AN INVESTIGATION OF ALUMINUM GRAIN REFINEMENT PROCESS AND STUDY OF THE ABILITIES OF ULTRASONIC DETECTION METHOD IN THIS PROCESS

by

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A thesis submitted in conformity with the requirements for the degree of Master of Applied Science
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An Investigation of Aluminum Grain Refinement Process and Study of the Abilities of Ultrasonic Detection Method in this Process

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Abstract

An investigation was carried out on the grain refinement mechanism in pure aluminum, using an ultrasonic detection system, and metallography tests. In this investigation the capability of the ultrasonic detection system in the grain refinement process was studied. The results show that the ultrasonic system, which effectively detects particles larger than 20μm in size, cannot detect the nucleants in the melt, but detects the movements and any cause of floating the particles, which provide more nucleants for the process. In the grain refinement process, the results show that there are other factors influencing the mechanism of grain refinement and fading phenomena, rather than TiAl₃ particles. Metastable phases containing titanium can play an important role in preventing the fading phenomena.
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1: Introduction

During the last few decades most of the improvements in science and technology have been related to the development of measuring and detecting devices. In biology and medicine the involvement of those devices in the researches and studies have been so important that new areas and branches were introduced to science and engineering, like biomedical engineering.

Waves have had an important role in detection devices. Light, electromagnetic, sound, and electrical waves are the ones which are used widely in detection systems. By transmitting them through a material or space, and analyzing the changes in their normal features, it is possible to get some data about the medium they traveled through, and to detect the entities inside that medium and their characteristics.

One of the wave propagating systems is the ultrasonic system. It has been widely used in science, industry, and medicine. The use of ultrasonic systems in liquid metals is in its earliest ages, and it can have a great future in being used by metallurgical industries, both for power forcing systems and also detection systems. Lately ultrasonics has been studied for detecting the cleanliness of metals in the liquid state.

This project is using the ultrasonic system in the grain refinement process for aluminum and studying its abilities of detection in this process.

Grain refinement is an old method which has been used to obtain a better structure in aluminum. Although this process has being used for several decades, still the mechanism of this process is not known well. Figure 1-1 illustrates the change in the structure of an aluminum cast due to the grain refinement process.

This study investigates the mechanism of this process and the fading phenomenon, which is happening in this process.
Figure 1-1: Two samples of the structure of an aluminum cast before and after grain refinement. (Adapted from Aluminum Association, TP-1, 1990)
2: Grain Refinement

2-1 Review of the literature

Grain refinement is a method for producing a structure with improved mechanical properties. In this method by adding some solid particles into the melt we provide a better heterogeneous nucleation opportunity for the melt. Therefore, by having more active nucleants, the grain size of the cast will be decreased.

In the aluminum industry grain refinement is very widely used. It makes a finer equiaxed structure (1) which:
- Ensures uniform mechanical properties
- Reduces ingot cracking
- Improves feeding to eliminate shrinkage porosity
- Distributes second phase and micro-porosity on a fine scale
- Improves machinability and cosmetic features

The traditional grain refiner for aluminum castings is TiAl₃. It is added in the form of a master alloy of Al-6%Ti. TiAl₃ is an effective nucleant as it has a low interfacial energy with aluminum. Amberg, Backerud, and Klang (2) showed that the aluminum atoms on the (011) planes of TiAl₃ match those on the (112) planes of solid aluminum (Figure 2-1).

They also showed that there could be three different types or shapes of TiAl₃, depending on the method of the master alloy production (2,3). Fast cooling of a solution from high temperature creates a form of petal-like shape. Slow cooling from high temperature makes plates, and production at low temperature causes chemical reactions which will produce blocky crystals of TiAl₃ (Figure 2-2). They also confirmed the previous study of Maxwell and Hellawell (4,5) that the grain refining of aluminum alloys is dependent on the morphology of TiAl₃. Petal and plate like shapes of TiAl₃ are slower in acting as a grain refiner but their efficiency in grain refinement lasts longer. On the other hand, the
Figure 2-1: TiAl₃ structure, which shows the (011) lattice planes (Ref. 2)

Figure 2-2: Schematic drawing of the different morphologies of TiAl₃ crystals. (a) Flake-like crystals. (b) Petal-like crystals. (c) Blocky crystals (Ref. 2)
refining action of blocky crystals is fast, but their effect fades very fast too. For faster use, using rod forms of master alloy, the blocky structure is used, and for the cases where furnace additions are made and it is necessary to keep the metal molten for a longer period, the plate–like form will be used.

The problem associated with this grain refiner is the process that is called fading. In this process, the refiner loses its efficiency gradually as time passes. In the literature, from 1951 (6) it has been stated that the reason for this process is the dissolution of TiAl3 in the aluminum melt and therefore disappearance of the nucleant particles. This reason seems acceptable according to the phase diagram of Ti-Al (Figure 2-3). As can be seen in the diagram, with the amounts of less than 0.15% Ti, which is the peritectic point, thermodynamically TiAl3 is not stable, therefore the added TiAl3 follows the peritectic reaction and is dissolved in the melt:

\[ L + \text{TiAl}_3 \rightarrow \alpha \]

Although to some extent this is an acceptable explanation, it should be considered that the phase diagram illustrates an ideal thermodynamically stable situation, regardless of the other elements in the melt and other factors like the rate of cooling and the settlement of the particles.

Also, even in the diagram at lower temperatures there is a dash-line between the two regions of \( \alpha \) and \( \alpha + \text{TiAl}_3 \) that indicates an unknown situation in that area of the diagram.

Also, there have been some experiments regarding the possibility of partial recovery of refining by stirring the melt, which will be discussed later.

Another master alloy, which has been used widely in industry, is an alloy of Al-Ti-B. The addition of boron by this master alloy delays the fading time enormously. Figure 2-4 shows an example of the addition of boron as the grain refiner together with titanium. In
Figure 2-3: The aluminum-rich side of the Al-Ti phase diagram. (Adapted from Sigworth, 1984)

Figure 2-4: Influence of boron content on the grain refining response of three master alloys in 99.7% aluminum (at 700°C melt temperature). (a) 0.01% Ti added as a 5.35%Ti master alloy, (b) 0.01% Ti added as a 5.4%Ti-0.034%B master alloy, (c) 0.01%Ti added as a 5.4%Ti-0.2% B master alloy. (Adapted from Guzowski and Sigworth, 1987)
spite of the importance of grain refinement in industry and a lot of studies in this area, still the mechanism of grain refinement by this master alloy is not clear. It is obvious that after addition of the grain refiner master alloy, the aluminum matrix dissolves and releases intermetallic particles into the melt. These particles can act as nucleants. But as Mohanty and Gruzleski claimed (1), exactly which particles are released, their physical and chemical characteristics, and their subsequent reaction with the melt are still disputed. Even some of the theories which were discarded, reappeared later in more advanced studies. There are different theories regarding grain refinement.

The first theory was the peritectic theory (or phase diagram theory), started in 1951 as explained earlier. For Al-Ti master alloy it was reasonable. Davis (7) and Maxwell and Hellawell (8) observed TiAl₃ particles in the center of α grains. Arnberg by publishing cooling curves showed that there is no nucleation below or at the melting temperature of the melt. He observed that nucleation took place around 665°C, which is the peritectic temperature and a little bit higher than the aluminum melting point. This shows that the interface of TiAl₃ and liquid aluminum is the place for nucleation of α and grain growth.

But it doesn’t have an acceptable explanation for the effect of boron. One theory suggests that the existence of boron causes a movement of the peritectic point to the aluminum side of the phase diagram (6). According to the phase diagram for Al-Ti-B, which has been predicted by various researchers, this is not possible (10-14). Still, Mondolfo insisted he observed the change of composition of the peritectic point in his experiments.

Backerud (15) proposed a new type of peritectic theory called the hulk theory. In this theory it is suggested that a layer of boride compound, presumed to be TiB₂, is formed at the interface between TiAl₃ particles and liquid aluminum. In fact a sheath layer of TiB₂ is formed, which can protect TiAl₃ from dissolution. Therefore, fine peritectic cells will be formed in this layer. By the diffusion of titanium and aluminum through this passive layer a Ti rich liquid layer is formed which is called the peritectic hulk. By decreasing
the temperature, the nucleation of α starts in this liquid hulk, and the dendrites form and grow with subsequent piercing of the passive layer.

Although it provided a logical explanation for the effect of boron, some studies brought up some suggestions against it. Mayes (16) observed TiB₂ crystals within TiAl₃ crystals using thin foils in his experiment using TEM for detection. This arrangement of crystals is not in agreement with the prediction of the hulk theory. Also, Johnson (17) performed experiments in which he re-melted and solidified the cast metal five times at 775°. According to the hulk theory, in the case of re-melting, the peritectic cells should be dissipated, because their higher concentration of Ti should be equilibrated with the melt. But Johnson didn’t observe any change in the grain size and the nucleation temperature (Tₙ) even after five cycles of re-melting. The other phenomenon, which is against this theory, is the effect of stirring in causing recovery of grain refinement, which has been observed by various researchers. Also thermodynamically, it is questionable how this phenomenon occurs (18).

Another theory suggested by Cibula (19,20) and followed by Jones (21) is that by the addition of Al-Ti master alloy, a reaction takes place with the residual carbon in the melt, causing the formation of TiC. When Al-Ti-B is added to the melt, TiB₂ and TiC particles, which both are insoluble in the melt, will disperse in the melt and act as heterogeneous nucleants. As they are not supposed to dissolve in the melt, the explanation of fading is because of settling of the particles and agglomeration. However, there has been controversy over the stability of TiC in the melt. Mohanty and Gruzleski (22) demonstrated by their experiments that TiC is not stable in aluminum melts, so that the carbide theory is invalid.

With respect to borides, there are three boride phases discussed, namely TiB₂, AlB₂, and (Al,Ti)B₂. Marcantonio and Mondolfo (23) and Cibula (19) regarded AlB₂ as a weak grain refiner in pure aluminum, which is only active in hypereutectic compositions. TiB₂ is the other phase, whose solubility is low in aluminum, and in some studies TiB₂ particles have been detected in the center of aluminum grains. But it has been shown in
some other experiments that it is not an effective nucleant alone, as TiAl₃ is. Because if the boride was more effective, it should cause $T_n \leq T_m$, where $T_n$ is nucleation temperature and $T_m$ is melting temperature, but it has been observed that $T_n > T_m$ (24). It has been established both in industry and research centers that extra Ti in excess of the stoichiometry of TiB₂ is necessary. Also, in some studies on grain refinement by Al-Ti-B master alloys it was observed that TiAl₃ particles were in the center of the grains, whereas TiB₂ particles were pushed to the grain boundaries. So, TiAl₃ is a more effective nucleant than TiB₂.

Another theory produced was the metastable boride theory (9). TiB₂ and AlB₂ are very similar from a crystallographic point of view. Both are hexagonal, with close a, b, and c. So there could be solid solution of (Ti,Al)B₂ which could be metastable and after some time is changed to TiB₂. It may act either as a nucleant or help to nucleate TiAl₃ on it. Still there is no established evidence of the existence of this type of boride. Also its potency as a nucleant should not be very different from TiB₂ as they have almost the same morphology.

One of the factors that appears more in recent discussions is recovery by stirring. The grain refining, depending on the alloy used, can be partly recovered by stirring the melt (25). Recently, Tzu-Hsin Wang and his colleagues (26) performed an experiment using Al-Ti and Al-Ti-B master alloys for commercially pure aluminum, and 5182 aluminum alloy. They claimed that in the case where Al-Ti master alloy was used, the stirring did not recover the fading of aluminum while the amount of Ti in the melt was constant. But by using Al-Ti-B master alloy, fading was decreased enormously, and when the stirring was kept continuous almost no fading was observed.

Poisoning will be another factor in disturbing the grain refinement process, if the poisoning element amounts are enough in the melt. This is mostly an issue in alloys. Zr, Ta and Cu are some of the elements which can remove the effect of nucleants.
Figure 2-5: Schematic of the inoculant addition set up  (Ref. 1)
Mohanty and Gruzleski promoted an experiment with a new technique (1). They added synthetic TiB$_2$ crystals into aluminum melt while preserving their physical characteristics and studied their behavior and the mechanism of grain refinement.

The experimental arrangement is shown in Figure 2-5. In this method the particles are of high purity HCT-20 type. Their sizes are 5-10 microns, and they have hexagonal platelet morphology. The principle of the inoculant addition is that first a bed of sized particles are heated in an inert atmosphere, and then are fluidized and blown by an inert carrier gas into the melt. In the melt, the particles are uniformly distributed by breaking up the bubbles of the fluidized mixture with the help of an impeller. The particles are about 1wt% of the melt and preheated at 200-250°C for 2-3 hours. The melts are 20 cm in depth and 8 cm in diameter. Commercially pure aluminum and Al-Ti master alloy are used in the experiments.

The process started with keeping the temperature of the melt at 770°C. Then the particles of TiB$_2$ were added, which caused the temperature of the melt to drop to 700-750. Holding the melt for 5-10 minutes allowed the temperature to reach 730°C and the melt was then cast into chill molds.

The next step was to re-melt the ingots and keep them molten for 6 hours to study the structure of the cast when there is no Ti added. During this period the number of TiB$_2$ particles remained almost the same (43/cm$^2$). Figure 2-6 shows the microstructure of the ingots. As can be seen, TiB$_2$ particles are engulfed in the grain boundaries indicating that they had been pushed away by growing dendrites of aluminum. Etching of the samples, using Kellers’ reagent, shows a high interfacial energy along the particle/matrix interface.

After that, Ti was added through Al-6%Ti master alloys in different amounts, and at the time of maximum addition of Ti, which was 2%, the temperature was raised to 900°C. Because of the excess of titanium, TiAl$_3$ was observed around the TiB$_2$ particles. In Figure 2-7 thin layers of TiAl$_3$ can be seen, which are formed between the Al matrix and the TiB$_2$ crystals. These could be seen at higher concentrations of Ti (0.05%), but the
Figure 2-6: Distribution of TiB$_2$ particles in pure aluminum matrix in the absence of Ti. (a) Single particle. (b) Particle cluster (Ref. 1)

Figure 2-7: Distribution of TiB$_2$ in pure aluminum matrix in the presence of Ti. (a) 0.01%Ti. (b) 0.05%Ti (Ref. 1)
researchers in this study believed that as this amount is much lower than the peritectic composition, it is reasonable to suppose that a similar but much thinner layer also forms at the normal Ti levels used in grain refining practice (around 0.01%). They supported this idea by observing TiB₂ crystals in the center of α grains at 0.01% Ti level (Figure 2-8). Figure 2-8 shows that at higher concentrations of Ti like 0.5%, that is much higher than the peritectic composition, TiAl₃ particles still preferred to nucleate on TiB₂ particles. At 2% Ti, TiB₂ particles were seen at both interior and exterior of TiAl₃.

The important point here is the interfacial energy between particle surfaces. If it is lower than the interfacial energy between the liquid matrix and the particles, thermodynamically particles are more likely to face each other. The term wetting is applied to this desire and θ is defined as the wetting angle. The lower the angle is, the more wetting ability the phases have. The interfacial energy between TiB₂ and α-Al is not known yet. Therefore, at present, we can't theoretically show that the interfacial energy of TiB₂ with liquid phase is lower or higher than that with TiAl₃ particles.

Mohanty and Gruzleski, referring to the microstructures in their studies, claim that as the α-Al phase pushes TiB₂ particles to the grain boundaries, it can be concluded that their interfacial energy is high. Also after the addition of TiAl₃ particles, all the TiB₂ particles stayed with TiAl₃ crystals, which shows lower interfacial energy between them.

Maxwell and Hellawell (30) tried to model the grain growth and showed a relation between the number of particles and the number of grains. They explained that there is an optimum number for the nucleants to act in the melt, and that those in excess of this optimum, are pushed to the grain boundaries. They stated that TiB₂ is a good refiner, being wetted by liquid aluminum well enough for nucleation. The excess, which is not necessary for nucleation, is pushed to the grain boundaries.

Mohanty and Gruzleski denied this idea referring to the existence of more than one TiB₂ particles inside some of the grains (Figure 2-9). They explained that even those particles, which are not nucleants, would be engulfed in the grains.
**Figure 2-8:** Nucleation of TiAl$_3$ on TiB$_2$ (grain refiner addition is at the level of 0.5%Ti). (a) Single nucleation. (b) Multiple nucleation (Ref. 1)

**Figure 2-9:** Spherical shape TiB$_2$ particles in the presence of Ti (Ref. 1)
They also discussed the validity of hypernucleation theory. Jones (27-29) brought up hypernucleation theory, mentioning that Ti atoms will segregate at TiB₂/melt interface, providing a stable Ti-rich layer, with up to 2% Ti, above the melting point of aluminum. He claimed that this layer can be a good nucleation site in the melt. Therefore, an imaginary metastable region of α-Al will be provided and the liquidus and solidus in the phase diagram will be like those shown in Figure 2-10. The existence of 2% Ti in the boride/liquid interface is assumed to be caused by different activities of Ti in the liquid and the Ti on the surface of TiB₂. This activity gradient causes the diffusion of Ti atoms toward the surface of TiB₂ and provides a high percentage of Ti there, which can form TiAl₃ crystals, or in other words, the sites of the nucleation.

Later Sigworth (31) published a paper critical of Mohanty and Gruzleski’s suggestions. He denied their conclusions and hypernucleation theory in general for four reasons.

The first reason is that he believes that hypernucleation is thermodynamically impossible. He claims that it is possible that boride crystals introduce compositional gradients at the boride/melt interface, but they cannot cause an activity gradient in Ti or TiAl₃. In fact,

$$a_{\text{TiAl}_3} = \frac{\%\text{Ti}}{\%\text{Ti}_p}$$

where %Ti is the percentage of Ti in the melt and %Tiₚ is the peritectic solubility of TiAl₃ given by the phase diagram, and the activities are constant.

The second reason is that he considers pure TiAl₃ crystals to be poor nucleants, and mentioned that without borides, providing duplex particles, they are not effective nucleants.

As the third reason he claims that TiB₂ is an effective nucleant in alloys. In casting alloys containing more than a few percent Si, Cu, or Si combined with Cu, unlike aluminides, borides are powerful nucleants.

The fourth reason concerns the Ti-rich layer on the boride surfaces. He explained the possibility of the formation of these Ti-rich layers during the cooling time and after
Figure 2-10: Hypothetical metastable phase diagram according to hypernucleation theory (Ref. 27)
solidification. In fact the Ti-rich regions of $\alpha$ may precipitate Ti on borides during the cooling time by the diffusion of Ti atoms.

In author's view, although Mohanty and Gruzleski's research has not proved the mechanism of the grain refinement yet, the reasons of Sigworth for not accepting their results don't seem very clear.

The first reason talks about an ideal thermodynamic situation that covers the whole melt. But in the melt, in real life, the situation is not like that. Thermodynamically, all the atoms of Ti should be uniformly distributed in the melt. Then there would be no activity gradient, of course. But with different concentrations of Ti in the melt, each region can have its own thermodynamic action.

The second reason is not valid, because according to most of the studies, when TiAl$_3$ particles exist in the melt, even without the existence of boron, they are good nucleants for grain refinement.

The third reason is just for the Al alloys and not for pure aluminum. In Al alloys the situation is more complicated, and as there are other elements existing in the melt in considerable amounts, it cannot be concluded firmly that TiB$_2$ is a powerful nucleant just by itself.

There is no evidence for the fourth reason so that it is only a speculation rather than a firm conclusion.

In the University of Cambridge, Schumacher and Greer (32) set up a new method of experiment for investigating the mechanism of grain refinement. They used metallic glasses instead of a regular aluminum melt. The crystallization from both occurs in an undercooled liquid, so that their nucleation mechanisms are identical. But in metallic glasses, the atomic mobility is lower and the microscopic studies of the nucleation process on added particles are easier.
Aluminum-based metallic glasses can be made by rapid quenching of the melt, applying melt spinning (in this study 105-106 Ks\(^{-1}\)). They used the TEM technique for detection of the particles in the glassy alloy (Al\(_{85}\)Y\(_{5}\)Ni\(_{5}\)Co\(_{2}\)). In their study they didn’t find any separate TiAl\(_3\), which indicates all of them have been dissolved in the melt. They were just detected on boride particles. On the other hand they detected the existence of TiB\(_2\) even when they kept the melt at 1300\(^\circ\) for one minute and then quenched.

They concluded that TiB\(_2\) particles survive and act as the centers from which Al grows. Also the peritectic reaction can occur and, although separate TiAl\(_3\) particles are all dissolved, they can be preserved in association with boride particles, and excess of Ti is necessary for effective nucleation of \(\alpha\)-TiAl\(_3\). The surface of \(\alpha\)-Al nucleation was regarded as the (112) TiAl\(_3\) face. They said that there are well-defined orientation relationships between TiB\(_2\), TiAl\(_3\), and \(\alpha\)-Al in which the close-packed planes and their directions are parallel. So TiAl\(_3\) as a strong potent nucleant can exist as a layer on TiB\(_2\). \(\alpha\)-Al, even at high undercooling is only on (0001) faces of TiB\(_2\) crystals, which are parallel to the (112) face of TiAl\(_3\) and the (111) of \(\alpha\)-Al.

In a previous study (33) and this one they found adsorbed traces of tantalum in the layer that is an impurity element in the yttrium, which has been used as a component of glassy matrix. They observed a perfect solid solubility of the isomorphous phases TiAl\(_3\) and TaAl\(_3\), which both cause a peritectic reaction with an Al-rich melt. Thus, they concluded that by the existence of any element which can promote formation of a phase isomorphous with TiAl\(_3\), like Ta or Zr, these elements can replace the excess Ti and act similarly.

Still they mentioned that the mechanism of formation or preservation of TiAl\(_3\) and possible influences of solute in the aluminide layer on the nucleation of \(\alpha\)-Al is not clear.

In another study, Gudmundsson et al. (34) used different amounts of Al-Ti-B master alloy, and by varying the holding time after melting, collected and measured the amount of the inclusions from the melt at different times. They were collected by a filtration
method. They established that by increasing the amount of 5/1 Al-Ti-B master alloy, inclusions are settling much faster in the furnace. There is an empirical equation for the rate of particle settling:

\[ C(t) = C_0 e^{-\alpha t} \]

where \( C(t) \) is the number of particles in the melt at time \( t \), \( C_0 \) is the initial inclusion content, \( \alpha \) is a constant, and \( \varepsilon \) is a constant which defined as the efficiency of holding time constant.

As the reason for this behavior they suggested two possibilities. One is that, as the grain refiners have been added to the melt, the presence of TiB_2 in excess of inclusions makes a higher number of inclusions per unit area. This causes the increase of the probability of collisions between particles and may result in agglomerates of inclusions. When these agglomerates reach the boundary layer they will have a greater tendency to settle out from the melt.

The second possibility that he proposed is the formation of a boride layer around the metal bath which traps the small or low density inclusions. Thus the particles of TiB_2 increase the removal efficiency in the boundary layer. These were just hypothetical suggestions, which are not proved yet.

Mohanty and his colleagues set up another method for detecting the particles (35). They set up a system, which is called LiMCA (Liquid Metal Cleanliness Analyzer). It can detect the amount of particles, which are distributed in the melt (Figure 2-11). As shown in Figure 2-11, there are two electrodes connecting to the analyzer system. One is inside the sample tube, and the other one outside of it in the melt. The orifice on the tube, which is under reduced pressure, allows the melt to pass through this hole and enter the tube. At the same time there is an electric current between two electrodes. Aluminum has a specific conductivity. Therefore, if any foreign particles pass through the orifice, it will cause a change in the current. In the analyzer system this will be shown as a current peak, either positive or negative, depending on the conductivity of the foreign particles.
Figure 2-11: Schematic set up of LiMCA detecting system (Ref. 35)
The orifices utilized were in the range 230-350 μm. The impeller helps to produce a better distribution of the particles in the melt.

Using this system, they tried to detect the grain refiner particles by counting the amount of particles and comparing them before and after the addition of the grain refiner. Figure 2-12 shows the particle counts vs. Ti content for different master alloys. It shows that among the three master alloys, Al-5Ti-1B produces the highest amount of particles and the master alloy without boron has the lowest amount. This agrees with the consideration of Al-5Ti-1B as the best optimized amount of Ti and boron in the master alloy.

Figure 2-13 shows the effect of time on the number of particles. As can be seen, the number of particles decreases with the passing of time, but in a stirring situation the amount of particles decreases more slowly, because it brings up the settled particles.

Although LIMCA is a good method for detecting the cleanliness of the melt, it can only detect a small zone in the melt. It cannot cover a large area of the melt. Also it is not clear how it can count the particles when a huge amount of very fine particles, just several microns in size, pass through the orifice. The peak in the analyzer may somehow change to show the conductivity change, but how it can analyze the number of particles?

2-2 Evaluation of Grain Refiner Performance

There are two main methods for evaluating the grain refiners; the Alcan test, and the Alcoa test.

In the Alcan method, a small melt is stabilized at about 730° and the grain refining master alloy is added. Then samples are taken from the melt at measured time intervals with a mold, which is preheated to 250°. The mold is shown in Figure 2-14. The mold is cooled
Figure 2-12: Particle counts vs Ti content for different master alloys (Ref. 35)

Figure 2-13: Effect of melt holding and stirring for different melts (Ref. 35)
in a quenched tank and the cast is sectioned at 25 mm from the bottom. Then the samples are prepared by grinding and etching.

![Diagram](image)

**Figure 2-14**: Alcan standard test mold

In the Alcoa method (Figure 2-15) an aluminum melt is prepared, and after the addition of grain refiner the samples are taken over an extended time period. The melt is kept quiescent during the experiment. The directionally solidified castings are sectioned longitudinally, through the central axis, and one face machined for macroetching to observe the structure of the metal. The Alcoa method needs more sample preparation, but can show the performance of the grain refiner in practice. In both methods the melt freezes in a unidirectional mode.
**Figure 2-15:** Schematic drawing of Alcoa standard test set up, and structures of the casts.

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**Figure 6**
Grain Structure Revealed in Unidirectionally Solidified Castings of 3004 Alloy
(a) Poured from Melt with No Grain Refiner Added
(b) Melt Grain Refined with a 0.01% Ti Addition of Al-5%Ti-0.2%B Rod
Ultrasound Theory (36-40)

Sound is a form of energy, which is transmitted as mechanical vibrations through matter. So it is not transferable through vacuum.

Ultrasound is a mechanical vibration or in other words a type of sound, in the range of frequencies higher than those audible to the human ear. So, the vibrations with frequencies more than 20 kHz are called ultrasound.

For the theory and discussions about ultrasound we can either use classical physics, or modern physics which uses quantum mechanics in ultrasound analysis. The classical mechanics is based on Newton's laws of motion, and the wave aspects of sound are considered. In quantum mechanics the molecular motion whose spectrum extends to about $10^{13}$ Hz (1) is discussed for the sound (Figure 3-1).

![Figure 3-1](image)

**Figure 3-1:** The density of phonon modes plotted against frequency for compression sound in aluminum. (Adapted from Kittel, 1971.)
Quantum mechanics deals mostly with the properties of very small objects in the level of atoms and molecules, and the motions which are close to the speed of light. In that regime, according to the quantum theory of heat, small particles, called phonons, are considered as the identity of sound. It is similar to photons as the light identity.

As our field of work is dealing with frequencies much lower than $10^{13}$, we don't need to use quantum mechanics, and classical physics is sufficient.

A simple harmonic motion of sound can be represented by the simple formula of waves:

$$a = A \sin \phi = A \sin \omega t$$  \hspace{1cm} (3.1)

\(a\) is the length of the vertical projection in the phase angle of \(\phi\) (particle displacement).
\(A\) is the amplitude of the wave, which is the maximum particle displacement.
\(\phi\) is the phase angle.
\(t\) is the time passed.
\(\omega\) is the angular frequency, and it can be given by \(\omega = 2\pi f\), in which \(f\) is the frequency of the wave.

![Simple harmonic motion (SHM)](image-url)

**Figure 3-2:** Simple harmonic motion (SHM).
Types of ultrasound waves

There are two general types of sound waves. One is longitudinal or compression sound, and the other one is transverse or shear sound. In longitudinal sound waves the direction of amplitude of the wave is parallel to the direction of its propagation. On the other hand, in transverse sound waves the amplitude direction of the wave is at right angle to its propagating direction (Figure 3-3).

**Figure 3-3:**

Pressure variation

**Figure 3-3(a):** Particle position, particle displacement, and spatial pressure variation plotted against position (x) for a single cycle, sinusoidal, plane-traveling wave in a fluid medium. (Adapted from Pierce, 1981a.)

**Figure 3-3(b):** Particle position, particle displacement, and spatial shear strain variation plotted against position (x) for a single cycle, sinusoidal, plane-traveling shear wave.
Shear waves generally are only able to pass through solid matter because liquids and gases do not usually support shear stresses, while compression waves can move through all type of liquids, gases, and solids. In very viscous liquids, shear waves can propagate for very short distances, often only a fraction of a millimeter.

It should be noted that it is the energy of the vibrations and not the particles in the material which move from the source to receiver. The particles themselves only vibrate about their positions with small displacement amplitudes.

**Wave characteristics**

The principle of characteristics of acoustic waves are particle displacement, particle velocity, and acoustic pressure (or stress). The particle displacement amplitude is shown in equation 3-1. The particle velocity is defined as the velocity of a vibrating particle in the medium at a given time and location. It should not be confused with the wave velocity. It can be defined by:

\[ u = u_0 \sin \omega(t - \frac{x}{c}) \]  

(3.2)

where \( u \) is the particle velocity at the particular time \( t \), \( u_0 \) is the maximum particle velocity that is called the particle velocity amplitude, \( c \) is the velocity of the wave in the medium (sound velocity), and \( x \) is the distance which the wave has traveled.

The acoustic pressure is the alternating excess pressure or stress due to the sound waves, which are carried by the material. It can be defined by:

\[ p = p_0 \sin \omega(t - \frac{x}{c}) \]  

(3.3)

where \( p_0 \) is the acoustic pressure (or stress) amplitude.
Usually in the equations acoustic pressure at the peak, $p_0$, is shown as $p$. It can be defined by:

$$p = \omega A \rho c$$  \hspace{1cm} (3.4)

where $\rho$ is the density of the medium.

**Specific acoustic impedance**

There is a similarity between sound wave characteristics and some of those used in electrical a.c. theory. Therefore, acoustic pressure may be regarded as being similar to electrical voltage, particle velocity to electrical current, and particle displacement to electrical charge. Using the acoustic equivalent of Ohm's law, a quantity known as the specific acoustic impedance $Z_a$, equivalent to electrical impedance, may be defined as:

$$Z_a = \frac{p}{u}$$  \hspace{1cm} (3.5)

The value of the characteristic impedance for a material depends only on its physical properties and thus to be independent of the wave characteristics and the frequency.

**Acoustic intensity**

Acoustic intensity is defined as the rate of flow of acoustical energy per unit area.

$$I = \frac{p_0 u_0}{2} = \frac{u_0^2 \rho c}{2} = \frac{p_0^2}{2 \rho c}$$  \hspace{1cm} (3.6)
It can be related to the root mean square (r.m.s.) values of acoustic pressure and particle velocity which are similar to Ohm's law in a.c. electrical circuits:

\[ I = p_{r.m.s} u_{r.m.s} = u_{r.m.s}^2 \rho c = \frac{p_{r.m.s}^2}{\rho c} \]  

(3.7)

**The decibel scale**

In ultrasonics, variations of intensity, acoustic pressure, etc., often take place in logarithmic manner and measurements are made in comparison with some fixed standard. An intensity \( I \) may be expressed in relation to a reference intensity \( I_0 \) as:

\[ \text{Intensity level} = 10 \log \frac{I}{I_0} \text{ decibels (dB)} \]  

(3.8)

It is usual to use an a.c. voltmeter or oscilloscope to measure a voltage which is proportional to the acoustic pressure, and therefore, the number of decibel change is obtained from pressure levels:

\[ \text{Pressure level} = 20 \log \frac{p_{r.m.s}}{p_{r.m.s}} \text{ dB} \]  

(3.9)

The number 20 in equation 3.9 replaces 10 in equation 3.8 because the intensity is proportional to the square of the r.m.s. acoustic pressure. Decibel is a unitless number, which is used for the acoustic measurements.

**Mode conversion**

Mode conversion is the conversion of one type of ultrasound into another. This can take place at the interface between two media. Figure 3-4 shows the reflection and refraction
refraction of ultrasound at a boundary between two materials. The acoustic velocities for the various beams are related to one another in the following manner:

\[
\frac{c_{1L}}{\sin i} = \frac{c_{1T}}{\sin l} = \frac{c_{2L}}{\sin r} = \frac{c_{2T}}{\sin r}
\]

(3.10)

where the velocities of longitudinal waves in the media A and B are represented by \(c_{1L}\) and \(c_{2L}\), respectively, and \(c_{1T}\) and \(c_{2T}\) for the velocities of transverse waves.

**Figure 3-4:** Double reflection and refraction of ultrasound at a boundary between two materials. L: Longitudinal waves. T: Transverse waves
Progressive and Standing waves

Progressive waves as the name shows, are a type of wave which can progress through a media, and transfer the energy.

Standing waves are a type of wave in which the pattern does not move to left or right and the amplitude of the oscillation is always zero at the nodes, while the peaks of the wave are regularly changing from a maximum in a positive direction to a minimum in a negative direction and vice versa. They are usually between two boundaries at right angles to the beam direction, where the distance between the boundaries is exactly an integral number of the half wavelength (Figure 3-5).

![Standing wave diagram]

**Figure 3-5:** A standing wave (stationary wave).

Standing waves are in a resonance situation. Resonance is a state in which the frequency of applied sound exactly matches one of the natural frequencies of vibration of the system. The lowest resonance frequency is that where half the wavelength fills the distance between boundaries.
Reflection and transmission at interfaces

When a beam of waves strikes a plane boundary separating two materials, some of the sound energy is transmitted forward and the remainder reflected backward (Figure 3-6).

\[ \frac{Z_2}{Z_1} \]

Incident beam 
\( (p_i & l_i) \)

Reflected beam 
\( (p_r & l_r) \)

Transmitted beam 
\( (p_t & l_t) \)

**Figure 3-6:** Reflection and transmission at an interface; normal incidence.

The ratio of the acoustic pressure of the reflected beam to that of the incident beam is called the pressure reflection coefficient and is given by:

\[
R_p = \frac{p_r}{p_i} = \frac{Z_2 - Z_1}{Z_2 + Z_1}
\]  
(3.11)

where \( Z_1 \) and \( Z_2 \) are the characteristic impedance for the two materials.

For the intensity reflection coefficient, as the intensity is related to the square of the acoustic pressure, it is:

\[
R_i = \frac{l_r}{l_i} = \frac{(Z_2 - Z_1)^2}{(Z_2 + Z_1)^2}
\]  
(3.12)

The pressure and intensity transmission coefficients are given by:
The equations show that the transmission coefficient approaches unity and the reflection coefficient tends to zero when the characteristic impedance values of the two media have approximately similar values. Therefore, the two materials are said to be well matched or coupled. On the other hand, when the two materials have substantially different characteristic impedance values, the transmission and reflection coefficients tend to zero and 100 percent, respectively.

**Pulses and tone bursts**

Pulses are used in many sensors as exciting waves. They usually continue for only several cycles and the amplitude is changing (Figure 3-7a). In some other sensors tone bursts are used. They are also called gated continuous waves. Like pulses they are usually short, but with constant amplitude and frequency (Figure 3-7b).

\[
T_p = \frac{P_r}{P_i} = \frac{2Z_2}{Z_2 + Z_1}
\]

(3.13)

\[
T_i = \frac{I_r}{I_i} = \frac{4Z_1Z_2}{(Z_2 + Z_1)^2}
\]

(3.14)

Pulses and tone bursts: (a) A pulse. (b) A tone burst.
Modulation

Modulation is a process in which the continuous wave itself carries another wave. It can be carried out in two forms. Amplitude modulation (AM), and Frequency modulation (FM). In AM the fluctuating of the amplitude of the carrier makes the other wave which is called envelope (Figure 3-8).

**Figure 3-8:** Amplitude modulation

In FM the frequency of the carrier wave is changing and the frequency is arranged to be proportional to the amplitude of the modulating signal (Figure 3-9).

**Figure 3-9:** Frequency modulation

The main reason of the modulation process is to move and transfer the wave more effectively in higher frequency and then demodulate the signals and extract the modulated wave which is the desired signal with lower frequency.

Fourier principle

The Fourier principle states that any continuous waveform signal can be divided into a number of simple harmonic motions of appropriate frequency, phase and amplitude (Figure 3-10).
The number of these simple waves can be very large and even infinite. It shows that a pulse can be broken down into simple waves. Therefore, a pulse which is used with a specific frequency, in fact, contains different components of lower and higher frequencies. The breaking down of the wave according to the Fourier principle is called Fourier analysis. Figure 3-11 shows two pulses and their frequency spectra. Frequency spectra illustrate the intensity of different frequencies in logarithmic scale. A wider spectrum shows that a higher range of frequencies, with relatively high intensity, are involved in the pulse, while a narrower spectrum illustrates higher intensities just around the main frequency. A longer pulse with a specific frequency can have narrower spectra than shorter pulse.

**Figure 3-10:** Fourier analysis of a pulse.

**Figure 3-11:** Frequency spectra (schematic). (a) A short pulse. (b) A longer pulse.
Attenuation

Ideally the intensity of a parallel beam of progressive plane waves should remain constant at all distances from the source. But in practice it will not happen because of the attenuation of ultrasound during its progress through a medium. Three causes of attenuation are absorption, scattering, and diffraction. During the motion of ultrasound in a media, a great amount of its energy will be absorbed by the media, or scattered and then may be absorbed. In both cases, the ultrasound converts to heat. The general equation for attenuation is:

\[ p = p_0 \exp(-\alpha x) \]  

(3.15)

where \( p \) is the initial pressure and \( p \) is the pressure of the wave after travelling distance \( x \), and \( \alpha \) is the attenuation coefficient that can be expressed in dB per mm.

Absorption is a characteristic of the physical properties and microscopic structure of the material, while scattering and diffraction are properties of the shape and macroscopic structure of the material, and the particles and phases in it.

Diffraction

A parallel beam of wave originating from a source vibrating in a piston-like manner diverges after travelling a specific distance \( d \) from the source. The value of \( d \) depends on the size of the source and the wavelength \( \lambda \). For a circular source it can be shown that:

\[ d = \frac{r^2}{\lambda} \]  

(3.16)

where \( r \) is the radius of the source.

The parallel part of the beam is called the near field or the Fresnel zone, and the divergent part is called the far field or the Fraunhofer zone (Figure 3-12). The divergence, which appears to originate from the center of the source, is called Fraunhofer diffraction. As
equation 3.16 shows, the directivity of the beam increases with the size of the source and decreases with wavelength, or in other words increases with frequency.

Figure 3-12: Diffraction of waves from a circular source vibrating in a piston-like manner
In the Fresnel zone there is no attenuation due to diffraction. In the Fraunhofer zone, the intensity decreases inversely with the square of the distance from the source due to the diffraction.

**Scattering**

Lord Rayleigh claimed that when there are a large number of particles with almost uniform size distributed homogeneously in the medium which beam passes through, there is a random reflection from the particles and sound is scattered uniformly in all directions. A condition for this manner is that the particle size should be less than 0.1 times the wavelength. The attenuation coefficient is related to the mean particle diameter D and the frequency f as:

\[ \alpha = Kf^4 D^3 \]  \hspace{1cm} (3.17)

where K is a constant for a particular material.

The processes of attenuation are considered to act independently of each other. Thus, when several attenuation mechanisms take place in the same system at the same time, the total attenuation coefficient is given by the sum of different attenuation coefficients.

Absorption in fluids occurs as a result of three types of relaxation mechanism. Two of them are due to viscosity and thermal conduction, which are called classical attenuation, and the other one involves a wide range of molecular effects in which the geometry of the molecules of the material temporarily changes. The viscosity effect is usually more important in absorption, and the thermal conduction can have a considerable effect just in liquid metals. Scattering in fluids can occur when a second phase exists in the fluid.
Beat frequencies

When two waves with the same amplitude and a little difference in frequency interfere each other, the result will be a wave as shown in Figure 3-13. It consists of an initial wave, which carries another wave. The frequencies of those waves are:

\[ f_b = f_1 - f_2 \]  \hspace{1cm} (3.18)
\[ f_{Initial} = \frac{f_1 + f_2}{2} \]  \hspace{1cm} (3.19)

\[ f_{Envelopes} \]

**Figure 3-13:** The generation of beat frequency
4: Ultrasonics

4-1 History of Ultrasonics

Ultrasonics became a subject when Galton was aware of its existence and used a whistle in his studies of the limits of the acoustic spectrum perceived by humans in 1883. This whistle can be regarded as one of the first man-made ultrasonic transducers, although the only application that it had at that time was to be used as a dog whistle!

For three decades after his work, ultrasonics remained an unimportant subject, because its development was impeded by the lack of progress in electrical technology. Therefore, when the piezoelectric and magnetostrictive effects were known, they were not utilized in the construction of useful ultrasonic instruments. As a result of the experiences of the First World War, an interest in this subject developed and in France Langevin investigated the use of quartz transducers to receive ultrasound waves, of relatively low frequencies, in water. This system was used for the detection of submarines and for under-water communication.

After the war, rapid developments took place in the fields of electronics and, in 1925, Pierce used quartz and nickel transducers for generating and detecting ultrasound at frequencies extending to the range of megahertz. At the same time, Debye and Sears, and also Lucas and Biquard working independently of one another, discovered the ultrasonic diffraction grating. The use of ultrasound to study the acoustical properties of liquids and gases progressed after that and by the 1930's, investigations into the properties of solids started. In 1934, Sokolov in the USSR published the first known work on ultrasonic flaw detection.

Between the two world wars, a considerable amount of work was done on the development of high-intensity ultrasonic generators, including whistles, sirens, and electric spark-gap devices. In 1927, Hartmann and Trolle produced details of their ultrasonic whistle, which proved capable of propagating ultrasound waves having powers
up to 50 W in fluids. However it did not have any application until the Second World War.

In 1958 Mountford and Calvert used the ultrasonic technique to investigate the existence of particles in the melt (41).

The use of pulse methods derived from radar techniques and after the war it was used widely in non-destructive testing of materials, in medical diagnosis, and in various forms of instrumentation and control. Later, other methods, including cleaning, emulsification, drilling, were developed. In 1960’s, new materials and techniques were discovered and, with the developments of microwave propagation, generating ultrasonic waves at frequencies of up to 100 GHz became possible. Applications of ultra-high frequencies are of considerable importance in fundamental researches in physics, communication, electronics and computer technology.

During the last few decades ultrasonic systems have improved and now play important roles in different areas of science and engineering and still remain as one of the front line research fields.
4-2 The Ultrasonic Detection System

The apparatus of our experimental system is illustrated in Figure 4-1.

**Figure 4-1:** Schematic of general set up of the ultrasonic system for aluminum trials.
The furnace used in the experiments is an electrical furnace. The oscilloscope, CRT, computer system, and electronic analyzer system are placed on the shelves of the system control box.

There are two guide-rods for transmitting and receiving the signals installed inside a ceramic tube, which keeps them stable and parallel to each other. The ceramic tube is held by a holding arm, which moves the rods into the melt, and out of it. A hand operated rotary wheel can control this arm.

The rods are cooled by a cooling system so that the transducers aren’t damaged by high temperature, and also the attenuation in the rods is less. The rods are made from mild steel.

There are two transducers, one the transmitter and the other one the receiver of the signals. They are placed on the top of the guide-rods and connected to the control box by two cables. The transmission transducer is connected to the voltage exciting circuit, and the receiver to the electronic analyzer system.

There are different types of transducers, for producing mechanical vibrations. The most widely used one, which we are using in our experiments too, is a piezoelectric transducer. It can be abridged to PE. A general schematic of a piezoelectric transducer for generating longitudinal ultrasound is illustrated in Figure 4-2.

When it is used as a transmitter, a suitably varying voltage is applied to its electrodes. Any applied exciting voltage can cause a change in the PE disc thickness. Therefore, the alternating voltage causes an alternating change in the PE disc thickness, which is a mechanical vibration with the same frequency as the varying voltage. Thus, electrical vibration will be changed to mechanical vibration.

When it is used as a receiver, the sound waves impinging on the front face of the transducer generate strains in the piezoelectric slice. The mechanical strain in PE slice
causes the creation of an e.m.f. which is transferred to the electronic system by the electrodes on the PE slice faces and the cables. The amount of generated e.m.f. is proportional to the change in the thickness of the transducer. Therefore, mechanical vibrations will be changed to electrical vibrations.

![Diagram of a piezoelectric transducer](image)

**Figure 4-2**: The ‘reference design’ piezoelectric transducer.

The damping part on the back of the PE slice is for the absorption of the backhits of the PE slice. Without damping part, the waves which are produced at the back of PE slice, hit the case and reflect back to the PE slice and disturb its vibration.

The best known material for piezoelectric materials is quartz, and it is generally used in most of the ultrasonic systems.

**The operation of the system**

The general description for ultrasound detection method is that signals are transmitted into a material, and after passing through that material they are received and analyzed by
electronic systems to detect the defects, impurities, second phases, any kind of irregularities, and attenuation.

There are two methods for transmitting and receiving ultrasound signals. One is the pulse-echo method in which one probe is used for both transmitting and receiving the signals. The other one, which we are using, has two probes one for transmitting and one for receiving the signals. This is called pitch-catch method.

In the pulse-echo method the advantage is that the same probe can very well detect the reflections directed back from the particles at the same direction that they were transmitted. But the problem is the interference between the signals in the same rod that causes disturbance in the signals.

In the pitch-catch method we can avoid the signal interference, which exists in the pulse-echo method. Also, in our experiments as we are dealing with very small particles with irregular shapes, we expect reflections toward different directions and the advantage of pulse-echo method is not important here. Therefore, pitch-catch method is the proper method for our experiments.

Thus, in our system the transmission transducer is excited by an e.m.f. and produces mechanical vibrations as a pulse. The pulse is travelling through the guide-rod and transfers into the melt. The pulse goes toward the bottom of the crucible and is reflected back from the bottom to the top of the crucible. By hitting the receiver probe, this mechanical signal is passing through the guide-rod and hits the receiver transducer. Then, it will be changed to an electrical signal and goes to the electronic data acquisition system.

As the amplitude of the received signal is very week, a pre-amplification is needed to get a useful amount of amplification before too much noise interferes. On the next step, electronic filter systems are used to eliminate the noises accompanying the main signal. Then another powerful amplification is used to prepare the waves for data analysing.
After that, other electronic processes are carried out to obtain the main data for the signal processes.

The transmitted signal is called the main bang and the reflected signal is the called bottom echo. The difference between the amplitude of these two signals indicates the amount of attenuation of the wave energy (Figure 4-3).

There were also some reflected signals from the particles inside the melt, which are received by the receiver probe before receiving the bottom echo. These signals are displayed on CRT with lower amplitude than main bang and bottom echo. In Figure 4-3 they are shown as particle reflections. The amount of these reflected signals indicates the amount of particles inside the melt.

Also, the bigger size the particle is, the higher amplitude of the reflected signal is. Therefore, the amplitude of the signals indicates the size range of the particles. The number of the peaks of these signals is proportional to the number of particles inside the melt.

In order to achieve proper signals regarding the particles reflections, we should choose a measuring period of time in which signals are reflected from the melt. It takes some time for the pulse to pass through the transmitter guide rod. Then it enters into the melt so that the reflected signals are received. In fact the measuring period of time is close to the bottom-echo and usually takes 30 μsec.

As mentioned before, the amplitude of the signals illustrates the size of the particles. Thus, by defining some thresholds levels, which are different percentages of the amplitude peak height, we can compare the amount of particles in different size ranges (Figure 4-4).

The attenuation of the beam happens due to the absorption of the sound energy by the melt, or scattering of the wave which later will be absorbed in the medium. To measure
the amount of the attenuation in the melt, the difference between the received bottom echo signal and the calibration reference that has been defined from a datum measurement is measured and illustrated by a unitless number, which is called Mag or N number. The higher attenuation gives a lower N number and vice versa.

**Figure 4-3:** CRT TRACE RECEIVED FROM ULTRASONIC PULSE

![CRT Trace Diagram]

**Figure 4-4:** Schematic of the counting mechanism
5: Experiments and Results

5-1 General description of the experiments

In all the experiments, pure aluminum, either commercial pure or super pure was used and melted, the grain refiner added to the melt, and after different intervals of time, samples were taken from the melt. The samples were poured into molds, and after complete solidification and cooling down, they were taken out and were prepared for metallography tests.

In order to study the structure of the solidified samples, they were cut and cross sectioned one to two centimeters from the bottom by handsaw, ground, polished and then macro-etched, consecutively. Some of the samples were prepared for micro-etch or SEM test too. The cross sections of all of the samples were taken under ASTM standard tests for grain size measurement.

The grain size results were illustrated as graphs for each experiment. Each graph shows the grain size versus the amount of time for keeping the melt at 720°C temperature in the furnace.

The polishing steps were carried out as follows:

1- Cutting by handsaw
2- Grinding by silicon carbide sand papers with the grits of 180, 320, 800, and 1200, consecutively.
3- Polishing on the cloths with diamond 6μm and 1μm, consecutively.
4- Final polishing with MgO 2μm.
5- Cleaning the sample surface by alcohol and vibrating cleaning system.

The etching solutions were:
For macro-etching: Poulton's reagent; 60% HCl, 30% HNO₃, 5% HF (48%), 5% H₂O.
For micro-etching: HF etch; 0.5% HF (48%), 99.5% H₂O.

For ultrasonic measurements, the system was used through the whole the time in which the aluminum was kept in the molten state in the furnace. The measurements were taken at almost the same intervals of time. Two measurements by ultrasonic system i.e.; N number (Mag), and particle counts are illustrated on the same graph sheets in order to be able to compare them more easily.

They are illustrated versus time. In some graphs the time is directly shown in minutes and in some other graphs it is replaced by the number of measurement counts, which are directly proportional to the time. The counts are easier to use, practically.

For particle counts, different threshold graphs are shown. Threshold 1 refers to the lower level peaks of reflections, which indicates the existence of smaller particles, and threshold 4 refers to high level peaks, which indicates the existence of bigger size particles in the melt.

Stirring is one of the factors that was applied to the melt at different times. By stirring the melt, the particles in the melt can be brought up from the bottom of the crucible, and be distributed in the melt which causes more attenuation of the ultrasound signals too.

Two types of mold were used in these experiments. One type, graphite molds, which were used for faster cooling rates, while the other type was sand mold for having slower cooling rate of the poured melt (Figure 5-1).
Materials used in the experiments:

Melts:
Commercial Pure Aluminum (99.7% Al, 0.18% Fe, 0.07% Si, 0.05% other elements)
Super Pure Aluminum (99.95% Al, 0.05% other elements)

Grain Refiners:
Al-6%Ti Master Alloy
Al-5%Ti-1%B Master alloy

Molds:
Graphite Mold
CO₂ Sand Mold
5-2 Experiments With Repeated Stirring

In these experiments the molten commercial purity aluminum was kept at 720°C and the grain refiner, Al-6%Ti, added to the melt. After that, the melt was continuously stirred at similar intervals of time. Each time two samples were taken, one immediately before, and one after the stirring.

Figures 5-2 and 5-3 show the results of one of these experiments. Mag and particle counts graphs are illustrated in Figure 5-2. To simplify the illustration, two thresholds are considered for the particle counts rather than the four thresholds, which are used for other experiments.

In the ultrasonic graphs it is obvious that after each stirring, the particle count graphs rise up rapidly and then go down again. At the same time the Mag lowers down after each stirring that indicates a higher attenuation of the ultrasound signals. This is very reasonable, in that the particles are being distributed well inside the melt by stirring. Therefore, there is a good match between ultrasonic graphs and the amount and distribution of particles in the melt.

As time passes, only small changes in particle counts graphs can be observed. The graph for threshold 1, which represents the smaller particles has a much higher level than threshold 2.

On the other hand, we see a decrease in the average level of Mag as the time passes. This indicates an increase in attenuation which can be caused by the distribution of more particles by repeated stirring, which are very small, even smaller than the ultrasonic particle counts range of detection i.e.; 20 μm.

In Figure 5-3, we see the effect of the grain refinement on the grain size of the samples. After addition of the grain refiner the grain size decreases rapidly. But the surprising point is that we don’t see any fading during more than 3 hours after grain refiner addition.
This experiment was carried out twice with the same experimental factors and the results were almost the same. Therefore, the results show that no fading is happening in this situation. The grain refinement is definitely related to the addition of the grain refiner as it is shown in Figure 5-3. So, faster cooling rate couldn't be the main cause of finer grain size, although it can be an important factor.

The curves for before and after stirring are not very different, and it shows that although the number of particles are much higher after stirring, the crystals, which act as heterogeneous nucleants, are available and floating in the melt even sometime after stirring. This is especially true for smaller particles which are settling at slower rates than bigger particles.

A number of experiments were carried out using Al-Ti-B grain refiner master alloy. The results were almost the same as later experiments, and it was in agreement with our expectations to observe those results. Previous studies had shown that the addition of boron delays the fading for a long period of time. Therefore the experiments were continued with the use of Al-Ti grain refiners.
Figure 5-2: In commercial pure aluminum, grain refiner Al-6%Ti added at the level of 0.02% Ti, with repeated stirrings. Melt temperature; 720°C, and poured in graphite mold.
Before Addition

Figure 5-3: Grain size of the structures at different times. Melt; commercial pure aluminum. Melt temperature; 720°C. Grain refiner added at the level of 0.02%Ti. Repeated stirring. Solidified in graphite mold.
5-3 Experiment Without Repeated Stirring

To study the effect of stirring on fading, an experiment was carried out with only one stirring after the grain refiner addition. Other factors were like the previous experiments. Commercially pure aluminum was melted and kept at 720°C, poured into graphite molds and prepared for tests as mentioned before. The grain refiner was Al-6%Ti rod master alloy, and the grain refiner added at the level of 0.02%Ti.

The ultrasonic and grain size graphs are shown in Figures 5-4 and 5-5. The grain size of the sample before grain refiner addition was 1500μm. In order to focus on the graph of the grain size versus time, the curve only shows the data after grain refiner addition.

In ultrasonic graphs we see a high level peak of particle counts and a low level peak for the Mag number that is the result of stirring and threshold 4 shows a high amount of big particles. But after that, the particle counts are very low until the end of the experiment, indicating the settling of the particles.

On the grain size graph, not a lot change after grain refinement can be seen. Only at the time 130 min we see a little decrease in the grain size and at the same time on ultrasonic graphs we observe a little higher amount of counted particles and higher level of attenuation. These can be caused by convection or any kind of movement in the melt and show the effect of movement of the melt on raising the number of particles, including those which act as nucleants.

But in general, fading is still not observed after almost three hours. This means that the nucleants are still existing and floating in the melt. Their size could be too small to be detected by the ultrasonic system. In that case they should be less than 20μm. In this experiment we also see the higher level of attenuation (lower Mag) at the later part of the experiments than the beginning (other than stirring time). This means more distribution of very fine particles in the melt.
Figure 5-5: Grain size of the structure at different times. Melt; commercial pure aluminum. Melt temperature; 720°C. Grain refiner; added at the level of 0.02% Ti. Solidified in graphite mold.
5-4 The experiment With Less Added Titanium

In this experiment commercially pure aluminum was melted and kept at 720°C, poured in graphite molds, the same as the previous experiments. The melt was stirred one time after the addition of the grain refiner and one time at count 28 before taking sample 7. But this time the grain refiner Al-6%Ti was added into the melt at the level of 0.01%Ti. Figures 5-6 and 5-7 illustrate the results of this experiment.

In Figure 5-7 we see a decrease in grain size after addition of the grain refiner. But it was not enough for the grain refinement process. The structure of the samples even after addition, were about half columnar and half equi-axed grains, which is not a proper structure after grain refinement. Therefore, the amount of Ti is very important in shaping the finer grain structure and it was not enough here.

In Figure 5-6, as in the previous ultrasonic graphs, high levels of particle counts and attenuation are observed after stirrings. But other peaks are also visible resulting from unexpected movements in the melt. At measurement count 24 there appears to be a disturbance in the melt so that the particle counts and the attenuation are high. At measurement count 25 the attenuation is lower (Mag is high), and thresholds 2 to 4 are low. Threshold 1 has a higher peak that shows the smaller particles still are not settled, but they are not distributed in the melt, so they are not increasing the attenuation very much.
Figure 5-5: In commercial pure aluminum, grain refiner Al-6%Ti added at the level of 0.01%Ti. Melt temperature; 720°C, and poured in graphite mold.
Figure 5-7: Grain size of the structure at different times. Melt; commercial pure aluminum. Melt temperature; 720°C. Grain refiner added at the level of 0.01%Ti. Solidified in graphite mold.
5-5 Experiment With Sand mold

In this experiment the commercially pure aluminum was melted and kept at 720°C. But this time it was poured into sand molds which were bigger than graphite molds and are dried with CO₂. Therefore the cooling rate of solidification was much lower than that obtained by using graphite mold. The melt was stirred two times, one time after addition of the grain refiner, and the other time before taking the last sample at measurement count 24. Also, this time the grain refiner Al-6%Ti was added at the level of 0.01%Ti.

Figures 5-8 and 5-9 illustrate the results of this experiment. On the grain size graph, the fading phenomenon can be seen. The structure of the samples taken between the measurement counts 10 to 15 were fine and uniform equi-axed. At the other measurement counts the sample structures were coarser equi-axed and less uniform.

In the ultrasonic graphs high level peaks are observed at the first stirring. At the second stirring the peak of threshold 3 is high, but threshold 4 unlike the first stirring has a low level peak. It indicates the existence of much lower amount of bigger particles compared to the first stirring.

At other times the levels of particle counts and attenuation are rather low while on the grain size graph the grain size is very low too. This indicates that the particles which are acting as nucleants are too small to be detected by the ultrasonic system. Therefore, whenever only those small nucleants with less than 20μm size are floating in the melt and bigger particles are still settled, they are not detected by the ultrasonic system.

The fading phenomenon here indicates the effect of cooling rate on the occurrence of the fading process. This can be the effect of the amount of undercooling which affects the critical size of the nucleation sites which can set as thermodynamically stable nucleants and be able to grow. Therefore, a higher amount of undercooling results in more nucleants and a finer grain size.
Figure 5-7: In commercial pure aluminum, grain refiner Al-6%Ti added at the level of 0.01% Ti. Melt temperature; 720°C, poured in sand mold.
Figure 5-9: Grain size of the structure at different times. Melt; commercial pure aluminum. Melt temperature; 720°C. Grain refiner added at the level of 0.01%Ti. Solidified in sand mold.
5-6 Experiment With Sand Mold and 0.02% level of Ti

This experiment was carried out with the same conditions as the previous sand mold experiment but with a different amount of titanium. This time Al-6%Ti master alloy grain refiner was added at the level of 0.02% Ti.

Figures 5-10 and 5-11 illustrate the results of this experiment. In Figure 5-10 we see three strong peaks with even a high peak level for threshold 4, which indicates the high amplitude of received pulses. The first and the last peaks were after stirring, but the other one at measurement count 26 could be due to a strong unexpected movement in the melt. The Mag number at measurement count 26 is rather low, indicating the distribution of a large number of particles inside the melt.

The situation at count 26 might be caused by providing more potent particles for acting as heterogeneous nucleants. In Figure 5-11, a low grain size is observed at the measurement count 26. In general, there were more particles available in the melt during the whole of the experiment time, and the higher amount of titanium could help the existence of more effective nucleants even at later times.

At lower times, the minimum grain size in both sand mold experiments with 0.01% and 0.02% Ti were almost the same. Therefore, the amount of 0.01%Ti at low cooling rates could be enough for grain refinement for a short time, but after a part of it is dissolved, even after stirring, the amount of it is not enough for recovery of the grain refinement.
Figure 5-9: In commercial pure aluminum, grain refiner added at the level of 0.02% Ti. Melt temperature; 720°C, and poured in sand mold.
Figure 5-11: Grain size of the structure at different times. Melt; commercial pure aluminum. Melt temperature; 720°C. Grain refiner added at the level of 0.02% Ti. Solidified in sand mold.
5-7 Experiment With Super Pure Aluminum

To study the effect of impurities in the aluminum melt on the grain refinement process, two experiments were carried out with super pure aluminum. In the first one the metal was melted and kept at 720°C, and poured into graphite molds. The grain refiner, Al-6%Ti was added at the level of 0.01% Ti. The melt was stirred two times, once after the addition of the grain refiner and again before taking the last sample at the measurement count 18. Figure 5-12 and 5-13 show the results of the experiment.

In Figure 5-13 a decrease in grain size is clear, but the grain refinement has not properly occurred. The cross section structures of the samples were all columnar. Only in the sample taken at the measurement count 9 some equi-axed grains in the middle of the cross section were observed. The structure and grains of the samples in this experiment were coarser than those in the experiment for commercially pure aluminum with 0.01% titanium. Also here the fading effect of partial refinement can be seen, indicating the dissolution of effective particles created by the addition of the grain refiner.

In Figure 5-12 the ultrasonic graphs illustrate two strong peaks after stirring, with a high level of threshold 4 which indicates stronger reflection signals and bigger particles. There are two other weaker peak levels at measurement counts 9 and 11 where the threshold 4 level is very low, but the other thresholds, especially threshold 3, have higher levels. At the measurement count 3 there is a minimum in the Mag number that shows a higher level of distribution of the particles. At this measurement time we see the lowest particle size in Figure 5-13. There are two other minimums at the measurement counts 6 and 12 in the Mag number graph. But the particle counts graphs are all down. This indicates the distribution of very small particles, which cause a little bit more attenuation.
Figure 5-11: In super pure aluminum grain refiner Al-6%Ti added at the level of 0.01% Ti. Melt temperature; 720 °C, and poured in graphite mold.
Figure 5-13: Grain size of the structure at different times. Melt; super pure aluminum. Melt temperature; 720°C. Grain refiner added at the level of 0.01%Ti. Solidified in graphite mold.
5-8 Experiment With Super Pure Aluminum and Higher Amount of Ti

This experiment was carried out with the same conditions as the previous experiment, except that the amount of grain refiner was at the level of 0.02\% Ti. Figures 5-14 and 5-15 illustrate the results of the experiment.

In Figure 5-14 we observe two peaks in particle counts graphs after stirring, and at other times the level of the particle counts are close to zero. This obviously indicates that there are very few particles with the size of more than 20\,\mu m floating in the melt. But the Mag (N number) graph shows some fluctuation in attenuation, which indicates variations in the number of very small particles, distributing and floating in the melt.

In graph 5-15 we observe a fine grain refinement. At measurement count 17, the sample shows a fading phenomenon in the melt. But after stirring the fading is recovered to some extent.

By comparing graphs 5-14 and 5-15 we see that between measurement counts 5 and 15 the particles which were counted by ultrasonic system were close to zero, while the grain refinement process takes place properly. Therefore, the potent particles for acting as nucleants were lower than 20\,\mu m in size which were not counted by the ultrasonic system.
Figure 5-13: In super pure aluminum, grain refiner added at the level of 0.02% Ti. Melt temperature: 720°C, and poured in graphite mold.
Figure 5-15: Grain size of the structure at different times. Melt; super pure aluminum. Melt temperature; 720°C. Grain refiner added at the level of 0.02%Ti. Solidified in graphite mold.
5-9 Experiment With Induction Furnace

To study the difference between an Induction furnace and an Electrical Resistance furnace, an experiment on the grain refinement process was carried using an Induction furnace. In this experiment only the grain size and structures of the samples were studied.

In this experiment commercially pure aluminum was used, melted and kept at 720°C. The grain refiner, Al-6%Ti, was added at the level of 0.02% Ti, and poured into graphite molds. In the Induction furnace the melt was already in a continuously stirred situation.

The results are shown in Figure 5-16. A perfect grain refinement followed by a perfect fading phenomenon is observed in the grain size versus time graph. This result indicates that the continuous stirring situation in grain refinement causes a faster dissolution process of the grain refiner. In this situation there is no opportunity for particles to settle down and recover the fading by being redistributed by stirring or movement in the melt.

The creation of metastable phases can be prevented by continuous movement and dissolving the phases. Therefore, the Induction furnace that is mostly used in practice, causes a much higher rate of fading phenomenon compared to the Electrical Resistance furnace.
C.P. Al in Induction Furnace. Al-6%Ti Grain refiner. 0.02% Ti added. Graphite Mold.

Figure 5-16: Grain size of the structure at different times. Melt; commercial pure aluminum. Melt temperature; 720°C. Solidified in graphite mold.
6: Discussion

The ultrasonic graphs indicate a good correlation between the amount of particles inside the melt and the number of counted particles greater than 20 μm in size. After each stirring, the number of particle counts jumps up. Also, the Mag (N number) shows more attenuation during stirrings and higher amount of distribution of particles inside the melt.

The particles inside the melt, which are below 20μm in size, can not be detected by our ultrasonic system. This is due to the restrictions that we are dealing with, in operating the ultrasonic system (42).

In order to achieve clear results from the electronic data analyzer, we should have clear and strong peaks with a high enough amplitude of reflected waves. Also, intruding noises and energy losses of the main reflection waves must be minimized.

By using higher frequency for the pulses, there would be a better discrimination for the wave analysis. But on the other hand it causes a higher amount of loss of energy due to the Kirchoff effect (43). When the frequency is higher, the regions of compression and rarefaction are closer to each other. Thus, the amount of heat flow from compression areas to rarefaction areas is higher and therefore, we have a higher loss in energy of the sound waves.

The other factor that plays the main role in detecting the smaller size of particles, is dB level (43). The higher the dB level is, the smaller size of particles that can be detected. But the higher amount of dB causes a higher level of noise too. Therefore, at higher dB levels, the lower level particle reflection peaks are lost among the noise waves.

In the electronic data analyzer system, there are effective electronic filter circuits used. But as both sound reflection and noise waves are in a wide range of different frequencies, it is not possible to remove all the extraneous noise. Thus, the elimination of noise on the
CRT is out of the question, and we are only able to detect the peaks which are higher than the level of the noise.

The best detection level can be chosen by using a proper level for frequency and dB and by having a good balance between dB and the noise level, and also between the frequency and the amount of the loss of energy. Figure 6-1 shows a comparison between two results of an experiment in water. As observed, the number of particle counts are very similar for the higher frequency and dB levels compared to those with the lower levels. In fact here, the higher dB covers the loss of energy caused by the higher frequency.

The ultrasonic and grain size graphs show us that in the case of finer grain size without stirring and movements in the melt, the level of particle counts are very low too. This indicates that the nucleant particles, which are smaller than 20μm in size, are still floating inside the melt and cause nucleation and refinement of the structure of aluminum.

The settling of the small particles can be explained by Stokes law. Stokes law determines the ultimate settling velocity of particles inside a melt by the following equation:

\[ u_p = \frac{d_p^2 \Delta \rho g}{18 \mu} \]

where \( u_p \) is the ultimate settling velocity, \( d_p \) is the diameter of the particle, \( \Delta \rho \) is the density difference between the particle (\( \rho_p \)) and the melt (\( \rho_m \)), \( \mu \) is the dynamic viscosity of the melt, and \( d_c \) is the critical diameter of the particle.
Figure 6-1: Comparison in the number of counted particles when two different frequencies are used in ultrasonic system.

Figure 6-2: Ultimate settling velocity of spherical particles with different density in molten aluminum ($\rho = 2.37 \text{ g/cm}^3$, $\mu = 2.5 \times 10^{-3} \text{ Pa-s}$)
Figure 6-2 shows the graphs for some particles inside the aluminum melt. The ultimate settling velocity of the particle is proportional to the diameter of the particle to the power of two, and to the density of the particle. It is observed that the settling velocity, \( u_P \), of the particles with diameters less than 20\( \mu \)m is very low. As Stokes formula is for spherical shapes and stable state of the melt without movement, the small irregular particles in a situation with slight movements of the melt can stay and float in the melt even for a longer time. This can cause the small effective nucleants to be available even for a long period of time after stirring.

The complicated aspect of the experiments is about the fading phenomenon which has happened in some cases and did not happen for other cases. This is related to the mechanism of grain refinement, which has been a matter of controversy.

In three cases we could see fading in the grain refinement process. One was in the experiment with sand molds with lower cooling rate than graphite molds. The other one was in super pure aluminum experiment with 0.01\%Ti, and also the experiment which was conducted in an Induction furnace. In the case of commercially pure aluminum with 0.3\% impurities which were conducted in a resistance furnace and the solidification took place in graphite molds, the fading phenomenon was not observed either with stirring, or without stirring.

The rate of cooling is an important factor in nucleation and growth. Higher cooling rate allows the melt temperature to go further below the melting point and causes a higher undercooling. Higher undercooling causes a lower critical radius for stabilizing the nucleant. Therefore, smaller sized heterogeneous potent embryos could become stable nucleants, and more nucleants are available to grow. Thus the grain size will be reduced because of the higher number of the nucleants.

Figure 6-3 shows the relation between growth temperature in which nucleant growth begins, and the square root of the cooling rate in pure aluminum (44). We observe that by
increasing the cooling rate the growth temperature is getting lower, and in fact we have a higher undercooling in solidification.

The difference between the root of cooling rate between our graphite mold and sand mold is about $1^\circ$C/s$^{1/2}$ i.e.; for sand mold 0.7, and for graphite mold 1.7. Therefore, the difference in undercooling is about 0.6°C. This amount of undercooling can lower the critical $\Delta G$ and therefore critical radius for stable nucleation, significantly.

Figure 6-3: Growth temperature versus root of cooling rate during the solidification of aluminum melt (99.995% Al) (Ref. 17)
Figure 6-4 illustrates the relation between undercooling and the nucleation rate in the melt for solidification, \( N \), (45). It can be seen that after starting the nucleation, either for homogeneous, or for heterogeneous nucleation, the nucleation rate increases very rapidly with only a small change in the amount of undercooling, and is exponentially related to it.

Therefore, it is a reasonable explanation that by a higher rate of undercooling in our grain refinement experiments, there were more potent nucleants available, which were stable and were able to grow to make more grains.

\[ \Delta G^* \]

\[ \Delta G_{\text{hom}} \]

\[ \Delta G_{\text{het}} \]

\[ \text{Critical value for detectable nucleation} \]

\[ N_{\text{het}} \]

\[ N_{\text{hom}} \]

**Figure 6-4:** (a) Variation of \( \Delta G^* \) with undercooling (\( \Delta T \)) for homogeneous and heterogeneous nucleation. (b) The corresponding nucleation rates assuming the same critical value of \( \Delta G^* \). (Ref. 45)
But still something is confusing and that is the dissolution of TiAl₃ particles in the melt. It is obvious that in all the experiments the grain refinement took place after the addition of the grain refiner. Also, the amount of Ti was an important factor. It should be high enough to have a fine grain structure after solidification. In almost all of the studies during the last few decades, with different theories and opposing ideas about the mechanism of grain refinement, one point was in common. That was the importance of Ti which has the key role in grain refinement.

To study the effect of TiAl₃ in grain refinement after the melt was kept for a significant time, the cross section of many samples were studied under optical microscope, and some of them by scanning electron microscope (SEM).

There was no trace of any TiAl₃ particles. Figure 6-5 shows a sample of x-ray test under scanning electron microscope. Most of the particles were the composed of aluminum, iron, and silicon. There was no titanium phase found in the structure.

The dissolution of TiAl₃ particles is reasonable according to the phase diagram of the Al-Ti system and in practice. But is it just TiAl₃ which can play the role of effective nucleant?

The author made a calculation regarding the amount and distribution of the TiAl₃ particles in the melt, considering different sizes of particles and different amount of Ti. The assumption is that all of the Ti content in the melt is changed to TiAl₃. Also, it is assumed that the particles are distributed uniformly in the melt perfectly, so that the distance between the particles is the same. The result of these calculations is shown in Figure 6-6.
Figure 6-5: A sample of SEM test on grain refined aluminum specimens.
Figure 6-6: The distance between titanium aluminide particles of different size at different levels of added titanium inside the aluminum melt after addition of the grain refiner in an ideal hypothetic situation.
The graphs in Figure 6-6 show that even in the assumed ideal situation that does not happen in real life, the distance between the particles is too large. According to the studies in the past, we know that just a small amount of TiAl₃ particles, i.e., about 1% of them, become effective nucleants and cause the grain growth. Therefore, the amount of the effective TiAl₃ particles for making nucleants is much lower than what is needed to be the main nucleant in the melt and change the grain size of the structure from more than a thousand micron to less than a hundred micron.

Also, in our experiments we observed that in commercially pure aluminum which contains more impurities like iron and silicon, there is a better situation for grain refinement than in super pure aluminum which has much less impurities. Therefore, the effect of other elements is clear, mostly in the situations with higher rates of cooling. The other elements like iron and silicon can make metastable phases with titanium together with aluminum. The surface of these metastable phases may have a higher interfacial energy with aluminum compared to that of TiAl₃, but it could be enough for stable nucleation, especially in situations like a higher amount of undercooling.

The situation in the induction furnace shows that the continuous stirring of the melt causes a faster dissolution of the potent nucleants in the grain refiner, and prevents the creation of metastable phases which can act as potent nucleants. That is the reason for a higher rate of fading in the induction furnace.
7: Conclusions

1- The ultrasonic system can detect the particles inside the melt during the grain refinement process and therefore detect any cause of distribution of particles, like movements inside the melt, or external oxides and other solid crystals.

2- In molten aluminum the ultrasonic beam can detect the particles above 20 μm in size. As the particles which act as effective nucleants are not detected by the system, they appear to be less than 20 μm in size. That is why they can float in the melt for a long time.

3- The higher rate of cooling during solidification causes a better opportunity for small crystals to be stable heterogeneous nucleants, which are more stable than TiAl₃ crystals in the melt and provide a better grain refinement with finer grain size.

4- The main nucleants, especially at higher cooling rates, could be some types of metastable phases consisting of aluminum, titanium, and other impurities like iron and silicon.

5- In the induction furnace the fading phenomenon is faster than in the electrical resistance furnace due to the continuous stirring of the melt. This condition does not let metastable phases form as stable nucleants, and causes a faster rate of particle dissolution.
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