9.94
		609.75	609.76	612.41	0.01	2.66	2.65	0.86	5.35	6.21
	6	610.05	610.25	615.13	0.20	5.08	4.88	2.71	5.94	8.65
		609.96	610.18	613.30	0.22	3.34	3.12	2.47	4.15	6.62
		607.24	608.09	611.06	0.85	3.82	2.97	6.43	5.24	11.67
	7	607.18	608.30	611.73	1.12	4.55	3.43	6.43	5.32	11.75
Al-		607.12	608.61	611.80	1.49	4.68	3.19	7.14	5.22	12.36
2.5%Ti	1	608.04	609.27	612.10	1.23	4.06	2.83	6.52	4.79	11.31
2.57611-	8	607.84	608.85	610.63	1.01	2.78	1.77	5.95	4.16	10.11
2.3%6	ļ	607.15	608.49	612.34	1.34	5.19	3.85	5.92	5.68	11.60
		607.70	609.18	611.03	1.48	3.32	1.85	6.85	4.35	11.20
	9	607.50	608.67	610.88	1.17	3.38	2.21	6.93	4.82	11.75
		606.00	607.29	610.15	1.09	2.80	1.91	7.45	9.71	10.90
		606.62	607.56	611.06	1.20	4.15	2.07	0.40	5.45	14.22
	10	606.00	607.64	610.41	1.03	4.53	3.50	7.20	5.05	14.32
		609.70	609.70	612.09	1.24	4.01	2.11	0.39	7.10	7.40
TiLite		600.70	600.70	614 75	0.00	5.50	5.30	2.50	7.13	0.76
75BC	11	600.04	609.30	612.21	0.00	2.55	3.45	2.04	5.15	3.10
1000		609.04	609.12	612.01	0.00	3.21	3.13	1.05	6.24	7.02
		609.62	609.27	612.09	0.03	3.43	3.42		5.63	5.63
	12	608.87	608.80	612.69	0.00	3.92	3.12	0.00	6.30	7 33
} _		605.12	606.41	P8 P0a	1 29	4 77	3.48	8 78	6.85	15.63
1	42	604 98	606.52	612.04	1.54	7.06	5.52	10.72	8.54	19.00
j	13	605.37	606 71	610.46	1.34	5.09	3.75	7.65	6.92	14.57
		604 91	606.43	610.36	1.52	5.45	3.93	10.86	7 10	17.96
AlTab	44	604.41	605.81	609.21	1.40	4.80	3.40	8.06	6.62	14.68
	14	604.68	606.14	610.65	1.46	5.97	4.51	7.85	7.05	14.90
		606.03	607.56	608.55	1.53	2.52	0.99	8.62	4.29	12.91
	15	605.60	607.38	609.89	1.78	4,29	2.51	8.60	6.07	14.67
]	()	605.63	607.02	609.40	1.39	3.77	2.38	8.54	5.82	14.36
		606.84	608.06	610.08	1.22	3.24	2.02	6.93	4.56	11.49
	10	606.35	607.96	609.43	1.61	3.07	1.46	6.70	4.11	10.81
		606.93	608.00	610.55	1.07	3.62	2.55	7.45	4.88	12.33
		606.84	608.26	611.28	1.42	4.43	3.01	8.12	5.21	13.33
AI-5%B	17	607.33	608.52	612.34	1.19	5.01	3.82	7.34	5.98	13.32
		606.66	607.99	609.43	1.33	2.76	1.43	7.58	3.85	11.43
		607.22	608.62	610.69	1.40	3.47	2.07	6.16	4.23	10.39
	19	607.91	608.94	612.71	1.03	4.80	3.77	6.66	6.28	12.94
	10	607.91	609.07	612.10	1.16	4.19	3.03	6.23	5.10	11.33

Grain	Sample	Tu	T _R	T _N	$\Delta T_{\rm P,11}$	$\Delta T_{\rm NJ1}$	$\Delta T_{N,P}$	t.	t ₂	ta
Refiner	I.D.	(°Č)	(°Ĉ)	(°Ĉ)	(°Ĉ)	(°C)	(°C)	(sec.)	(sec.)	(sec.)
		607.05	607.17	610.67	0.12	3.62	3.50	5.03	17.22	22.25
Ν/Δ	0	608.05	608.23	612.10	0.18	4.05	3.87	6.71	22.27	28.98
	, , , , , , , , , , , , , , , , , , ,	607.50	607.60	611.53	0.10	4.03	3.93	4.59	21.25	25.84
		608.87	609.43	611.85	0.56	2.98	2.42	9.69	15.86	25.55
	1	609.27	609.75	612.13	0.48	2.86	2.38	9.14	16.25	25.39
		608.98	609.58	612.46	0.60	3.48	2.88	10.85	18.53	29.38
AL-6%Ti		609.87	610.50	611.91	0.63	2.04	1.41	10.20	11.10	21.30
/	2	609.73	610.24	611.00	0.51	2.79	2.28	10.74	16.12	26.86
		610.07	610.43	611.90	0.30	1.84	1.55	7.95	12.03	23.00
	•	610.24	610.51	611.51	0.24	1.04	0.87	9.31	9.22	18.53
	3	610.53	610.96	612.95	0.43	2.42	1.99	10.02	13.65	23.67
		610.13	610.53	612.81	0.40	2.68	2.28	9.57	15.28	24.85
	Λ	610.21	610.62	612.28	0.41	2.07	1.66	8.62	11.93	20.55
		610.12	610.48	612.71	0.36	2.59	2.23	9.50	14.97	24.47
		610.29	610.58	612.38	0.29	2.09	1.80	9.12	12.43	21.55
AI-5%11-	5	610.36	610.75	612.32	0.39	1.96	1.57	8.66	11.01	19.67
1%B		610.48	610.68	612.71	0.20	2.23	2.03	9.85	12.77	22.62
		610.60	610.94	612.67	0.34	2.07	1.73	9.96	12.64	22.60
	6	610.68	611.05	612.42	0.37	1.74	1.37	10.12	12.96	23.08
		610.66	600.95	611.05	0.22	1.92	1.70	8.58	13.44	22.02
	_	609.23	609.00	611.05	0.62	2.00	1.20	10.02	12.51	21.99
	7	609.23	609.01	611.03	0.50	1 70	1.42	10.23	11 22	23.74
Al-		609.17	609.68	610.95	0.50	1.70	1.20	940	11.22	20.73
2.5%Ti-		609.16	609.63	612.54	0.47	3 38	2.91	11 33	20.24	31.57
2.5%B	0	609.19	609.69	611.12	0.50	1.93	1.43	9.53	11.62	21.15
		609.69	610.14	612.22	0.45	2.53	2.08	9.00	15.79	24.79
	9	609.54	610.11	612.32	0.57	2.78	2.21	9.41	15.02	24.43
		609.62	609.96	612.36	0.34	2.74	2.40	8.49	16.28	24.77
		609.63	610.12	611.44	0.49	1.81	1.32	11.01	12.82	23.83
	10	609.51	610.12	612.19	0.61	2.68	2.07	10.95	14.17	25.12
		609.56	610.21	611.90	0.65	2.34	1.69	11.16	13.42	24.58
Til ite		609.79	610.24	612.20	0.45	2.41	1.96	10.72	14.88	25.60
75BC	11	609.87	610.37	612.67	0.50	2.03	1.53	10.01	12.50	23.11
1000	·	609.85	600.80	611.89	0.40	2.02	2.42	9.63	16.16	20.95
	10	609.80	609.03	612 12	0.15	2.15	2.00	10.51	16.10	26.88
	12	609.72	609.95	611.77	0.23	2.05	1.82	11.12	14.48	25.60
		609.41	609.97	611.81	0.56	2.40	1.84	11.07	14.30	25.37
	12	609.57	610.15	611.60	0.58	2.03	1.45	11.12	12.13	23.25
	15	609.57	610.05	611.74	0.48	2.17	1.69	10.72	14.81	25.53
		608.59	608.96	611.94	0.37	3.35	2.98	8.32	18.93	27.25
Allab	14	608.69	609.22	611.53	0.53	2.84	2.31	10.70	17.24	27.94
		608.69	608.93	611.16	0.24	2.47	2.23	7.25	16.37	23.62
		608.65	608.87	611.19	0.22	2.54	2.32	7.75	17.11	24.86
	15	608.70	609.01	612.07	0.31	3.37	3.06	8.73	19.22	27.95
	<u> </u>	600.05	610.00	611.45	0.57	2.00	1.40	10.49	12.04	21.13
		609.45	600.00	611.45	0.55	2.00	2 07	10.00	15 40	26.38
	16	609.58	610 16	611.85	0.40	2.47	1.69	10.03	12.75	23.30
		609.49	610.00	612.19	0.51	2.70	2.19	10.18	14.81	24,99
AI-5%B	47	609.40	609.90	611.38	0.50	1.98	1.48	11.32	12.77	24.09
	17	609.55	610.08	612.07	0.53	2.52	1.99	9.72	13.18	22.90
		609.58	609.92	612.11	0.34	2.53	2.19	9.47	13.57	23.04
	18	609.46	609.87	611.38	0.41	1.92	1.51	10.27	12.75	23.02
		609.67	610.10	612.38	0.43	2.71	2.28	9.13	14.36	23.49

Grain	Sample	Τ _u	T _R	T _N	$\Delta T_{\rm BJI}$	$\Delta T_{\rm NJI}$	$\Delta T_{\rm N,P}$	t,	t ₂	t,
Refiner	I.D.	(°Č)	(°Ĉ)	(°Ĉ)	(°Ĉ)	(°C)	(°C)	(sec.)	(sec.)	(sec.)
		613.77	614.97	616.41	1.20	2.64	1.44	5.71	3.89	9.60
NI/A	0	613.68	615.06	616.95	1.38	3.27	1.89	5.82	4.40	10.22
19/7	0	613.83	615.25	619.39	1.42	5.56	4.14	5.46	6.69	12.15
		613.81	615.01	616.52	1.20	2.71	1.51	5.60	4.18	9.78
	1	614.31	615.32	617.64	1.01	3.33	2.32	6.32	4.63	10.95
	• •	614 28	615 09	618 28	0.81	4 00	3 19	5 58	6 51	12.09
		613.56	614.50	616.61	0.94	3.05	2.11	6.74	4.57	11.31
AI-6%11	2	615.22	616.16	616.86	0.94	1.64	0.70	5.04	3.02	8.06
		614.90	615.98	617.78	1.08	2.88	1.80	5.33	4.33	9.66
		615.82	616.63	618.36	0.81	2.54	1.73	5.64	3.72	9.36
	3	615.88	616.51	620.16	0.63	4.28	3.65	3.95	5.71	9.66
		615.57	616.15	618.33	0.58	2.76	2.18	4.84	4.45	9.29
		614.26	615.27	619.01	1.01	4.75	3.74	6.94	6.64	13.58
	4	613.70	614.84	616.84	1.14	3.14	2.00	6.83	4.68	11.51
		613.29_	614.66	615.46	1.37	2.17	0.80	6.60	3.75	10.35
		614.26	615.56	616.79	1.30	2.53	1.23	5.40	3.62	9.02
AI-5%11-	5	614.02	615.26	617.02	1.24	3.00	1.76	6.18	4.23	10.41
1%B	•	614.09	615.03	617.22	0.94	3.13	2.19	6.64	4.68	11.32
		615.59	616.24	617.39	0.65	1.80	1.15	4.53	3.39	7.92
	6	616.11	616.56	619.38	0.45	3.27	2.82	4.72	4.91	9.63
	•	616.29	616.60	619.76	0.31	3.47	3.16	4.22	5.28	9.50
		615.63	616.02	618.12	0.39	2.49	2.10	3.80	4.18	7.98
	7	615.99	616.12	620.23	0.13	4.24	4.11	3.19	5.76	8.95
A1		615.42	615.80	618.18	0.38	2.76	2.38	3.35	4.09	7.44
		615.25	615.48	619.16	0.23	3.91	3.68	3.8 9	6.56	10.45
2.5%11-	8	615.05	615.42	618.21	0.37	3.16	2.79	3.10	4.97	8.07
2.5%B	5	614.74	614.98	618.40	0.24	3.66	3.42	2.78	5.55	8.33
		615.03	615.43	619.28	0.40	4.25	3.85	4.56	7.21	11.77
	a	615.21	615.69	618.40	0.48	3.19	2.71	4.63	5.19	9.82
		615.18	615.72	618.63	0.54	3.45	2.91	4.90	5.79	10.69
		613.13	614.61	615.97	1.48	2.84	1.36	4.15	3.62	7.77
	10	614.49	615.70	617.58	1.21	3.09	1.88	5.93	4.42	10.35
	10	614.42	615.38	617.60	0.96	3.18	2.22	5.46	4.38	9.84
		615.22	615.98	618.39	0.76	3.17	2.41	3.29	4.72	8.01
liLite	11	614.79	615.60	618.09	0.81	3.30	2.49	4.14	4.65	8.79
75BC		615.16	615.74	618.61	0.58	3.45	2.87	5.71	5.11	10.82
		614.85	615.54	617.24	0.69	2.39	1.70	5.63	3.78	9.41
	12	615.34	615.86	617.42	0.52	2.08	1.56	3.43	3.41	6.84
	, –	615.33	615.71	618.39	0.38	3.06	2.68	4.03	4.49	8.52
		613.53	614.59	616.66	1.06	3.13	2.07	6.51	4.49	11.00
	13	613.97	615.0 9	617.21	1.12	3.24	2.12	5.54	4.68	10.22
		613.73	614.95	617.39	1.22	3.66	2.44	6.55	5.36	11.91
A 177 . 1		613.41	614.76	615.44	1.35	2.03	0.68	5.99	3.52	9.51
Allab	14	614.55	615.96	617.49	1.41	2.94	1.53	6.63	4.22	10.85
		614.55	615.98	617.17	1.43	2.62	1.19	5.61	3.78	9.39
		614.22	615.66	616.66	1.44	2.44	1.00	5.81	4.17	9.98
	15	614.58	616.00	618.06	1.42	3.48	2.06	8.21	4.91	13.12
		614.45	615.61	617.01	1.16	2.56	1.40	5.76	3.78	9.54
		615.64	615.67	619.25	0.03	3.61	3.58	0.86	5.74	6.60
	16	615.86	615.91	620.03	0.05	4.17	4.12	1.67	6.23	7.90
		616.27	616.30	620.03	0.03	3.76	3.73	0.92	5.83	6.75
		615.72	615.83	618.97	0.11	3.25	3.14	1.88	4.94	6.82
AI-5%B	17	615.44	615.65	618.80	0.21	3.36	3.15	2.24	5.04	7.28
]		615.82	615.82	618.67	0.00	2.85	2.85	0.00	5.89	5.89
		615.54	615.59	619.08	0.05	3.54	3.49	1.81	5.53	7.34
	19	615.41	615.68	619.38	0.27	3.97	3.70	2.36	5.67	8.03
		615.33	615.46	618.38	0.13	3.05	2.92	1.72	6.80	8.52

Grain	Sample	Tu	T.	TN		<u>Λ</u> <i>Τ</i>	ATup	t .	ta	t.
Refiner	I.D.	(°Č)	(°Ĉ)	(°C)	(°Ĉ)	(°C)	(°C)	(sec.)	(sec.)	(sec.)
		615.77	616.07	617.28	0.30	1.51	1 21	7 77	13.37	21 14
NI/A	0	616.58	616.80	618.30	0.22	1.72	1.50	7.16	13.22	20.38
	0	615.64	616.03	617.30	0.39	1.66	1.27	7.83	13.92	21.75
		616.49	616.83	617.93	0.34	1.44	1.10	7.51	11.12	18.63
	1	616.37	616.66	617.58	0.29	1.21	0.92	7.40	10.75	18.15
		616.48	616.78	617.32	0.30	0.84	0.54	9.33	9.42	18.75
AL 6% Ti		617.28	617.58	618.98	0.30	1.70	1.40	7.82	14.20	22.02
	2	617.29	617.47	619.20	0.18	1.91	1.73	6.68	16.99	23.67
		617.44	617.74	618.61	0.30	1.17	0.87	10.48	11.56	22.04
	_	617.05	619.02	610.62	0.13	1.01	1.48	7.18	12.33	19.51
3	3	618 14	618.18	619.62	0.07	1.07	1.00	0.30	17.06	10.21
		616.45	616 75	617.76	0.04	1 31	1.00	7 90	10.31	18.21
		616.43	616 76	617.55	0.00	1.31	0.79	9.37	9.33	18 70
	4	616.51	616.76	618.23	0.25	1.72	1.47	6.48	13.74	20.22
		617.71	618.05	619.49	0.34	1.78	1.44	8.52	12.36	20.88
Al-5%Ti-	5	616.95	617.49	618.91	0.54	1.96	1.42	10.79	13.25	24.04
1%B	5	617.29	617.66	618.74	0.37	1.45	1.08	11.53	11.26	22.79
		618.31	618.56	619.57	0.25	1.26	1.01	8.65	10.04	18.69
	6	618.32	618.71	620.08	0.39	1.76	1.37	10.39	14,17	24.56
		618.43	618.75	620.16	0.32	1 73	1.41	9.62	13.13	22.75
		617.34	617.58	618.95	0.24	1.61	1.37	10.34	13.89	24.23
	7	617.37	617.51	618.60	0.14	1.23	1.09	9.16	10.87	20.03
AI-		617.07	617.36	618.51	0.29	1.44	1.15	8.74	11.66	20.40
2 5%Ti-		617.85	618.15	619.45	0.30	1.60	1.30	8.79	9.94	18.73
2.57011-	8	617.26	617.58	619.40	0.32	2.14	1.82	11.06	16.53	27.59
2.5%0		617.84	619.02	610.19	0.27	1.67	0.61	8.53	8.9/	17.50
		617.56	617.99	619.51	0.19	1.07	1.40	12.00	14.45	26.54
	9	617.00	617.71	619.43	0.32	2.03	1.03	9.58	13.75	20.34
		616 59	616 91	617.84	0.32	1.25	0.93	9.56	9.22	18 78
	10	616.07	616.35	617.51	0.28	1.44	1.16	7.72	11.46	19,18
		616.24	616.47	617.82	0.23	1.58	1.35	8.97	13.49	22.46
		617.07	617.39	618.13	0.32	1.06	0.74	9.60	8.91	18.51
TiLite	11	616.77	617.09	618.20	0.32	1.43	1.11	11.03	12.75	23.78
75BC		616.95	617.08	618.40	0.13	1.45	1.32	7.28	13.41	20.69
		617.23	617.48	618.38	0.25	1.15	0.90	8.35	10.27	18.62
	12	617.25	617.44	618.04	0.19	0.79	0.60	9.29	8.39	17.68
		617.01	617.37	618.51	0.36	1.50	1.14	10.41	12.09	22.50
		615.94	616.40	617.60	0.46	1.66	1.20	10.14	12.11	22.25
	13	616.28	616.49	617.27	0.21	0.99	0.78	1.70	9.94	1/ 04
		617.20	617.74	610.11	0.43	1.43	1.00	0.91	9.4/	20.26
AlTab		616 32	616.84	617.63	0.44	1 31	0.70	9.60	10.74	20.20
	14	616.00	616.52	617.46	0.32	1.31	0.79	8.05	0.35	17.40
		616 77	617.04	618 12	0.40	1.35	1.08	7 12	11 22	18.34
	45	616 12	616.43	617 15	0.31	1.00	0.72	8.71	9.90	18.61
	15	616.07	616.47	617.39	0.40	1.32	0.92	8.38	9.78	18.16
		616.83	616.99	618.45	0.16	1.62	1.46	7.20	12.17	19.37
	16	616.27	616.43	617.67	0.16	1.40	1.24	6.93	12.58	19.51
	10	616.45	616.54	617.95	0.09	1.50	1.41	6.60	15.73	22.33
		616.43	616.62	618.48	0.19	2.05	1.86	7.36	15.80	23.16
AI-2%B	17	616.08	616.27	617.82	0.19	1.74	1.55	7.25	14.52	21.77
		616.01	616.16	617.75	0.15	1.74	1.59	8.12	15.08	23.20
		615.74	615.90	617.66	0.16	1.92	1.76	7.87	14.59	22.46
	18	616.30	616.49	618.36	0.19	2.06	1.87	6.38	14.84	21.22
		616.01	616.17	617.45	0.16	1.44	1.28	8.07	13.11	21.18

Appendix E Results of Coherency Point Determination for Samples Solidified at 1.0 °C/s

Grain Refiner	Sample I.D.	Temperature at Coherency Point (°C)	Time from Nucleation to Coherency Point (sec.)
		602.2	36.2
N/A	0	602.5	36.0
		602.5	37.3
		603.1	34.4
	1	601.0	40.6
		602.8	36.3
AL 6% Ti	İ	501.3	40.0
AI-0 /011	2	599.0	4/.1
	_	602.7	38.0
		601.8	40.3
	3	602.5	37.4
		605.3	29.0
		600.1	42.0
	4	602.4	
		601.3	39.8
AI-5%Ti-		601.3	42.1
10/ 0	5	600.2	42.5
1700		602.6	38.0
		602.4	39.0
	6	601.0	44.4
		601.4	41.6
		599.8	42.2
	7	601.7	39.2
AI-		603.8	33.7
2 5% Ti		604.4	32.3
2.57611-	8	602.6	36.8
2.5%B		602.5	37.2
		603.1	36.0
	9	605.1	30.8
		605.5	30.5
		599.2	43.2
	10	604.8	
		602.9	
Tilito		600.3	43.3
TILILE	11	602.1	39.6
75BC		595.0	55.0
		600.7	42.1
	12	605.4	28.0
	ļ	601.0	41.0
		603.9	30.6
	13	603.2	36.6
		601.2	41.2
AITab		604.7	29.1
ALLAD	14	602.2	36.8
	L	604.2	31.0
		602.4	35.3
	15	602.8	34.3
		603.7	31.1
		603.1	33.8
	16	599.9	40.2
		601.5	39.7
		604.3	31.0
AI-3%B	17	601.2	41.3
		603.5	31.6
		604.4	29.8
	18	603.7	35.9
		604.6	32.2

356 Alloy,	Fast Cooling	Rate (~1.0	°C/s)
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Grain	Sample	Temperature at	Time from Nucleation to
Refiner	I.D.	Coherency Point	Coherency Point
		(°C)	(sec.)
		610.4	39.7
NI/A		609.5	43.5
IN/A	0	610.5	42.7
		611.6	34.3
	1	611.1	36.2
	I I	612.2	35.5
AL 00/ T		609.6	44.4
AI-6% I I	2	611.5	35.9
		610.5	41.5
		613.1	31.6
	3	6119	35.0
		613.0	33.0
		609.9	43.5
	4	611.6	33.3
		611.8	31.2
AL 5% TI.	1	611.3	36.4
AI-570 I I-	5	611.2	36.9
1%B		611.9	33.0
		612.1	35.6
	6	613.0	33.8
		609.4	48.0
		610.2	42.1
	7	611.8	36.5
Al-		610.9	41.9
2 5%Ti-		611.6	35.2
2.570 TF	8	612.1	34.5
2.370D		610.7	38.0
		612.6	35.6
	9	611.5	39.4
		611.3	40.4
		609.6	39.7
	10	6110	39.1
		612.0	45.5
Til ite		606.2	50.2
75BC	11	610.4	40.9
7500		611.9	35.0
		609.0	45.8
	12	609.4	45.0
	 		34.0
		609.5	44.5
	13	609.1	<u>458</u>
		610.4	36.9
AlTab		611.3	38.1
	14	610 4	<u>41</u> 9
		611 4	37.6
	1	611.3	40.0
	15	612.0	35.2
	1	612.2	36.5
		610.5	44.6
	16	608.5	49.1
		612.1	36.3
Al-5%B		611.5	37.2
	1/	611.8	35.5
		612.2	34.1
		608.4	50.6
	18	609.4	44.6
		1 003.4	

Appendix F Results of Latent Heat and Fraction Solid Determination

$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$		1	Laten	t Heat E	volved (W/g)	,	Fraction	Solid
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$			At	At	At	At	At	At
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Grain Refiner	Sample I.D.	Τ _υ	T _R	Coherency Point	Τu	T _R	Coherency Point
N/A 0 35.7 195.0 358.9 0.03 0.14 0.26 22.0 218.3 366.1 0.02 0.16 0.26 27.2 118.6 307.2 0.02 0.09 0.26 27.2 118.6 357.2 0.02 0.09 0.26 21.0 114.6 343.6 0.02 0.09 0.26 22.7 113.2 425.3 0.02 0.09 0.26 22.5 107.2 349.7 0.02 0.08 0.24 23.8 115.7 342.2 0.02 0.08 0.25 3 20.1 98.5 338.0 0.01 0.07 0.25 39 100.5 377.7 0.02 0.07 0.26 20.8 85.6 340.2 0.02 0.07 0.26 22.5 63.4 373.1 0.02 0.04 0.26 22.5 71.7 360.7 0.02 0.04 0.26			44.2	222.1	360.5	0.03	0.16	0.26
N/A 0 32.0 218.3 366.1 0.02 0.16 0.26 28.4 130.8 304.3 0.02 0.10 0.22 28.4 130.8 304.3 0.02 0.09 0.26 26.2 137.8 336.4 0.02 0.09 0.26 28.2 137.8 336.4 0.02 0.09 0.23 21.0 114.6 343.6 0.02 0.09 0.26 22.7 119.2 425.9 0.02 0.08 0.24 22.5 107.2 349.7 0.02 0.08 0.25 3 20.1 98.5 338.0 0.01 0.07 0.25 3 17.2 92.7 278.8 0.01 0.07 0.26 3 100.5 377.2 0.02 0.06 0.26 20.8 85.6 340.2 0.02 0.07 0.23 4 25.5 71.7 360.7 0.22 0.05 <td>NI/A</td> <td>0</td> <td>35.7</td> <td>195.0</td> <td>358.9</td> <td>0.03</td> <td>0.14</td> <td>0.26</td>	NI/A	0	35.7	195.0	358.9	0.03	0.14	0.26
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$		0	32.0	218.3	366.1	0.02	0.16	0.26
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$			28.4	130.8	304.3	0.02	0.10	0.22
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		1	27.2	118.6	357.2	0.02	0.09	0.26
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$			26.2	137.8	336.4	0.02	0.09	0.23
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$			21.0	114.6	343.6	0.02	0.09	0.26
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	AI-07611	2	22.7	119.2	425.8	0.02	0.09	0.30
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$			23.8	115.7	342.2	0.02	0.08	0.24
3 20.1 98.5 338.0 0.01 0.07 0.25 17.2 92.7 278.8 0.01 0.07 0.26 4 25.8 96.7 330.4 0.02 0.07 0.26 20.8 85.6 340.2 0.02 0.07 0.23 20.8 85.6 340.2 0.02 0.06 0.26 22.5 63.4 373.1 0.02 0.06 0.26 32.9 41.5 310.3 0.02 0.04 0.26 32.9 41.5 310.3 0.03 0.05 0.23 6 19.8 50.2 364.1 0.01 0.04 0.26 $2.5%$ Ti- $2.5%$ Ti- 319.8 0.01 0.07 0.25 $2.5%$ Ti- $2.5%$ Ti- 306.2 0.01 0.08 0.22 $2.5%$ Ti- $2.5%$ Ti- 30.62 0.01 0.08 0.22			22.5	107.2	349.7	0.02	80.0	0.25
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		3	20.1	98.5	338.0	0.01	0.07	0.25
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$			17.2	92.7	278.8	0.01	0.07	0.20
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$			33.9	100.5	377.2	0.02	0.07	0.26
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		4	25.0	90.7	330.4	0.02	0.07	0.23
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$			20.0	62.4	340.2	0.02	0.00	0.26
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	AI-5%Ti-		32.5	71.7	360.7	0.02	0.04	0.20
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	1%B	5	25.5	67.7	325.5	0.02	0.05	0.28
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	1/00	ļ	32.0	41.5	310.3	0.03	0.03	0.23
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$			20.8	53.5	355.6	0.03	0.03	0.24
Al- 26.6 109.9 375.3 0.02 0.08 0.28 21.3 106.2 354.7 0.01 0.07 0.25 21.3 106.2 354.7 0.01 0.07 0.25 25%Ti- 19.9 119.3 319.8 0.01 0.08 0.22 2.5%B 21.4 95.9 324.8 0.02 0.07 0.24 2.5%B 21.4 95.9 324.8 0.02 0.07 0.24 9 21.4 95.9 324.8 0.02 0.07 0.24 9 20.8 104.2 267.2 0.02 0.08 0.20 23.2 96.5 258.3 0.02 0.09 0.29 10 27.3 131.8 276.3 0.02 0.09 0.29 11 26.8 128.3 402.9 0.02 0.04 0.24 29.8 58.5 446		6	19.8	50.2	364.1	0.02	0.04	0.26
Al- 2.5%Ti- 2.5%B $\begin{array}{r} 7 \\ 21.3 \\ 19.9 \\ 19.9 \\ 19.9 \\ 119.3 \\ 19.4 \\ 19.9 \\ 21.4 \\ 95.9 \\ 21.4 \\ 95.9 \\ 21.4 \\ 95.9 \\ 22.48 \\ 19.3 \\ 102.0 \\ 336.2 \\ 0.01 \\ 0.07 \\ 0.24 \\ 0.07 \\ 0.24 \\ 0.07 \\ 0.24 \\ 0.07 \\ 0.24 \\ 0.07 \\ 0.24 \\ 0.07 \\ 0.24 \\ 0.07 \\ 0.25 \\ 0.01 \\ 0.07 \\ 0.24 \\ 0.07 \\ 0.25 \\ 0.02 \\ 0.07 \\ 0.19 \\ 0.26 \\ 0.20 \\ 0.02 \\ 0.08 \\ 0.20 \\ 0.02 \\ 0.09 \\ 0.29 \\ 0.20 \\ 0.02 \\ 0.09 \\ 0.29 \\ 0.20 \\ 0.02 \\ 0.09 \\ 0.29 \\ 0.20 \\ 0.02 \\ 0.09 \\ 0.29 \\ 0.21 \\ 0.02 \\ 0.09 \\ 0.24 \\ 0.04 \\ 0.26 \\ 0.20 \\ 0.02 \\ 0.09 \\ 0.29 \\ 0.22 \\ 0.02 \\ 0.09 \\ 0.29 \\ 0.24 \\ 0.04 \\ 0.25 \\ 0.02 \\ 0.04 \\ 0.23 \\ 0.23 \\ 0.03 \\ 0.03 \\ 0.03 \\ 0.25 \\ 0.02 \\ 0.01 \\ 0.01 \\ 0.00 \\ 0.21 \\ 0.01 \\ 0.20 \\ 0.21 \\ 0.01 \\ 0.02 \\ 0.01 \\ 0.02 \\ 0.02 \\ 0.01 \\ 0.02 \\ 0.02 \\ 0.02 \\ 0.02 \\ 0.01 \\ 0.03 \\ 0.25 \\ 0.02 \\ 0.02 \\ 0.01 \\ 0.03 \\ 0.03 \\ 0.25 \\ 0.02 \\ 0.02 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.02 \\ 0.02 \\ 0.01 \\ 0.03 \\ 0.03 \\ 0.25 \\ 0.02 \\ 0.02 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.00 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\ 0.01 \\$			26.6	109.9	375 3	0.07	0.04	0.28
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		-	21.3	106.2	354.7	0.02	0.00	0.25
Al- 2.5%Ti- 2.5%B 19.4 108.9 306.2 0.01 0.08 0.22 2.5% Ti- 2.5%B 8 21.4 95.9 324.8 0.02 0.07 0.24 19.3 102.0 336.2 0.01 0.07 0.24 9 21.4 95.9 324.8 0.02 0.07 0.24 9 21.4 95.9 324.8 0.02 0.07 0.24 9 20.8 104.2 267.2 0.02 0.08 0.20 23.2 96.5 258.3 0.02 0.07 0.19 26.8 128.3 402.9 0.02 0.09 0.29 27.3 131.8 276.3 0.02 0.09 0.24 10 226.0 123.1 329.2 0.02 0.04 0.24 $75BC$ 11 34.2 64.8 341.4 0.02 0.04 0.23	• •	1	19.9	119.3	319.8	0.01	0.08	0.23
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Al-	}	19.4	108.9	306.2	0.01	0.08	0.22
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	2.5%Ti-		21.4	95.9	324.8	0.02	0.07	0.24
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	2.5%B	0	19.3	102.0	336.2	0.01	0.07	0.25
9 20.8 104.2 267.2 0.02 0.08 0.20 23.2 96.5 258.3 0.02 0.07 0.19 26.8 128.3 402.9 0.02 0.09 0.29 27.3 131.8 276.3 0.02 0.10 0.20 26.0 123.1 329.2 0.02 0.09 0.24 49.1 52.4 355.4 0.04 0.04 0.26 11 34.2 64.8 341.4 0.02 0.04 0.23 75BC 12 38.4 49.9 349.5 0.03 0.04 0.25 12 32.9 32.9 230.5 0.02 0.02 0.17 39.3 48.8 352.3 0.03 0.03 0.25			17.4	103.5	307.2	0.01	0.08	0.24
Image: Figure 10 Image: 23.2 96.5 258.3 0.02 0.07 0.19 10 26.8 128.3 402.9 0.02 0.09 0.29 27.3 131.8 276.3 0.02 0.09 0.29 26.0 123.1 329.2 0.02 0.09 0.24 49.1 52.4 355.4 0.04 0.04 0.26 11 34.2 64.8 341.4 0.02 0.04 0.23 75BC 11 29.8 58.5 446.6 0.02 0.04 0.25 12 32.9 32.9 230.5 0.02 0.02 0.17 39.3 48.8 352.3 0.03 0.03 0.25		0	20.8	104.2	267.2	0.02	0.08	0.20
TiLite 10 26.8 128.3 402.9 0.02 0.09 0.29 7.3 131.8 276.3 0.02 0.10 0.20 26.0 123.1 329.2 0.02 0.09 0.24 49.1 52.4 355.4 0.04 0.04 0.26 75BC 11 29.8 58.5 446.6 0.02 0.04 0.23 12 38.4 49.9 349.5 0.03 0.04 0.25 12 32.9 32.9 230.5 0.02 0.02 0.17		5	23.2	96.5	258.3	0.02	0.07	0.19
10 27.3 131.8 276.3 0.02 0.10 0.20 26.0 123.1 329.2 0.02 0.09 0.24 49.1 52.4 355.4 0.04 0.04 0.26 75BC 11 34.2 64.8 341.4 0.02 0.04 0.23 75BC 11 29.8 58.5 446.6 0.02 0.04 0.23 12 32.9 32.9 230.5 0.03 0.04 0.25 12 39.3 48.8 352.3 0.03 0.03 0.25	······································		26.8	128.3	402.9	0.02	0.09	0.29
TiLite 10 26.0 123.1 329.2 0.02 0.09 0.24 TiLite 11 52.4 355.4 0.04 0.04 0.26 75BC 11 29.8 58.5 446.6 0.02 0.04 0.23 12 38.4 49.9 349.5 0.03 0.04 0.25 12 32.9 32.9 230.5 0.02 0.02 0.17		10	27.3	131.8	276.3	0.02	0.10	0.20
TiLite 11 52.4 355.4 0.04 0.04 0.26 75BC 34.2 64.8 341.4 0.02 0.04 0.23 75BC 29.8 58.5 446.6 0.02 0.04 0.23 12 38.4 49.9 349.5 0.03 0.04 0.25 12 32.9 32.9 230.5 0.02 0.02 0.17		10	26.0	123.1	329.2	0.02	0.09	0.24
11 34.2 64.8 341.4 0.02 0.04 0.23 75BC 11 29.8 58.5 446.6 0.02 0.04 0.33 38.4 49.9 349.5 0.03 0.04 0.25 12 32.9 32.9 230.5 0.02 0.02 0.17 39.3 48.8 352.3 0.03 0.03 0.25			49.1	52.4	355.4	0.04	0.04	0.26
75BC 29.8 58.5 446.6 0.02 0.04 0.33 38.4 49.9 349.5 0.03 0.04 0.25 12 32.9 32.9 230.5 0.02 0.02 0.17 39.3 48.8 352.3 0.03 0.03 0.25	liLite	11	34.2	64.8	341.4	0.02	0.04	0.23
38.4 49.9 349.5 0.03 0.04 0.25 12 32.9 32.9 230.5 0.02 0.02 0.17 39.3 48.8 352.3 0.03 0.03 0.25	75BC		29.8	58.5	446.6	0 02	0.04	0.33
12 <u>32.9</u> <u>32.9</u> <u>230.5</u> <u>0.02</u> <u>0.02</u> <u>0.17</u> <u>39.3</u> <u>48.8</u> <u>352.3</u> <u>0.03</u> <u>0.03</u> <u>0.25</u>			38.4	49.9	349.5	0.03	0.04	0.25
39.3 48.8 352.3 0.03 0.03 0.25		12	32.9	32.9	230.5	0.02	0.02	0.17
			39.3	48.8	352.3	0.03	0.03	0.25
<u>36.9</u> <u>151.3</u> <u>298.1</u> <u>0.03</u> <u>0.12</u> <u>0.23</u>			36.9	151.3	298.1	0.03	0.12	0.23
		13	34.8	1/3.0	337.4	0.02	0.12	0.23
		·	28.8	124.1	349.9	0.02	0.09	0.27
AlTab 35.3 177.4 291.3 0.02 0.12 0.20	AlTah		35.3	1/1.4	291.3	0.02	0.12	0.20
	711100	14	33.1	130.7	350.0	0.02	0.10	0.20
		 	21.2	135.4	294.0	0.02	0.10	0.21
			21.5	140.7	320.0	0.02	0.10	0.20
$15 \qquad 132 \qquad 149.7 \qquad 300 \qquad 0.02 \qquad 0.10 \qquad 0.23 \qquad 0.01 \qquad 0.02 \qquad 0.10 \qquad 0.23 \qquad 0.01 \qquad 0.02 \qquad 0.10 \qquad 0.02 \qquad 0.01 \qquad 0.0$		15	27.0	193.7	270.0	0.02	0.10	0.23
		<u> </u>	21.9	1127	217.2	0.02	0.10	0.21
			20.9	112.6	317.3	0.02	0.00	0.22
16 20.0 113.0 300.2 0.02 0.00 0.27		16	20.0	1120	351.0	0.02	0.00	0.27
			20.6	127 A	289.4	0.02	0.00	0.23
AI-5%B 23.4 120.4 365.3 0.02 0.08 0.26	AI-5%B	47	23.4	120.4	365.3	0.02	0.08	0.26
	· · · · · · · ·	17	18.7	115.8	290.3	0.01	0.09	0.22
			18.8	103.5	288.4	0.01	0.08	0.21
			29.3	116.3	326.6	0.02	0.08	0.22
		0	20.1	103.1	295.5	0.01	0.08	0.22

		Latent Heat Evolved (W/g)		Fraction Solid			
		At	At	At	At	At	At
Grain Refiner	Sample I.D.	Τ _υ	T _R	Coherency Point	Τυ	T _R	Coherency Point
· · · · ·		13.1	78.8	313.6	0.01	0.05	0.22
N/A	0	11.2	78.4	325.0	0.01	0.06	0.24
	-	13.3	78.1	318.6	0.01	0.05	0.22
		12.7	73.6	254.8	0.01	0.05	0.17
	1	21.4	83.5 77.5	2/0.0	0.01	0.05	0.19
		12.6	81.0	317.3	0.01	0.05	0.17
Al-6%Ti	2	11.3	62.1	249.1	0.01	0.00	0.19
	2	12.8	71.1	298.9	0.01	0.05	0.21
	3	12.1	72.0	241.8	0.01	0.05	0.17
		14.8	57.3	276.5	0.01	0.04	0.19
- <u>-</u>		14.7	62.2	237.9	0.01	0.04	0.17
		15.4	87.1	296.1	0.01	0.06	0.20
	4	13.8	87.0	251.4	0.01	0.06	0.18
		13.5	82.8	230.5	0.01	0.05	0.16
Al-5%Ti-	-	11.0	77.6	202.0	0.01	0.05	0.21
1%B	5	14.5	83.6	246.5	0.01	0.05	0.13
.,		12.4	57.0	245.7	0.01	0.04	0.18
	e	16.2	65.2	254.9	0.01	0.04	0.17
	0	17.2	59.2	335.3	0.01	0.04	0.22
		14.5	51.3	292.9	0.01	0.04	0.22
	7	16.6	47 4	263.4	0.01	0.03	0.18
AI-		13.9	48.6	315.1	0.01	0.03	0.22
2 5%TL		21.9	57.6	234.0	0.02	0.04	0.17
2.57611-	8	15.4	45.8	245.0	0.01	0.03	0.18
2.3700		27.3	717	2/3./	0.01	0.05	0.19
		17.9	62.9	230.5	0.02	0.05	0.17
	9	19.0	66.4	278.9	0.01	0.05	0.19
	<u> </u>	11.5	65.0	328.3	0.01	0.04	0.22
	10	10.6	74.3	274.6	0.01	0.06	0.21
		11.9	71.9	344.2	0.01	0.05	0.23
TUBO	11	15.6	52.3	293.9	0.01	0.03	0.20
		13.7	58.9	392.2	0.01	0.04	0.27
75BC		16.9	76.2	306.3	0.01	0.05	0.20
	12	13.0	/0.9	262.1	0.01	0.05	0.18
		14.5	40.7	333.5	0.01	0.03	0.24
		13.8	85.7	267.3	0.01	0.06	0.18
	13	15.5	78.2	343.4	0.01	0.05	0.22
		16.9	89.4	241.5	0.01	0.06	0.16
· · · ·	14	13.1	77.1	270.2	0.01	0.06	0.21
Allab		14.0	91.5	304.0	0.01	0.06	0.20
		11.2	75.6	313.5	0.01	0.05	0.22
	15	15.7	80.8	281.0	0.01	0.06	0.20
1		12.4	100.4	293.0	0.01	0.07	0.20
	16	13.3	79.7	287.9	0.01	0.05	0.19
		17.0	24.1	240.4	0.01	0.02	0.10
AI-5%B		23.2	31.0	359.7	0.01	0.02	0.20
	17	15.3	32.7	259.7	0.02	0.02	0.19
		17.1	38.9	275.5	0.01	0.03	0.19
		23.8	23.8	232.8	0.02	0.02	0.18
	18	19.7	36.4	252.6	0.01	0.03	0.18
		15.8	39.5	347.1	0.01	0.03	0.23
		27.6	40.0	271.2	0.02	0.03	0.20

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	<u> </u>	Latent Heat Evolved (W/g)			Fraction Solid		
		At	At	At	At	At	At
Grain	Sample	τ _u	T _R	Coherency	Τ _U	T _R	Coherency
Refiner	<u> </u>			Point			Point
		3.3	6.1	Not Calculated	0.01	0.01	Not Calculated
N/A	0	2.8	6.1		0.01	0.01	**
		3.3	5.7		0.01	0.01	
		2.4	7.7		0.01	0.02	
	1	2.5	87		0.01	0.02	
		2.0	79		0.01	0.02	
Al-6%Ti	2	22	7.9		0.00	0.02	· · ·
	2	2.0	7.5		0.00	0.02	
		2.0	5.2	ua ut	0.01	0.02	46 H
	2	1.8	6.2		0.00	0.02	4.4
	5	2.4	7.8	**	0.01	0.02	
		2.3	7.1	**	0.01	0.02	
	Δ	2.2	6.9		0.01	0.02	
	-	1.9	6.5	- +	0.00	0.02	**
		2.1	6.6	4.4	0.01	0.02	
AI-5%11-	5	2.1	6.8	ut +4	0.01	0.02	• •
1%B		2.2	7.1		0.01	0.02	4.4
		2.1	7.1	4 44	0.01	0.02	14 14
	6	1.9	6.5	**	0.01	0.02	14 H
		2.2	6.2		0.01	0.02	u #
	7	1.7	7.6		0.00	0.02	
		2.1	7.0		0.01	0.02	
Al-		1.9	1.4		0.01	0.02	
2 5%Ti-		1.7	0.4		0.00	0.02	
2.5%B	8	<u> </u>	7.0		0.01	0.02	
2.5700		1.7	6.0		0.00	0.02	
		1.9	6.0		0.00	0.02	
	9	1.9	5.8		0.00	0.02	····
	<u> </u>	1.5	6.9		0.00	0.01	
	40	21	83		0.00	0.02	
	10	2.0	7.9	4.4	0.00	0.02	4.4
		2.0	7.3		0.00	0.02	
TiLite	11	1.8	7.1	16 4	0.00	0.02	
75BC		2.2	7.1		0.01	0.02	
	12	2.7	6.8		0.01	0.02	4 14
		2.7	7.0		0.01	0.02	14 18
		2.3	7.3	**	0.01	0.02	
	13	2.0	7.7	4.4	0.00	0.02	
		1.9	7.9	4.4	0.00	0.02	••
		2.2	7.3		0.01	0.02	4 Hi
		2.7	7.1	**	0.01	0.02	**
	14	2.3	7.8	**	0.01	0.02	
		2.3	5.6		0.01	0.01	
	15	2.7	<u>6.2</u>		0.01	0.02	
		2.9				0.02	
	16 17	2.0	0.0			0.02	
		1.0	72	ui ui		0.02	
		2.2	1.3		0.01	0.02	
		2.1	70			0.02	
AI-5%B		17	7 2			0.02	
		22	77		0.00	0.02	4 44
	18	19	68	**	0.01	0.02	
		21	72	<u> </u>	0.00	0.02	+++
		22	71		0.01	0.02	4 4

		Latent Heat Evolved (W/g)			Fraction Solid		
		At	At	At	At	At	At
Grain Refiner	Sample	τ _υ	T _R	Coherency	Tu	T _R	Coherency
		16	45	Not Calculated	0.01	0.01	Not Calculated
N/A		1.0	4.5	" "	0.01	0.01	""
	0	1.5	4.3		0.01	0.01	
		1.6	4.5	16 16	0.00	0.01	
	1	1.6	4.4		0.01	0.01	
		1.9	5.4		0.01	0.02	
		1.8	4.8	18 46 	0.01	0.01	u u
AI-6%11	2	2.1	4.5		0.01	0.01	**
		1.3	4.6		0.00	0.02	
		2.2	5.1		0.01	0.02	
	3	2.3	4.4		0.01	0.01	
		2.7	3.3		0.01	0.01	
		1.1	4.1		0.00	0.01	
	4	1.6	3.9		0.01	0.02	
		1.5	52		0.00	0.01	4.4
Al-5%Ti-	-	1.0	6.4		0.00	0.02	· · · · · · · · · · · · · · · ·
1%B	5	14	57		0.01	0.02	
		1.4	4.6		0.00	0.01	4.4
	^	1.5	53	4.4	0.00	0.02	4 4
	Ь	1.8	5.6		0.00	0.02	+4 16
		2.0	5.7		0.01	0.02	
	7	2.3	5.8	N 18	0.01	0.02	-4-14
	1	1.5	4.8		0.00	0.01	
Al-		2.2	6.8		0.01	0.02	4.4
2.5%Ti-	8	1.9	6.0		0.01	0.02	
2.5%B	0	1.8	5.0	14 44	0.01	0.01	
		1.7	4.0		0.00	0.01	ve +6
	9	1.7	6.3		0.01	0.02	* *
		1.9	6.0	**	0.01	0.02	**
		1.3	5.4		0.00	0.02	
	10	1.6	4.7	10 10	0.00	0.01	
		1.7	4.7		0.00	0.01	
Tilita		1.9	5.9		0.01	0.02	
7500	11	1.6	5.4		0.01	0.02	
7360		1.1	4.1		0.00		
	12	1./	4.9			0.02	·
		1.9	5.4	**	- 0.01	0.02	
		1.7	6.1		0.01	0.02	
AiTab	13	1.0	3.8	· · · · · · · · · · · · · · · · · · ·	0.00	0.02	•••
		17	59	и и	0.00	0.02	
	┝	1.7	5.7	4.14	0.00	0.02	
	14	1.9	6.3		0.01	0.02	·····
	14	2.1	6.2		0.01	0.02	+ +
	15	2.2	5.1		0.01	0.01	• •
		1.3	4.3		0.00	0.01	• •
		1.3	4.8	H H	0.00	0.02	4.8
	16	2.3	5.3	uL 16	0.01	0.01	
		2.0	4.4		0.01	0.01	••
		2.1	4.1		0.01	0.01	
		2.3	5.2		0.01	0.02	**
Al-5%B	17	2.1	4.9	4.	0.01	0.01	
		2.0	4.9	**	0.01	0.01	
		2.0	5.0	<u> </u>	0.01	0.02	ļ
	18	2.9	5.7		0.01	0.02	
		1 2.0	4.8	-	0.01	1 0.01	