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Characterisation of Al-Ti-B grain refiners prepared by aluminothermic reduction of TiO2 and B2O3

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2. LITERATURE REVIEW

2.1 Fundamentals of Nucleation

Nucleation can be defined as the formation of a new phase in a distinct region, separated from the surroundings by a definite boundary. When a liquid cools a change of state from liquid to solid may occur corresponding to a discontinuity in free energy. This results in the formation of small particles surrounded by liquid. Nucleation is of two types, namely, homogeneous nucleation and heterogeneous nucleation.

Homogeneous nucleation does not involve foreign atoms, particles or surfaces. Heterogeneous nucleation is achieved through the influence of foreign particles and/or surfaces. A good understanding of how and when nucleation takes place necessitates a look at the problem from both the thermodynamic and the kinetic point of view.

2.1.1 Homogeneous nucleation

When a pure metal cools down in the liquid state, it will transform to the solid state at some temperature. From thermodynamics[17], there is only one temperature at which a pure solid metal can co-exist with pure liquid metal. At this temperature, corresponding to the equilibrium melting temperature T_m, the free energies of liquid and solid are equal. At temperatures lower than T_m, the solid has a lower free energy and will be the stable state (Figure 2.1). T_m is also the temperature of melting of the solid on heating. A metal will tend to solidify when its temperature is below the melting point because there is a decrease in free energy associated with the solid-to-liquid transformation. The larger the degree of undercooling, the larger the driving force to transform from liquid to solid.

2.1.2 Heterogeneous nucleation

In the usual casting processes, nucleation is heterogeneous and occurs on solid surfaces in the liquid. Foreign substances, either the container or insoluble impurities, provide such surfaces. For a metal to solidify on a foreign substance, it is essential that the surface of the substrate should be wetted. The angle of contact θ between the substrate and the solid metal being deposited is important (Figure 2.2). When θ is small, the interface energy between the solid and the substrate is low. Under these conditions, the atoms in the liquid readily form a solid-metal nucleus on the surface of the substrate. If $\theta = 180°$ the solid/substrate interfacial energy is high and nucleation is in effect homogeneous. The effectiveness of any particle as a nucleation catalyst is a function of

the contact angle, which is determined by factors such as the lattice spacing of the two structures (substrate and solid metal) and the chemical nature of the substrate surface.

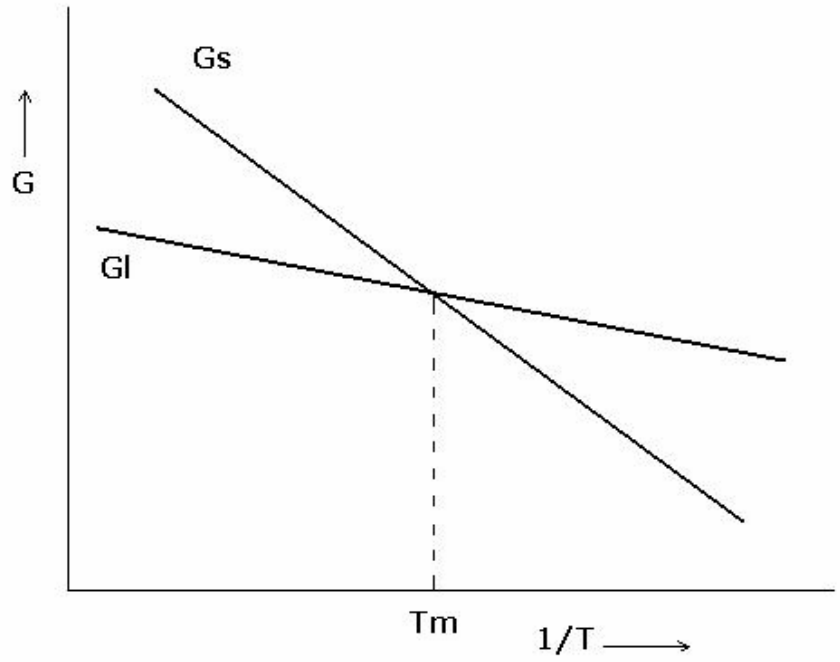


Figure 2.1: Variation of free energy for a pure liquid (G_l) and a pure solid (G_s) as a function of 1/T; T_m is the equilibrium melting temperature [18]

When the contact angle is small, nucleation will occur with a small amount of undercooling; if the contact angle is large a greater amount of undercooling will be necessary. Most commercial metals contain a sufficient number and variety of insoluble impurities for nucleation to occur at undercooling of 0.5-5.5°C. If the number of nuclei is insufficient for a given purpose, nucleating agents may be added to the melt.

2.1.3 Properties of the interface in heterogeneous nucleation[18]

It is of interest to consider the concept of coherency in heterogeneous nucleation. A coherent interface is one in which there is matching between atoms on either side of the interface. If there is only partial matching, the interface is considered to be semi-coherent. For a coherent interface, there is elastic strain energy due to misfit across the interface. For semi-coherent interface, part of the matching is taken up by the coherency strains and part by introducing

dislocations. The energy of these dislocations is calculated in the total change of free energy in nucleation.

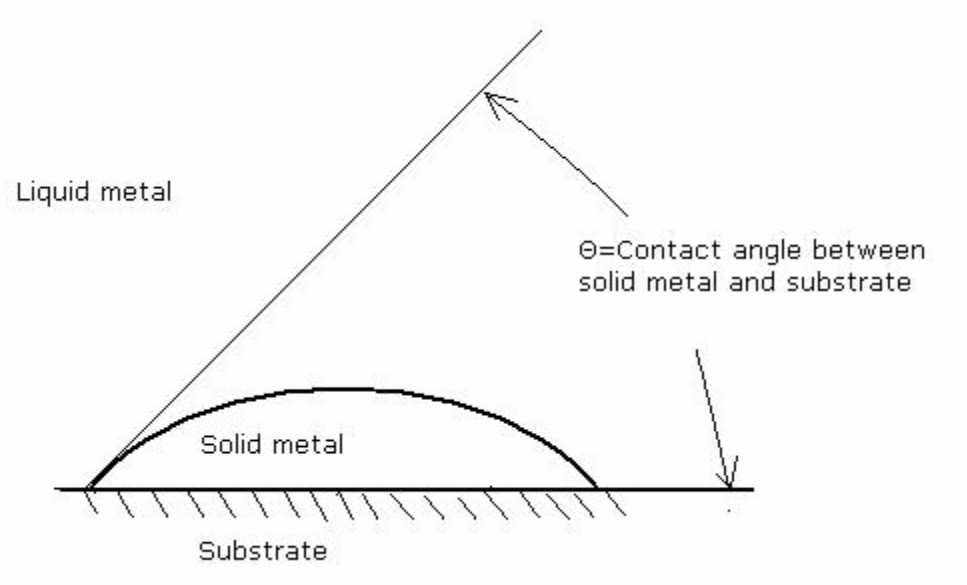
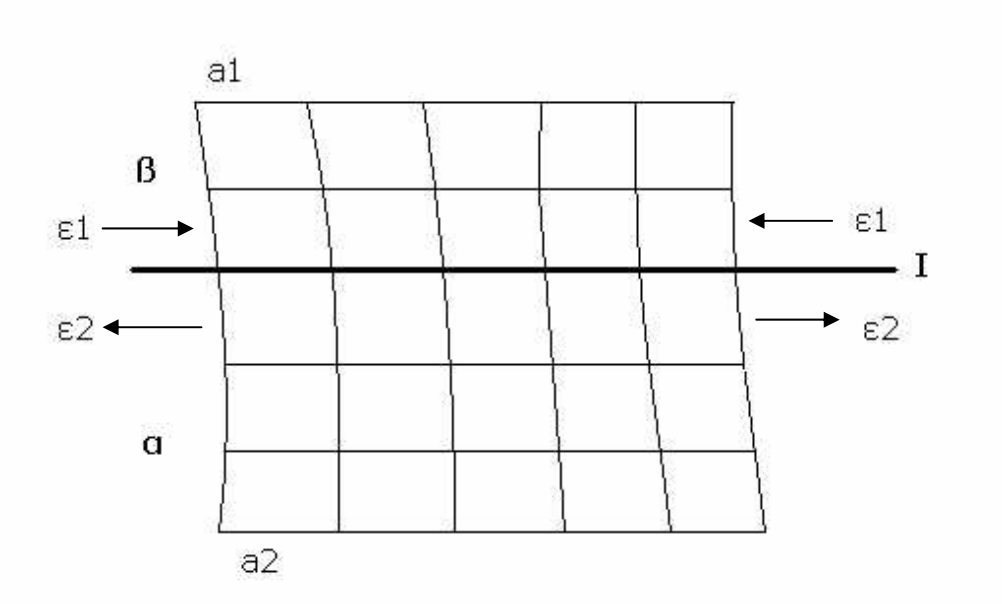


Figure 2.2: Contact angle between substrate and solid metal in heterogeneous nucleation

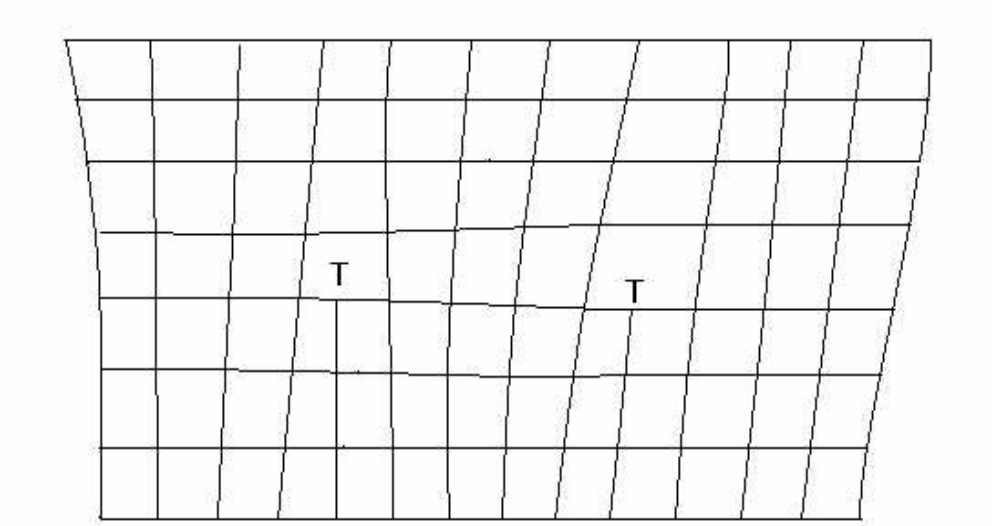
In a coherent interface, two phases α and β having lattice constants a_1 and a_2 respectively, can be made to correspond across an interface I (Figure 2.3) if a_1 and a_2 do not differ substantially. In this case, a strain ε_1 is imposed on α and a strain ε_2 on β. The total interface strain is then $\varepsilon_1+\varepsilon_2$. The disregistry or lattice mismatch δ is given by $\delta = (a_1 - a_2)/a_2$. In semi-coherent interfaces, regions of coherency exist within a network of dislocations. The latter are necessary to account for the remaining strains. The interface energy is now made up of two terms, one due to the matching in the coherent region (σ_E) and a second term due to the energy of the dislocations (σ_S). The total interfacial energy σ is equal to $\sigma_E + \sigma_S$.

2.1.4 Nucleation on a coherent and a semi-coherent interface

For coherent nucleation, the strain energy is the dominant term and is the one of importance in nucleation calculations. In semi-coherent nucleation with a small mismatch, coherency is favoured since the strain energy is small and the energy of nucleation has its smallest value. As δ increases, dislocation geometry becomes more favourable for taking the misfit at the interface. The critical free energy for nucleation then becomes dependent upon this term.



(a) Coherent interface



(b) Semi-coherent interface

Figure 2.3: Model of coherent and semi-coherent interfaces between two phases[18]

2.1.5 Nucleating agents or inoculants

As indicated in previous paragraphs, a nucleating agent is a substance which can be intentionally added to the liquid to act as a nucleation site. The substance may be a compound that

is insoluble in the melt and will produce a small contact angle, or it may be a material that will react with the liquid to form a nucleation catalyst. The nucleation potency of inoculants is strongly dependent on the contact angle θ, and chemical parameters such as the bond type and the bond strength. For easy nucleation, a low contact angle is required. When chemical parameters of the nucleated crystal and the substrate are similar, the lattice mismatch between the crystal and substrate is small and nucleation is easy. Practically, controlled nucleation is of great importance. It is found that the grain size and the grain shape together with segregation effects occurring during casting can have a significant influence on the physical, mechanical and chemical properties of the product. In practice, one of the most important technical aspects considered in casting is the control of nucleation. The reason is that the amount of nucleation controls the final structure and thus the properties of the solidified metal. Each grain or crystal grows from a single nucleus, and the number of nuclei available in the melt determines the final grain size. Most commonly, control is exerted by use of nucleating agents. The addition of known nucleation agents is a standard method for producing the correct grain size in a casting, but vibration techniques may be used as well. . Table 2.1 gives compounds used to study the heterogeneous nucleation of aluminium from its melt with their respective lattice mismatch.

Table 2.1: Compounds used to study the heterogeneous nucleation of aluminium.

Compound	Crystal structure	δ for close-packed planes	Nucleating effect
VC	Cubic	0.014	Strong
TiC	Cubic	0.060	Strong
TiB_2	Hexagonal	0.048	Strong
AlB_2	Hexagonal	0.038	Strong
ZrC	Cubic	0.145	Strong
NbC	Cubic	0.086	Strong
W_2C	Hexagonal	0.035	Strong
Cr_3C_2	Complex	-	Weak or nil
Mn_3C	Complex	-	Weak or nil
Fe_3C	Complex	-	Weak or nil

For many purposes, particularly for strength, a small grain size is desired, and this means that a large number of nuclei must be made available and the cooling rate must be controlled to allow the nuclei to act. Rates of cooling are important in nucleation since it is likely that all the nuclei do not act at exactly the same time, perhaps because the whole of the liquid is not at the same temperature or because all the nuclei do not operate at the same degree of undercooling. The first crystals to nucleate will grow until they meet the other crystals that have nucleated. If the time between nucleation events is long the crystals become large and absorb some of the nucleating sites, which might have produced nucleation. If the cooling rate is rapid, a large number of nuclei are given the opportunity to act as nucleation centres before the advancing grains absorb them.

2.2 The Mechanism of Grain Refinement of Aluminium Alloys

Since the works of Cibula[1] in the late 1940s and early 1950s, many theories have been proposed to explain the mechanism of refinement and the subject has been controversial over the years. It is well known now that the refinement of grains during solidification of aluminium alloys is due to the presence in the melt of many nucleation sites that impart to the solidifying metal a fine structure. The proposed mechanisms for grain refinement can be divided into two groups. First are those which assume that the nucleant particle is of ultimate importance. These theories form the "nucleant paradigm". Second, there are those which recognise the solute elements as essential for the achievement of a fine-grained microstructure. This group forms the "solute paradigm". The nucleant paradigm includes the following theories:

- Boride/carbide theory
- Phase diagram/peritectic theory
- Peritectic hulk theory
- Hypernucleation theory
- Duplex nucleation theory

The solute paradigm assumes that the mechanisms are driven by constitutional undercooling.

The boride/carbide theory was first postulated by Cibula[1] in 1949. According to this theory, TiC and/or TiB_2 crystals nucleate solid aluminium by heterogeneous nucleation after the addition of Al-Ti-B master alloy. TiC is thought to be formed from the added Ti and carbon impurities always present in the melt. Soon after the addition of the master alloy, the $TiAl_3$ particles begin to dissolve rapidly, thereby creating a constitutionally favourable growth condition for α-aluminium

to grow on these TiB_2 and TiC particles.

The peritectic nucleation theory proposes that grain refinement is achieved by the action of certain transition elements such as Ti, Zr, Cr, Mo and W, which undergo a peritectic reaction with aluminium. In a melt containing Ti (the most common grain refining element), the reaction that occurs can be illustrated by the Al-Ti phase diagram as follows:

$Al_{(liquid)} + TiAl_3 \rightarrow Al_{(solid\ with\ titanium\ in\ solution)}$

The peritectic reaction occurs at approximately 665°C at a minimum concentration of 0.15wt%Ti. The α-aluminium (with Ti in solid solution) nucleates on the dissolving $TiAl_3$ particles. A layer of α-aluminium then forms and completely encloses the surface of the particle. This theory faces a big problem. According to the binary Al-Ti phase diagram, the liquid aluminium should contain a minimum 0.15wt%Ti at the peritectic temperature. Since the amount of titanium added to the melt is usually 0.01wt%Ti, it was suggested that, by adding Al-Ti-B master alloy during the grain refinement of aluminium, boron caused a shift in the peritectic reaction to a composition below 0.15wt%Ti. Figure 2.4 shows the aluminium-rich side of the Al-Ti phase diagram with the peritectic point at 1.2 % Ti and 665°C and the minimum Ti content of 0.15% required for the peritectic reaction to take place.

The peritectic hulk theory proposes that the nucleation occurs inside a boride shell via the peritectic reaction. The titanium is present inside the boride shell after $TiAl_3$ dissolution at the peritectic concentration. While recognizing $TiAl_3$ as a better nucleant than TiB_2, the peritectic hulk theory explains how the boride slows down the dissolution of aluminide. It suggests that borides form a shell around the dissolving aluminides, thus slowing down the dissolution of the latter as diffusion needs to proceed through the boride shell. The aluminide finally dissolves leaving a cell of approximately peritectic composition inside the boride shell. The peritectic reaction takes place to form α-aluminium and growth occurs from there.

The hypernucleation theory was proposed and named as such because of the disproportionate effect that very small amounts of titanium and boron have on the grain size of aluminium. Hypernucleation theory proposes that nucleation occurs on the borides. Titanium segregates down the activity gradient to the borides (TiB_2) particles, thus forming a suitable interface for nucleation of α-aluminium. Solutes of similar atomic size to aluminium lead to hypernucleation whereas solutes of grossly mismatching size will destroy the hypernucleation process. The atomic size of titanium is very similar to that of aluminium and hence promotes hypernucleation. There is no experimental evidence to support this theory.

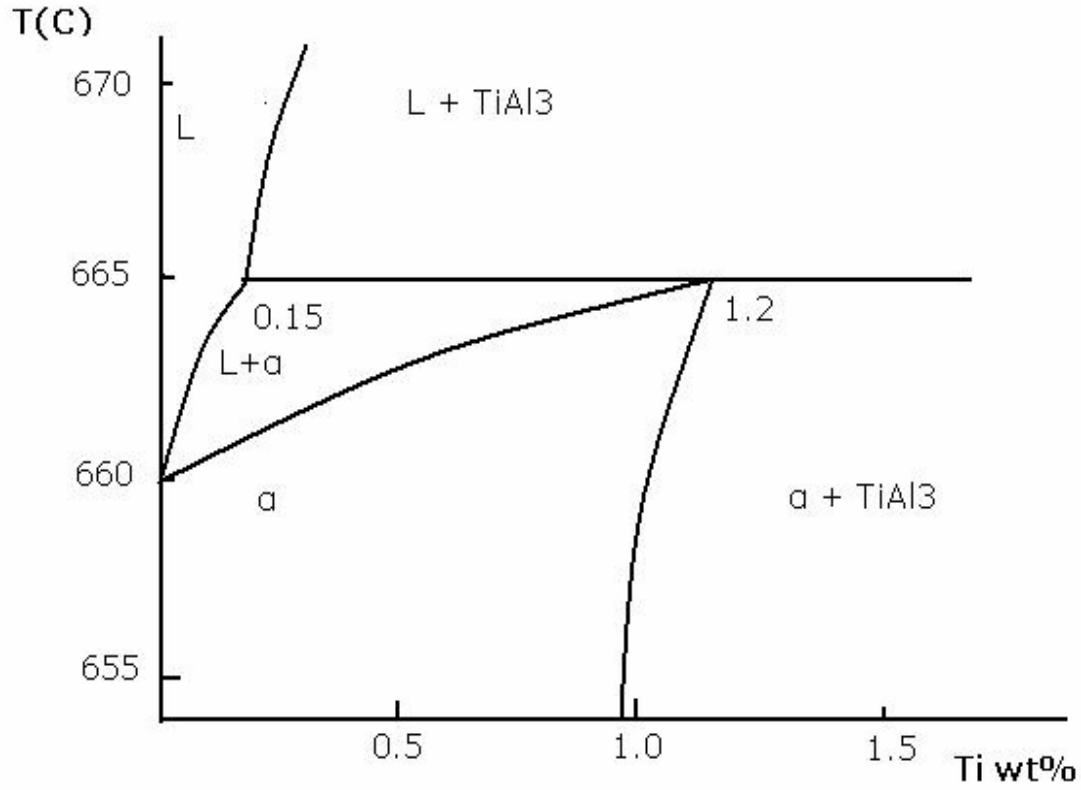


Figure 2.4: Detail of Al-Ti phase diagram showing the minimum Ti content for the peritectic reaction at 0.15% and 665°C[19]

The duplex nucleation theory suggests that nucleation takes place on $TiAl_3$ particles that surround TiB_2 particles. The basic idea is that, in the absence of titanium in the aluminium melt, TiB_2 does not act as a nucleating site and is pushed to the grain boundaries. However, with the titanium at the peritectic concentration, TiB_2 was observed at the centre of aluminium grains with a $TiAl_3$ layer on the boride.

The solute paradigm is based on the constitutional undercooling mechanism. It suggests that both the nucleants and the segregation of solute influence grain refinement. In the solute theory, it is believed that the equi-axed crystal can nucleate in the solute-enriched liquid ahead of a growing solid/liquid interface. Solute elements like Ti, Si and Fe have a restrictive effect on the solidifying metal. They segregate to the nucleant/melt interface and restrict the growth of dendrites, thus effecting constitutional undercooling at the solid / liquid interface: they build up a constitutionally undercooled zone in front of the interface. This undercooled zone facilitates nucleation and the new grains do the same to neighbouring grains, thus providing many nucleating grains and producing a wave of equiaxed grains advancing towards the centre of the melt. The

extent of segregation is measured in terms of a growth-restricting factor (GRF). The GRF is a measure of the growth restricting effect of solute elements on the growth of the solid-liquid interface of the new grains in the melt. Experimental work on the GRF has shown that grain size drops dramatically with increase of that factor, but begins to increase after a certain value[20]. Solutes like Ti, Si and Fe have been found to restrict dendrite growth with additive effect, which is quantified, by the growth-restricting factor. Particularly, the role of Ti in grain refinement has been attributed to its strong tendency to segregate.

The solute theory suggests that, during casting, the driving force for nucleation at the beginning of solidification is usually thermal undercooling in the melt at the mould wall[21]. Thermal undercooling is quickly dissipated by latent heat evolution and, in the absence of solutes; there can be no further nucleation, even though there may be large numbers of potential nucleants in the melt. Columnar grains will then grow until solidification is complete. However, when the melt contains solute, the chill crystals reject solute as they grow forming a solute-rich layer surrounding the crystal surfaces within which constitutional undercooling may reach a level sufficient for nucleation on particles present in this layer.

2.3 New Understanding of Nucleation of Aluminium by Inoculation

A new approach has been set forward to explain which of the two compounds, $TiAl_3$ and TiB_2, is the primary nucleant. Based on the quantities of grains of aluminium and of TiB_2 and $TiAl_3$ particles added in the grain refining process, Lee and Chen[22] concluded that $TiAl_3$ particles couldn't be the primary nucleating substrate for grain refinement using Al-Ti-B grain refiners. This explanation is based on the fact that the introduced quantities of $TiAl_3$ are much lower than the amount of grains and the number of grains was lower than that of TiB_2 particles. Furthermore, when only TiB_2 is used, the grain refining performance is very poor or even nil. It was thus concluded that the nucleation mechanism for Al-Ti-B grain refiners must be based on TiB_2 as the nucleating substrate while the titanium in excess has some effect on the surface of TiB_2 particles. TiB_2 is then said to be the primary substrate.

This approach is in agreement with the finding of Schumacher *et al*[23] in their micro-structural studies of nucleation mechanisms in a glass matrix. In these studies, TiB_2 is seen having well defined faces and ledges. Aluminium crystals appear to nucleate on the basal faces of the boride. The α-aluminium nucleates on a thin layer of $TiAl_3$ coating the boride. Only the basal plane of the TiB_2 has a favourable interfacial energy with $TiAl_3$ and nucleation is observed on the flat

portion of the ledges, not in the corners. These observations in metallic glasses suggest the following overlapping stages in the mechanism of nucleation:

- $TiAl_3$ dissolves in the melt and provides excess titanium.
- TiB_2 particles are distributed uniformly in the melt.
- A thin layer of $TiAl_3$ coats any TiB_2 particles not already coated and grows or dissolves to a characteristic thickness: this layer is stabilised by a favourable chemical interaction between the close packed planes of $\{112\}_{TiAl3}$ and $\{001\}_{TiB2}$. The exposed $\{112\}_{TiAl3}$ faces are non-equilibrium and are stabilised by the TiB_2 substrate; they are highly effective substrates for heterogeneous nucleation of α-aluminium.
- The melt is cooled and a driving force for the formation of α-aluminium develops when the temperature decreases below the α-aluminium liquidus
- α-aluminium nucleates on $\{112\}_{TiAl3}$ faces so that the close packed planes of TiB_2 {0001}, $TiAl_3$ {112} and α-aluminium {111} are parallel.
- α-aluminium grows, the release of latent heat increasing the temperature and stifling further nucleation; the excess titanium in the melt retards the growth via constitutional effects.

While Youssef *et al*[24] have found the existence of an orientation relationship between TiB_2 particles and aluminium suggesting a direct nucleation of aluminium by TiB_2 particles, Arnberg *et al.*[5] have found a preferred orientation between the $TiAl_3$ crystals and the surrounding aluminium grains with no such relationship between TiB_2 and aluminium. As a result, whenever $TiAl_3$ is present, crystals of this phase, rather than TiB_2 particles will nucleate aluminium. In this regard, the role of excess titanium in the melt is that it permits the formation of a thin layer of $TiAl_3$ on the boride particles. Increasing titanium content in the liquid, up to the solubility limit at the peritectic temperature would have the effect of retarding growth and improving refinement. Thus the nucleation mechanism must be degraded as the level of titanium in the melt increases beyond the small value necessary to ensure the formation of the $TiAl_3$ layer on the borides. When the aluminide layer is thin, the interatomic spacing in its {112} plane is stretched by its epitaxy on the TiB_2 and more closely matches the $\{111\}_{\alpha\text{-aluminium}}$ plane. For thicker layers, this effect disappears.

2.4 Methods of Preparation of Grain Refiners

Grain refiners commercially available at present are Al-Ti-B, Al-Ti and Al-Ti-C.

2.4.1 Al-Ti and Al-Ti-B grain refiners

Different methods of preparation of Al-Ti and Al-Ti-B grain refiners are proposed in the literature. Among these methods are:

- Reaction of fluoride salt with aluminium (Al-Ti)
- Reaction of molten aluminium with titanium oxide (Al-Ti)
- Melting of high purity aluminium and titanium iodide together under argon (Al-Ti)
- Melting of aluminium and titanium sponge together (Al-Ti)
- Electrolysis of TiO_2 and B_2O_3 in cryolite alumina melts in the presence of aluminium at 1000°C (Al-Ti-B)
- Aluminothermic reduction of TiO_2 and B_2O_3 in the presence of cryolite (Al-Ti-B)
- Reaction of B_2O_3 and TiO_2 with molten aluminium (Al-Ti-B)
- Melting of aluminium and titanium sponge together and the reaction of the melt with KBF_4 (Al-Ti-B)

Among the above techniques, those involving the reaction of halide salts with molten aluminium have become quite popular and most commercial grain refiners are prepared by this technique. The salt route uses low melt temperatures (in the range 750-800°C) and utilises the exothermic nature of the reaction between the salts and the molten aluminium. Commercial production of Al-Ti-B master alloy involves the addition of the inorganic salts potassium fluorotitanate K_2TiF_6 and potassium fluoroborate KBF_4 to molten aluminium at temperatures in excess of 700°C. Aluminium reduces the fluoride salts to yield a melt consisting of molten aluminium and dispersed particles of $TiAl_3$ and TiB_2. Clean melt with good control of alloy composition is usually achieved by this technique. The reaction products and unreacted salts are in the molten state and float on the melt owing to their lower density and hence can easily be separated from the melt.

The reaction temperature, stirring of the melts and sequence of addition of salts are important factors which influence the chemical composition, the microstructure and the grain refining performance of grain refiners. Salt addition at 750°C, leads to the formation of blocky $TiAl_3$ particles whereas at an addition temperature of above 900°C, $TiAl_3$ particles are acicular or flaky. TiB_2 particles are not influenced by the reaction temperature in the preparation of the master alloy. Boride crystals formed at higher temperature (about 1100°C) show the same

morphology, size and frequency of twinning as crystals formed at lower temperature (750°C)[3].

Good stirring of the melts leads to uniformly dispersed $TiAl_3$ and TiB_2 particles in the melt by preventing the sinking of particles due to their higher densities. The particles formed depend on the salt addition sequence. When K_2TiF_6 and KBF_4 react with aluminium individually, $TiAl_3$ and AlB_{12} are formed respectively while $TiAl_3$ and TiB_2 form instead of AlB_{12} when both salts react with aluminium simultaneously[9].

2.4.2 Al-Ti -C grain refiner

There is no detailed literature on the production of Al-Ti-C grain refiner as the process is usually proprietary to the producer. However, it is known that Al-Ti-C grain refiner is prepared by first melting aluminium with titanium scrap and adding carbon either as graphite or some other form of fixable carbon. Banerji and Reif [4] have prepared Al-Ti-C by reacting carbon particles of 20 μm average size with Al-(5 to 10 %)Ti alloy melts while the melt was vigorously stirred. The microstructure of these master alloys, (containing 5 to 8% Ti and 0.4 to 2.0% C) showed $TiAl_3$ particles and TiC particles of average size lower than 1 μm. This preparation involved the melting of Al-Ti alloys in a medium frequency induction furnace at temperatures between 750 and 1000°C and mechanical stirring so that a deep vortex was generated. Graphite powder of 20μm average particle size, suitably preheated to expel the absorbed moisture was added to the vortex in small batches and stirred into the melt in succession to effect the graphite/melt reaction. TiC particles were found to be poisoned at the normal melting temperature of 1000°C or below due to their higher free energy of formation than that of Al_4C_3. This situation led to the formation of Al_4C_3 and Ti_3AlC compounds on the particle surfaces according to the reactions:

$$3TiC + 4\ Al = Al_4C_3 + 3\ Ti$$

$$9\ Ti + Al_4C_3 = 3Ti_3AlC + Al$$

Further the melt was superheated to higher temperatures (between 1200 and 1400 °C) and held there for 5 to 10 minutes for rejuvenation of active nucleants before casting redissolving the Al_4C and Ti_3AlC. In a recent work, Zhang *et al*[25] have prepared Al-Ti-C grain refiners by aluminothermal reaction of K_2TiF_6 salt, graphite powder and aluminium containing 5-7% Ti at reaction temperatures of 750-950°C. The reaction of K_2TiAl_6 with molten aluminium releases titanium which dissolves into the aluminium melt. When the solubility limit of titanium in liquid aluminium at the reaction temperatures is exceeded, $TiAl_3$ precipitates as follow:

$$Ti_{(d)} + 3Al_{(l)} = TiAl_{3(s)}$$

Titanium carbide is formed as follows:

$C_{(s)} + Ti_{(d)} = TiC_{(s)}$

Where d is dissolved, l is liquid and s is solid.

Stirring the melt after the addition of graphite enabled the carbon to penetrate the melt. The reaction for TiC formation was made easier at the graphite/melt interface[4], the only place where the reaction will occur. Furthermore, continuous stirring of the melt causes better wetting of TiC particles, good dispersion of these particles in the melts owing to the low solid-liquid interface energy, and uniform mixing due to the stirring. Without stirring both, TiC particles and primary $TiAl_3$ precipitates tend to settle to the bottom of a static melt owing to their higher densities.

2.5 Characterization of Grain Refiners

2.5.1 Methods of characterization

Basically, there are 3 methods of characterizing a grain refiner for aluminium alloys:

- Chemical analysis
- Microstructure
- Grain size measurements in the as-cast alloy

The examination of the microstructure of master alloys is one of the principal methods of evaluating and classifying these alloys and may be used to determine the effects of manufacturing conditions, cold working and heat treatment on their behaviour as grain refiners. Three methods may be used for microstructure analysis: optical microscopy, SEM and TEM. It is also important to know the elemental composition of the grain refiner since there is a link between the chemical elements present in the alloy, their combination and the different phases present. The chemical composition of a master alloy can be determined by a variety of methods such as:

- Mass spectrometry (MS)
- Energy-dispersive spectrometry (EDS)
- Atomic absorption spectrography (AAS)

The grain size of a treated aluminium alloy gives a good indication of the performance of the grain refiner used. Grain size measurement can be performed using methods described in ASTM Standard E112 and the results can be reported in one of several ways[26]:

- Average intercept distance
- Calculated average diameter
- ASTM grain size number
- Grains per unit area

Murty *et al.*[27] describe a number of reliable methods for evaluating grain size of sectioned surfaces. These include:

- The Alcan test
- The Alcoa test
- The KBI ring test
- The Aluminium Association test or TP-1 test

Recently, theoretical models have been set forward as means for characterizing grain refiner efficiency based on the Microstructural features[12,13].

2.5.2 Microstructural characterisation

2.5.2.1 Al-Ti and Al-Ti-B grain refiners

Microstructural characterisation is very important and allows one to trace the history of the master alloy[28]. The phases encountered in Ti-Al grain refining master alloys are $TiAl_3$ intermetallic particles dispersed in the aluminium matrix. The $TiAl_3$ particles can be needle-like or plate-like and grow in thickness as the Ti concentration in the alloy increases. The microstructure of Al-Ti-B grain refiners generally consists of $TiAl_3$ and TiB_2 particles dispersed in an aluminium matrix. The morphology, size and size distribution of the intermetallic particles depend on preparation conditions. $TiAl_3$ particles are either flaky or blocky but have the same crystal structure and composition [3]. Petal-like particles which form by twinning have also been observed. The sequence of salt addition and the addition temperature play a crucial role in determining the microstructure. In their study on intermetallic compounds, Mayes *et al* [29] observed aluminides in rod-like grain refiners containing nominally 5%Ti and 1%B. These were found to contain aluminide particles of either a blocky or a facetted blocky morphology with entrained platelets, believed to be boride due to the presence of boron in the alloys. The platelets were observed both within the $TiAl_3$ phase and at the interface between α-aluminium and $TiAl_3$. The definition of the exact nature of boride phases in Al-Ti-B grain refiners is a controversial issue. While the boride phase is now admitted to

be hexagonal plates of TiB_2, hexagonal plates of $(Ti,Al)B_2$ and AlB_2 are also found in master alloys cast after a short holding time indicating the presence of a continuous series of solid solution from TiB_2 to AlB_2[30]. But opinions are divided on the existence of this series or whether the two compounds are present as two distinct phases[31]. The melting point of TiB_2 is 3225°C and that of AlB_2 is 975°C. Most probably, formation of (Al, Ti)B_2 starts with the formation of a titanium boride into which diffusion of Al takes place to bring the crystals to equilibrium composition. Many researchers could not distinguish between borides TiB_2 and AlB_2, or the mixed boride (Ti, Al) B_2. Other work carried out on this issue has led to the conclusion that (Ti, Al) B_2 transforms to TiB_2.

2.5.2.2 Al-Ti-C grain refiners

The microstructure of Al-Ti-C grain refiners consists of an aluminium matrix, $TiAl_3$ particles, needle-like in shape embedded in the aluminium matrix, TiC particles dispersed in the aluminium matrix and Al_3C_4 if the holding time of the melt is long[32,33,34]. Mayes *et al*[32] identified the phases in Al-Ti-C grain refiners as an aluminium matrix and $TiAl_3$ particles, 50-100 μm long embedded in the aluminium matrix. Some aluminide particles had well defined facets whereas others were much rougher with pitted surfaces. Banerji and Reif [4] developed Al-Ti-C master alloys of different compositions which showed primary $TiAl_3$ particles of a needle-like form and TiC particles 200nm in size within the aluminide phase. These had the NaCl crystal structure with a lattice parameter of 0.433 nm. They found that TiC particles segregated to the cell or grain boundaries. The TiC particles were octahedral with well-defined facet planes[35] and were mostly found in clusters, with faces touching, the largest clusters being ~1.5μm across[35]. Individual TiC particles are smaller than the TiB_2 particles and bound by the {111} faces[36]. They also exhibit spherical or round shape[6]. Backscattered electron images (BEI) produced by SEM at 2000x magnification showed that the maximum size of TiC particles was 0.59 μm in Al-3.0%Ti-0.15%C and 0.26 μm in Al-6.0%Ti-0.2%C. The number of TiC particles in Al-3.0%Ti-0.15%C was approximately three times greater than that in Al-6.0%Ti-0.2%C for a similar area of analysis resulting in improved grain refining performance[37].

2.5.3 Chemical composition

The chemical composition of master alloys, especially their Ti, C and B contents, plays an important role in influencing their grain refining performance. The level of refinement achieved for the same level of Ti addition varies with Ti/B ratio for the Al-Ti-B master alloy and Ti/C ratio

for the Al-Ti-C master alloy. For example, Al-3%Ti-1%B master alloy has been found to grain refine better than Al-5%Ti-1%B aluminium alloys containing poisoning elements such as Zr, Cr, Li and Si[27]. The amount of boron present in commercial Al-Ti-B grain refining master alloy varies widely. Generally, the ratio of titanium to boron ranges from 1:1 to 50:1. This ratio has a significant impact on grain refining effectiveness. The stoichiometric ratio of Ti:B in wt % for the formation of TiB_2 is 2.22. Above this ratio, the remaining Ti contributes to the formation of $TiAl_3$ in the grain refiner. Al-Ti-B grain refiners with titanium-to-boron ratio lower than 2.22 have a microstructure of an aluminium matrix with only dispersed particles of TiB_2. In actual commercial grain refiners the titanium-to-boron ratio is above 2.22. Table 2.2 gives titanium and boron content of different commercially available Al-Ti-B master alloys.

Table 2.2: Al-Ti-B master alloys of different titanium-to-boron ratios

Types	Ti (%)	B (%)	Ti: B
Al2.5Ti2.5B	2.5	2.5	1
Al3TiB series	3	1.0	3
	3	0.5	6
	3	0.2	15
	3	0.1	30
Al5TiB series	5	1.0	5
	5	0.5	10
	5	0.2	25
	5	0.1	50

Master alloys with different Ti:C ratios are also available. But the range of ratios is not as wide as that for Al-Ti-B master alloys. Table 2.3 gives Ti/C ratios for commercial Al-Ti-C master alloys, which range from 15:1 to 300:1. Al-Ti-C grain refiners with very high titanium content have been used to grain refine aluminium alloys. However, a low ratio of Ti /C in Al-Ti-C master alloy has been developed to avoid high titanium additions and yet to provide enough TiC nuclei for control of the grain structure[37]. Table 2.3 gives titanium and carbon content of different commercially available Al-Ti-C master alloys.

Table 2.3: Al-Ti-C master alloys of different titanium-to-carbon ratios

Types	Ti (%)	C (%)	Ti: C
Al3TiC series	3	0.2	15
	3	0.15	20
Al5TiC series	5	0.2	25
Al6TiC series	6	0.02	300

2.5.4 Grain refining performance

The requirements of an inoculant for it to act as an effective nucleating agent are the following [9]:

- It should have a melting point higher than the alloy being treated
- It should be able to initiate freezing at minimal undercooling
- It should contain a sufficient number of nucleating particles
- The nucleating particles should be larger than a critical size, which depends on the undercooling of the melt.

In the treatment of aluminium with grain refiners the alloy is normally cast a certain time after the addition of the grain refiner. The grain size obtained is a function of the type of grain refiner and holding time. The grain size decreases to a minimum as holding time increases and increases when the holding time exceeds a certain limit. The minimum grain size is referred to as ultimate grain size for that system. The time required to reach ultimate grain size is referred to as optimum contact time [9]. Figure 2.5 illustrates the optimum contact time and fading characteristics for three different alloys. From these definitions, a grain refiner is termed “fast-acting” if the optimum contact time is very short, or “slow-acting” if it is not. It is termed “long-lasting” when the grain refining effectiveness is kept for a long period of time. In this case, the potency of the grain refiner is not lost even after a very long holding time. An ideal grain refiner is that which is fast acting with a long lasting effect on the melt following the addition of the master alloy. A master alloy is said to be effective in grain refining if the resulting grain size is below the acceptance level of 220

μm in a TP-1 test[9]. The effectiveness of a grain refiner is therefore quantified by the grain size achieved at a given refiner addition level. The refining efficiency can be defined as the fraction of particles which become active during solidification of the alloy. In this regards the number of grains corresponds to the number of nucleant particles which become active. Only 1% of the particles present in a commercial grain refiner are said to be active[15]. Hence, when comparing the grain refining efficiency of any two grain refiners, that which gives a lower grain size in aluminium alloys for the same addition level has the higher grain refining efficiency and effectiveness. Figure 2.6 shows the grain refining efficiency of three different grain refiners used in 99.7% Al at an addition temperature of 720°C. Al-5%Ti-1%B shows the highest efficiency.

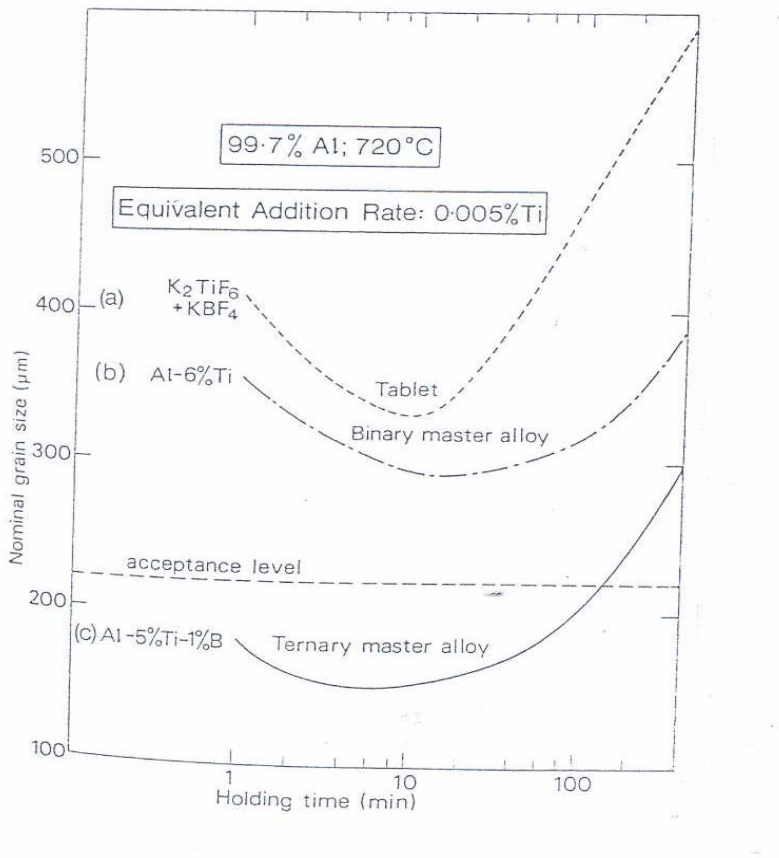


Figure 2.5: Optimum contact time and fade characteristics according to titanium-to-boron ratio

2.5.5 Important factors in the use of grain refiners in aluminium alloys

2.5.5.1 Microstructure of grain refiners

During the inoculation of aluminium and aluminium alloys with grain refiners, the microstructure of the grain refiners influences its grain refining performance. It has been shown

that Al-Ti-B master alloys containing mostly blocky aluminides are associated with good grain refinement after a short optimum contact time, but the grain refining ability fades rather quickly when contact time increases. Master alloys with flake-like or petal-like crystals need a longer contact time to develop maximum grain refinement[3].

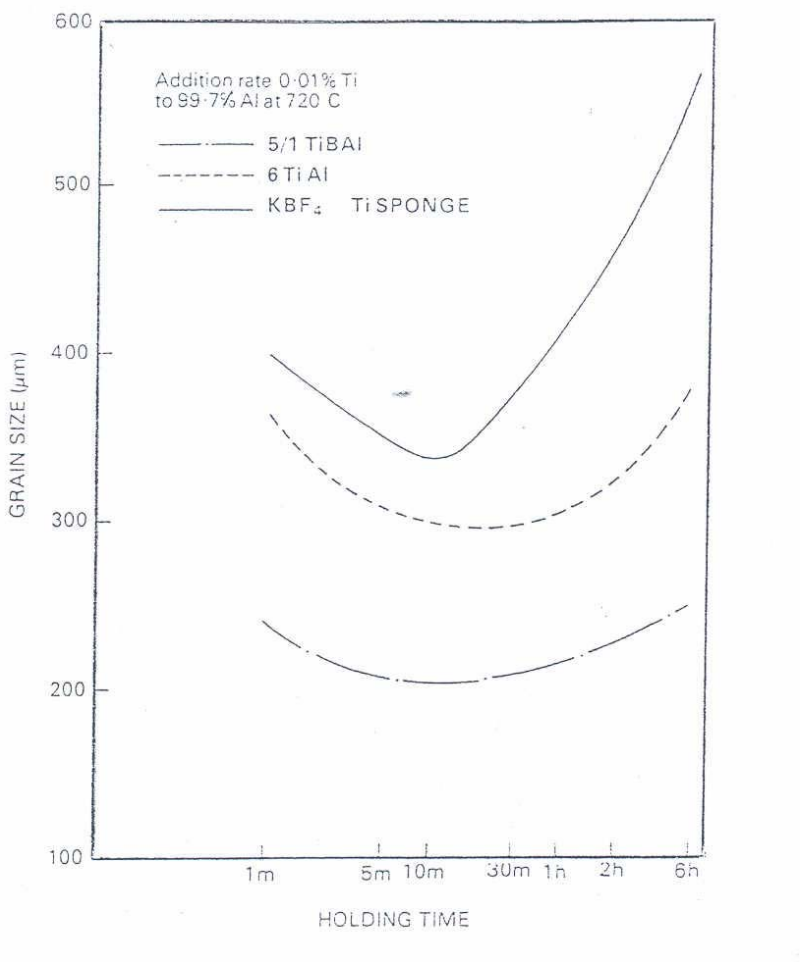


Figure 2.6: Grain refining efficiency of different inoculants at equivalent addition rate.

The efficiency of Al-Ti-C master alloys is greatly influenced by the simultaneous presence of TiC and $TiAl_3$ in the aluminium matrix. Al-Ti-C master alloys with the two phases in the microstructure have been found to be more efficient than those having only TiC particles dispersed throughout the α-aluminium matrix [6]. The refining efficiency results from the combined action of Ti and TiC in the aluminium melts. The $TiAl_3$ particles give excess Ti upon dissolution in the aluminium melt. In refined aluminium, TiC particles are located at the grain centre and nearly all the excess Ti added to the melt through the grain refiner is segregated at the surface of TiC particles forming rose-like Ti-rich structures around the TiC particles. The way TiC particles appear in the aluminium matrix also plays a part in influencing the refining performance. TiC

particles distributed in the matrix give good refining results whereas agglomerated TiC reduce refining performance.

2.5.5.2 Addition temperature and holding time of the melt

It is important to establish the optimum addition temperature in order to achieve good grain refining performance. Experience has shown that good grain refining efficiency is achieved when inoculation is carried out in the temperature range of 700 to 750°C and the grain refining effect continues even after 240 minutes of holding time. If the same master alloy is added at a higher temperature (above 800°C), the grain refining efficiency is lost after just 10 minutes[27]. The longer the grain refining effectiveness of the master alloy lasts, the longer may be the holding time after the master alloy addition. This is very important in foundry practice because operations before the casting of the metal are time-consuming. London & Scandinavian Metallurgical (LSM) recommends an addition temperature of 720°C for Al-Ti-B regardless of the Ti/B ratio. In experiments on the refining of aluminium by Al-5%Ti-0.5%B, Sivaramakrishnan *et al*[38] obtained good refining results at an addition temperature of 700°C with no holding time, the inoculating addition being made during the pouring of the melt. They also obtained grain refinement at the addition level of 0.2 to 0.5 % when pouring in the temperature range of 680 to 700°C into a mould at room temperature. This indicated that additions at higher temperature required more inoculant to achieve grain refinement.

In a systematic and comparative study of the behaviour of Al-Ti-B and Al-Ti-C grain refiners, Schneider *et al*[39] have shown that the level of refinement achieved depends on the addition temperature and the grain refiner addition rate. Total grain refinement was observed in the addition temperature range of 670-675°C for Al-3%Ti-1%B. At this addition temperature, Al-3%Ti-1%B gave results as good as Al-Ti-C. At higher melt temperatures, Al-Ti-C was less efficient than Al-Ti-B. TiC particles, responsible for nucleation when using carbon-based grain refiners, appear to be susceptible to reaction with aluminium at high temperature. High ratios of titanium-to-boron or titanium-to-carbon gave less refinement for lower addition temperatures. In the same study, the grain refining performance of a master alloy was found to increase with increasing addition rate for the same addition temperature.

2.5.5.3 Alloying elements in the melt

Certain alloying elements in aluminium alloys are deleterious to the grain refining efficiency of Al-Ti-B master alloys. However, in unrefined castings, impurities decrease the

undercooling required to nucleate grains and decrease the grain size[40]. They promote grain refinement in the absence of Al-Ti-B grain refiners. This is the case with zirconium[41]. However, Delamore and Smith[26] found that Al-Zr and Al-Cr master alloys did not produce any enhancement of grain refinement in the absence of boron compared to Al-Ti master alloys. Some alloying elements have a beneficial effect on the grain refining efficiency of Al-Ti-B master alloys, when dissolved in the melt. Fe, Mg, Cu and low levels of Si are in this category. Si improves the grain refining behaviour of aluminium when added in quantity as small as 0.2%[40]. However recent studies have shown that Fe has also a poisoning effect on grain refinement[41]. Progressive reductions in ultimate grain size and optimum contact time are observed with increasing content of these alloying elements[42]. These solute elements, like Ti, segregate to the nucleant/melt interface and affect the growth of dendrites by increasing constitutional undercooling at the solid-liquid interface[20].

When a number of solute elements are in the melt, their effects are additive (assuming no interaction between them)[11,43] Experimental data show that there is an initial decrease in grain size with the number of solute elements in the melt until a certain value of the growth-restricting factor is reached. Further additions of solute produce no effect and the grain size begins to increase [20]. Figures 2.7 shows the effect of normal alloying elements on the grain refining efficiency of a master alloy when Al-5%Ti-1%B master is added at 0.005%Ti.

2.5.5.4 Poisoning and fading effects

Zirconium, chromium, lithium and vanadium are among elements known to have poisoning effects on the nucleant particles in the Al-Ti-B master alloys[42]. Silicon also has a poisoning effect on grain refining performance, but to a lesser extent. In practice the detrimental influence of these poisoning elements can be overcome by adding the grain refiners into the melt at the last possible moment before casting provided the grain refiner has a short optimum contact time. This reduces the time for the poisoning elements to interact with the nucleants.

In the refinement of Al-Si alloys[40], a poisoning effect is observed in alloys containing 7% Si or more and the extent of poisoning increases with an increase in the silicon content. The reason for the reduction in the nucleation efficiency is probably that a complex intermetallic phase AlSiX (where X=Fe, Cr, Mn, and /or Zn) nucleates and grows on potent TiB_2 particles, effectively decreasing their nucleation potency. The TiB_2 particles may nucleate the unidentified intermetallic phase, which then coats the surface of the TiB_2 particles effectively, deactivating or “poisoning” them, thus causing an increase in grain size. Mg can counteract the poisoning effect of Si. The

optimum level of Mg required to overcome the poisoning effect depends on the silicon content of the alloy. Higher level additions of a grain refiner can overcome the poisoning effect of silicon and the level required to achieve good grain refinement is a function of the silicon and magnesium contents of the alloy.

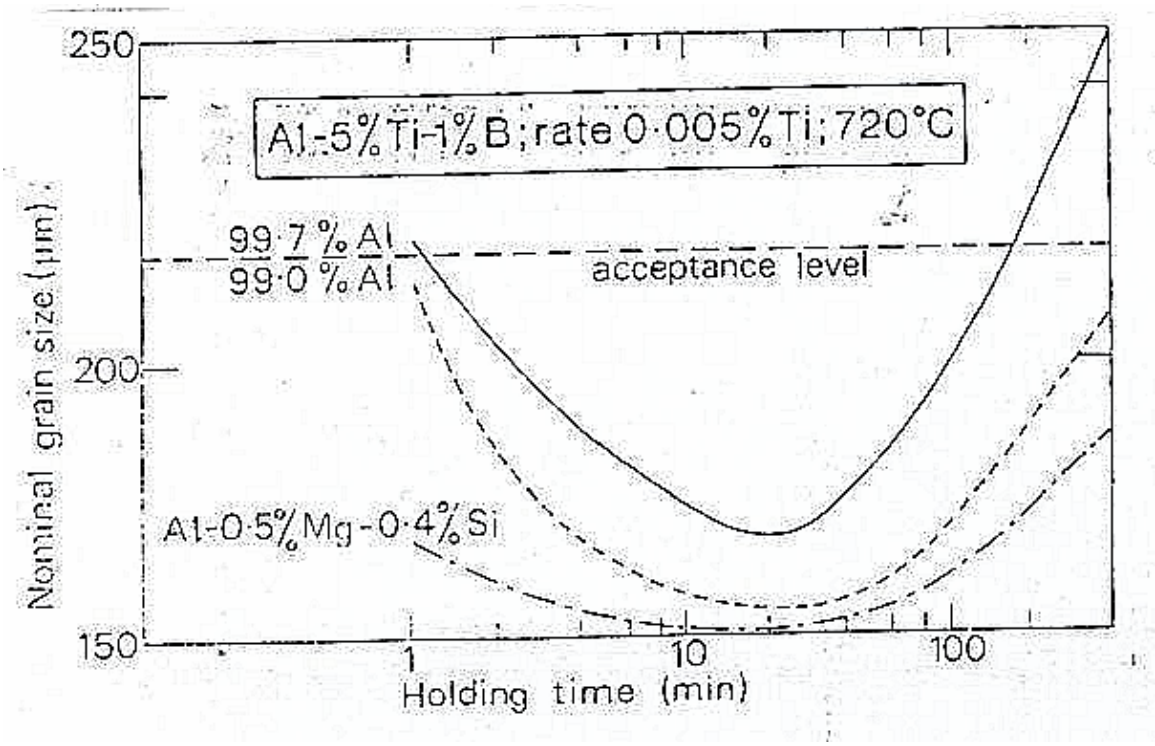


Figure 2.7: Effect of alloying elements on the grain-refining efficiency of a master alloy [32]

When the casting procedure necessitates the addition of grain refiner to the holding furnace, a decline in grain refining efficiency can be expected with prolonged holding time. In most cases, if the melt is held for a long time after the addition of the grain refiner, the casting will develop a coarse grain structure instead of the otherwise fine grain structure observed if the melt is poured within a short period after the addition. In some cases, the extent of fading can be very large, resulting in completely columnar structures. This means that the number of potent nucleating sites decreases with holding time. The phenomenon is usually attributed to either dissolution or settling/floating (or both) of nucleating particles during prolonged holding[9]. Agglomeration and settlement of TiB_2 is one of the causes of fading. It is observed that as the amount of Al-Ti-B grain refiner added to the melt and the holding time increase, a distinct layer tends to form at the bottom of cast ingots. The boron content tends to decrease rapidly in the early stages of holding as a result of TiB_2 settlement. On holding of the melt, TiB_2 particles which are dispersed singly or as agglomerates in the molten metal grow into larger agglomerates and settle out. When the size

distribution of TiB_2 is not affected by the length of holding time, the grain refining effects are good.

$TiAl_3$ has been reported not to be stable in the melt and to dissolve after a certain melt holding time. This time has been the subject of controversial reports. While some researchers suggest that it takes a very short time for the $TiAl_3$ particles to dissolve others report that it will take several hours for the particles to dissolve. According to Murty *et al*[9], the difference in dissolution times reported by several investigators could be attributed to the difference in $TiAl_3$ particle size and the presence of alloying elements/impurities which are expected to have a strong influence on the dissolution kinetics.

The fading of refining efficiency of Al-Ti-C grain refiner is due to the conversion of TiC to Al_4C_3 on prolonged holding in the melt[35]. This conversion is observed in the preparation of the grain refiner itself[25]. The rate of conversion is highly temperature dependent. At temperatures normally used in industrial processing of aluminium alloys (<750°C), the transformation is so sluggish that it poses no threat to the effective grain refinement by the TiC particles[11].

In a recent study, Hardman and Young[44] have performed grain refinement on a series of grain refiners with different compositions. In these experiments, Al-Ti-C was found to achieve better refinement than conventional Al-Ti-B in the early stage of holding (0-5minutes) but quickly lost efficiency on prolonged holding, becoming less effective than Al-Ti-B. However, Hadia *et al*[34] have found Al-Ti-C master alloys to be effective at short and prolonged holding time. They have also found these master alloys to be effective in grain refining at a range of temperature covering the pouring temperatures of almost all aluminium alloys.

The mechanism of fading in Al-Ti-C master alloys is still a controversial issue. While Banerji and Reif[4] explain the loss of refining efficiency by the reaction of TiC with the aluminium melt forming a sheath of Al_4C_3 on TiC particles, Tronche *et al* [35] in a recent study concluded that the conversion of TiC to Al_4C_3 takes place first by the dissolution of TiC particles in the melt and development of separate unrelated Al_4C_3. Conversion of TiC to Al_4C_3 is not possible due to the very different crystallography of the two carbides.

2.5.6 Influence of mechanical and thermal treatments on the microstructure of grain refiners

The general types of heat treatments applied to aluminium and its alloys are:

- Preheating or homogenizing, to reduce chemical segregation of cast structures and to improve their workability.

- Annealing, to soften strain-hardened and heat treated alloy structures, to relieve stresses and stabilize properties and dimensions.

- Solution heat treatments, to effect solid solution of alloying constituents and improve mechanical properties.

- Precipitation heat treatments, to harden alloys by precipitation of constituents from solid solution.

Since the grain refining performance of master alloys is dependent on their microstructure, anyone of these treatments could have an influence on the grain refining performance. Mechanical and thermal treatments which have an influence on the phases and particles present in the master alloy can be expected to affect the performance of master alloys. In a recent study, Venkateswarlu *et al*[16] showed that a substantial change in the microstructure of an Al-5%Ti master alloy occurs after rolling it at 300°C. While poor grain refining performance was observed in the as cast Al-5%Ti master alloy, rolling at 300°C to 20% reduction produced a grain refiner which completely converted the coarse columnar structure to a fine equiaxed structure upon holding for 2 minutes at that temperature. The fine equiaxed structure was retained for up to 120 minutes of holding. In the rolled master alloys with improved grain refining performance, the morphology of $TiAl_3$ was blocky and fine. This was attributed to the fracture of plate-like aluminide particles in the as cast master alloys during rolling.

The microstructure of Al-5%Ti was the same after heat treatment at 300, 400, 500 and 600°C for 4 hours. Precipitation of $TiAl_3$ from supersaturated aluminium occurred. Thus an increase in grain refining performance was observed when the heat-treated master alloy was used. The grain structure became completely fine and equiaxed after 60 minutes of holding, beyond which no significant change was observed. In addition the grain structure appeared to be finer for aluminium grain refined with master alloys heat-treated at higher temperature.

2.6 Theoretical Models of Heterogeneous Nucleation

Recent studies[12,13] have proposed theoretical models for predicting the rate of heterogeneous nucleation. These models assume that a comprehensive characterisation of nucleation substrates can be obtained using a unimodal size distribution function. The substrate size distribution can be considered as a quantitative feature of the undercooled melt, which accounts for the nucleation stage during solidification. A model applied to aluminium casting was developed for prediction of as-cast grain size in inoculated melts. In this model[12] , the appearance of the grains is controlled by the free growth model rather than by nucleation and by taking a

distribution of inoculant particle diameters. The number of grains is then limited by recalescence of the melt. In idealised grain refiners the TiB_2 particles are considered as disks of different diameter size with a normal distribution. The average diameter of the TiB_2 particles and the width of the distribution are of great importance. The general trend is an increase of grain size of inoculated aluminium with increasing width of the distribution[45]. A narrow distribution results in improved grain refining performance. Without adjustable parameters, the model fits quantitatively the measured grain size in the TP-1 standard tests on commercial purity and other alloys inoculated with Al-5Ti-1B grain refiners. The effectiveness of a refiner may be optimized at a particular size of TiB_2 particles, 2μm for the commercial Al-5Ti-1B grain refiner.

2.7 Corrosion Mechanisms of Aluminium Alloys and Particle Extraction

In order to extract particles of $TiAl_3$ and TiB_2 from the master alloys, an understanding of the corrosion behaviour of aluminium is necessary. From a purely electrochemical point of view[46,47], aluminium is corrosion resistant due to its oxide layer, but if exposed to aggressive environments, it may corrode. In oxygen containing environments (air, water), aluminium is rapidly covered with a dense oxide layer. The thickness of the layer may vary as a function of temperature, environment and alloying elements.

Acid (pH<4) or alkaline (pH>9) environments as well as aggressive ions (chlorides, fluorides) may attack aluminium oxide and thereby cause corrosion. Intermetallic phases in the aluminium alloys act as local cathodes while the surrounding aluminium matrix undergoes localized attack. So, corrosion of aluminium alloys is a microgalvanic process occurring between different phases in the alloy. The following factors are also important in influencing the aluminium alloy corrosion trend:

-An intermetallic phase may corrode preferentially.

-A corroding phase may serve as a sacrificial anode and provide cathodic protection to the surrounding material.

-Due to the electrochemical reactions at the corroding sites and the cathodes, the composition and the pH of the electrolyte adjacent to the reaction sites may become different from the bulk electrolyte.

-Active components of the matrix and the intermetallic phases may corrode selectively (dealloying), resulting in changed corrosion properties.

Pitting is a highly localized type of corrosion in the presence of aggressive chloride ions. Pits are initiated at weak sites in the oxide by chloride attack. Pits propagate according to the

ractions:

$Al = Al^{3+} + 3e$ (1)

$Al^{3+} + 3H_2O = Al(HO)_3 + 3H^+$ (2)

While hydrogen evolution and oxygen reduction are the important processes at the intermetallic cathodes:

$2H^+ + 2e = H_2$ (3)

$O_2 + 2H_2O + 4e = 4OH^-$ (4)

As the pit propagates, the environment inside the pit (anodes) changes. According to reaction (2) the pH will decrease. To balance the positive charges produced by reactions (1) and (2), chloride ions will migrate into the pit. The resulting HCl formation inside the pit causes acceleration of pit propagation. The reduction reaction (4) will cause local alkanisation around cathodic particles. Aluminium oxide is not stable in such environment and aluminium around the intermetallic particles will dissolve creating alkaline pits. The aluminium component of the particle will also dissolve selectively.

Microgalvanic cell action at the grain boundaries causes intergranular corrosion. Grain boundaries are sites for precipitation and segregation, which make them physically and chemically different from the matrix. Precipitation of noble intermetallic particles at the grain boundaries depletes the adjacent zone of these elements and the depleted zone becomes electrochemically active. The opposite case is also possible: precipitation of active particles at the grain boundaries would make the adjacent zone noble. Advantage can be taken from these observations to cause the sedimentation of noble intermetallic particles in an electrolytic cell whose soluble anode will be an aluminium based alloy. Marcantonio and Mondolfo[30] isolated $TiAl_3$ and TiB_2 particles by dissolving the aluminium matrix of an Al-Ti-B master alloy in hydrochloric acid.

2.8 Foundry Practice

2.8.1 General considerations

In foundries, furnaces are huge and melt enormous quantities of metal. Alloy melts are treated by adding grain refiner waffles to the furnace 30 minutes before casting to allow ample time for dissolution. Thus problems associated with holding time are encountered including:

- Inadequate mixing in the charge
- Settling and agglomeration of the heavy TiB_2 particles
- Poisoning effects

- Eventual interaction between solute elements

The master alloy in rod form is injected at the launder in the molten metal. In this technique a 9.5 mm diameter rod of Al-Ti-B master alloy is fed to the molten metal stream between the casting furnace and the casting machine. To achieve good results the rod is added against the direction of metal flow as near the furnace tap as possible. In this position, the velocity is greatest and the metal temperature highest. This is essential to melt the rod quickly, allowing dispersion of the titanium borides evenly throughout the metal stream. The rod addition eliminates furnace contamination due to the settlement of titanium boride particles and allows more precise control of alloying addition. Launder addition of a grain refiner rod clearly requires that the master alloy should have a short contact time. The time between the addition and the solidification is usually less than 5 minutes and can often be as short as 1-2 minutes.

2.8.2 Grain refiner addition

The type and amount of grain refiner required for a given operation depends on the composition, solidification rate and the proportion of recycled material in the melt[19]. Excessive additions of grain refiners frequently result in gravity segregation of intermetallic compounds, especially in more complex alloys, which can give hard spots in the castings and hence reduced machinability. Kawecki Billiton recommend the addition levels indicated in Table 2.4 for Al-Ti-B master alloys in foundry practice [19]. London & Scandinavian Metallurgical Co Limited (LSM) recommends addition levels of Al-Ti-B in the range of 0.25-3 kg/ton.

Table 2.4: Addition levels for specific aluminium alloys

Aluminium Association Alloy	Titanium content (%)	Al-Ti-B addition (kg/ton)
319	0.015-0.025	3-5
356	0.010-0.020	2-4
413	0.005	1
360	0.005-0.010	1-2
514	0.015-0.025	3-5
295	0.015-0.025	3-5

2.8.3 Recycled materials

Controlling the titanium level in the melts containing a significant amount of recycled scrap can sometimes pose a problem in production. A possible solution to this problem, as often promoted by a number of master alloy producers, is the use of a grain refiner with a very small concentration of titanium in excess of the stoichiometric level. Master alloys of stoichiometric composition have been reported to be ineffective in grain refining or at best to produce poor results [3] . When properly done, the residual titanium in scrap should compensate for the reduced concentration of titanium in the master alloy. Hardman and Young found that the use of recycled scrap containing TiC particles actually enhances the grain refining performance of Al-Ti-C master alloy[44].

In the cast house practice, criteria of assessment of grain refiner go beyond the fundamental definitions and take into account the consistency, versatility and cost-effectiveness of the grain refiner as well as the cleanliness of the inoculated alloy. Tests by various methods will assure process control and product performance. In the same series of commercial grain refiners, the technology used in casting will also determine the exact type of refiner to use. Therefore the product form is also important. For continuous injection into the metal stream, coiled rod will be used while for furnace and launder additions waffle plate, cast cut bar or cut rods will be used.