5 DISCUSSION

5.1 Phase Identification

In commercial Al-Ti-B grain refiners, the nucleants are known to be TiB$_2$\textsuperscript{3,5}. In newly developed Al-Ti-C grain refiners, the nucleants are TiC particles. The titanium-to-boron ratio in Al-Ti-B master alloys and the titanium-to-carbon ratio in Al-Ti-C master alloys vary and the performance of the grain refiners depends on these ratios\textsuperscript{9,37}.

The samples analyzed showed the following phases:
- An aluminium matrix
- TiAl$_3$ particles dispersed in the aluminium matrix
- TiB$_2$ particles dispersed in the aluminium matrix
- Agglomerates of TiC particles in the aluminium matrix
- Silicon particles mostly at the grain boundaries

5.2 Origin of TiAl$_3$ and TiB$_2$ Particles

The origin of TiAl$_3$ and TiB$_2$ is found in the following reaction occurring during the aluminothermic reduction of TiO$_2$ and B$_2$O$_3$ in the aluminium melt to produce the Al-42%Ti-11%B\textsuperscript{48,4950}:

\begin{align*}
4\text{Al} \hspace{0.5em} &\rightarrow 3\text{Ti} + 2\text{Al}_2\text{O}_3 \\
2\text{Al} \hspace{0.5em} &\rightarrow \text{B}_2\text{O}_3 + 2\text{B} + \text{Al}_2\text{O}_3 \\
3\text{Al} \hspace{0.5em} &\rightarrow \text{TiAl}_3 \\
\text{Ti} \hspace{0.5em} &\rightarrow \text{TiB}_2
\end{align*}

Where (l), (s) and (d) denote liquid, solid and dissolved in the melt respectively. Boron affinity for Ti is higher than that for Al and so AlB$_2$ could not be formed.

5.3 Origin of Titanium Carbide and Silicon

During the aluminothermic reduction the processing temperature in the button arc furnace favoured the formation of TiC and not Al$_4$C$_3$ in the presence of carbon, according to the Ellingham diagram for carbides. The reaction is:

\[ \text{Ti} + \text{C} \rightarrow \text{TiC} \]

As shown in the microstructure of Ind2B and Arc2B, TiC particles were enormous indicating agglomeration of individual TiC. The agglomeration of TiC particles was a consequence of low processing temperature and long holding time of the melt in the dilution process of the Al-42%Ti-11%B alloy. In the first step, which was the preparation of the Al-42%Ti-11%B alloy, the
processing temperature was above 1773ºK, which favoured the formation of isolated TiC particles. Since the operating temperature in the dilution process was 1273ºK in induction furnace, less than that in the resistance furnace, TiC particles was expected to agglomerate and eventually Al₄C₃ to form on TiC particle surface on holding of the melt. In the case of the arc furnace where the processing temperature was above 1773ºK, only agglomeration of TiC particles was expected to take place on holding of the melt.

Since the carbon was not part of the feed materials, its origin was exogenous. It probably came from the graphite electrodes during the aluminothermic reaction in the arc furnace. The formation of TiC was likely to take place during this stage of preparation rather than during the dilution process.

As for carbon, silicon was not part of the feed materials in the preparation of grain refiners and was therefore of exogenous origin. It came from the Al-42%Ti-11%B whose silicon content was high. This contamination took place during the aluminothermic reduction of TiO₂ and B₂O₃.

5.4 Morphology and Size of TiAl₃ Particles

The morphology of TiAl₃ particles was needle-like as could be expected because the processing temperature in the dilution stage was very high in all cases. During the preparation of Al-Ti-B grain refiners, the TiAl₃ morphology is strongly temperature dependent. When the alloy is cooled from relatively low temperature (680-750°C) the TiAl₃ particles are blocky in shape. When cooled from higher temperature (above 750°C) the flake-like or needle-like morphology is found²⁹. All the experimental grain refiners were cooled from temperature of 850°C and 950°C for the electric resistance furnace, 1000°C in the induction furnace and 1500°C in the arc button furnace. The thickness and the length of titanium aluminide particles increased with titanium content.

5.5 Morphology, Size and Size Distribution of TiB₂ Particles

The TiB₂ particles had prismatic morphologies. Some showed a cuboidal shape, other appeared as hexagonal platelets. The melting point of TiB₂ is about 3225°C. This means that the TiB₂ particles form in the liquid prior to the start of solidification. Once they are formed, their morphology and size do not depend on the temperatures of subsequent steps in the preparation, provided that these temperatures are below the melting points of TiB₂.⁵ Since the TiB₂ particles were formed during the first stage of preparation, that is, during the aluminothermic reduction of TiO₂ and B₂O₃, the dilution process should not affect the formed TiB₂ in size or in morphology but
only change the weight ratio between the aluminium and the TiB2 particles present in the master alloy.

As indicated earlier, during the aluminothermic reduction in the arc furnace, the first intermetallic to form will appear at a very high temperature corresponding to the processing temperature in the furnace. These first boride particles will have enough time to grow to a relatively large size. As cooling of the melt continues more and more TiB2 forms from it with progressively shorter time for growth until all the melt solidifies. As a consequence, TiB2 particles appear in the solidified grain refiner with a wide range of sizes and different morphologies corresponding to their level of growth after solidification is complete.

In commercial grain refiners (Al-5%Ti-1%B), the mean size of TiB2 particles is about 1µm with size range of 0.2 - 6.0µm, meaning the presence of very few particles bigger than 3µm. The size range of 0.05 - 3.00µm was also reported. In experimental grain refiners, the size ranges varied from 0.10 - 6.72µm to 0.10 - 14.60µm and the means of size distributions of TiB2 particles were all above 1µm. This indicated the presence of coarse particles. Skew values obtained in Table 4.4 were all different from 0, indicating asymmetrical distributions. Values of standard deviation were all different from 0 and relatively high indicating distribution spread apart from the means. Finally, in each case, the mean size of TiB2 particles was higher than the median, indicating positively skewed distribution.

Analysis of these statistic parameters showed that the size distribution of TiB2 particles in the experimental grain refiners was not normal as in ideal grain refiners or narrow as in commercial grain refiners. Instead, it was skewed and spread towards the high values of particle sizes.

**5.6 Influence of Mechanical and Thermal Treatments on Microstructure**

Substantial changes in the microstructure were observed after mechanical treatment. After rolling at 80% reduction, the zebra-striped and flaky TiAl3 particles observed were replaced by broken particles of TiAl3 aligned in the rolling direction and showing rough edges. The morphology and size of TiB2 particles were not affected by the rolling process.

The changes in microstructure of the worked materials were due to plastic deformation and stresses introduced as a result of plastic deformation. The plastic deformation of the soft aluminium matrix produced shear and tensile stresses in the TiAl3 particles causing them to fragment. This resulted in an increase of hardness as a consequence of many defects and deformations in the aluminium matrix. Under the same conditions the TiB2 particles remained unaffected due to their low aspect ratio and their extreme hardness and strength. The reason for the
different responses of TiB$_2$ and TiAl$_3$ particles to rolling is the difference in their morphology and hardness. The TiAl$_3$ particles mostly elongated, readily broke during the rolling process whereas the TiAl$_3$ particles, cuboidal and hexagonal in shape, were unaffected by the rolling process. Also, TiB$_2$ has a very high hardness (HV=3000) compared to TiAl$_3$ (HV=400). Alignment of TiAl$_3$ and TiB$_2$ particles was a natural consequence of the plastic deformation of the aluminium matrix.

TiAl$_3$ particles were also influenced by heat treatment but TiB$_2$ particles were not. After heat treatment the rough edges of TiAl$_3$ particles were smoothed and rounded probably due to dissolution and re-precipitation. TiB$_2$ particles remained unchanged in size and morphology due to their high stability. TiB$_2$ has a very high melting point (3225ºC). At the temperature of heat treatment (625ºC), TiB$_2$ particles were very stable and did not undergo any change. The only effect of heat treatment on those particles was the reduction of interfacial energy generated by the plastic deformation in the aluminium matrix.

In this work, the grain refiners were soft. Hardness values obtained were all below 50. Observation of Tables 4.1 and 4.8 shows that alloys of low titanium content gave low hardness values and alloys of high titanium content gave high hardness values. High titanium and boron contents can be expected to result in harder alloys due to the formation of higher quantities of the harder intermetallic phases. The size and size distribution of these particles will affect the hardness as well, with fine, evenly distributed particles resulting in harder materials. This situation explains why alloy Ind2A with low titanium content was harder. Alloys Ind1A and Ind2B with titanium content close to Ind2A gave low values of hardness due to the presence of high amount of coarse TiB$_2$ particles as can be seen in Figure 4.15. A uniform distribution of fine TiB$_2$ particles can be expected to give material of higher hardness while coarse TiB$_2$ particles will result in lower hardness for the same volume fraction especially if they are unevenly distributed. For this reason, alloys Elec1A and Elec1B gave low values of hardness.

The values of hardness in experimental grain refiners were close to values obtained with commercial grain refiners with finer TiB$_2$ particles. The presence of TiC and Silicon particles may have made a contribution to the hardness of the experimental grain refiners.

### 5.7 Grain Size of Inoculated Aluminium Castings

In almost all cases the grain size achieved with the experimental grain refiners was above the acceptance level of 220 µm$^9$. From the thermodynamic point of view, during the nucleation stage of aluminium, there is a close relationship between undercooling and nucleation rate. The nuclei in the experimental grain refiners appears to have nucleated at different degree of
undercooling giving rise to long time between nucleation events and therefore promoting growth at the expense of nucleation. The growing crystals would become large and absorb other nucleating site, which might have produced nucleation. This fact was observed in the experimental grain refiners themselves where the microstructure showed large clusters of coarse TiB$_2$ particles completely engulfed in grains, indicating the poor ability TiB$_2$ particles to nucleate aluminium in the grain refiners themselves.

Although the average size of TiB$_2$ particles varied between 1.5 and 3 $\mu$m in experimental grain refiners, the grain size achieved by inoculation with them was bigger than that achieved in commercial and ideal grain refiners for the same average size of TiB$_2$ particles at TP-1 test’s cooling rate of 3.5K$^{-s}$ $^{15}$. The morphology of TiAl$_3$ particles, the morphology, size and size distributions of TiB$_2$ particles appear to be responsible for this difference. In idealised grain refiners, TiB$_2$ particles are considered to be disks whose thickness is proportional to their diameters and size distribution of TiB$_2$ particles is assumed to be perfectly normal. In commercial grain refiners, TiB$_2$ particles are hexagonal platelets with a narrow distribution and TiAl$_3$ are blocky. In this work, TiAl$_3$ particles had flaky or needle-like morphology, which is not the targeted morphology for good refining results. In addition, the experimental grain refiners had spread size distributions of TiB$_2$ particles with relative great amounts of coarse particles.

In samples with more than 20% of TiB$_2$ particles with size beyond 3$\mu$m, poor refining performance was observed. This was due to the phenomenon of agglomeration and settling of finer TiB$_2$ particles in the melt on holding. In their study on agglomeration and settlement of TiB$_2$ particles in molten aluminium, Tanaka et al $^{53}$ have shown that the bulk of nucleation in the material was achieved through TiB$_2$ particles bigger than 1 $\mu$m in size. Smaller TiB$_2$ particles either came in clusters to build up large agglomerates and settle to the bottom of the melt or were rejected in the last zone to solidify. In grain refiners where particles less than 1 $\mu$m represent a small proportion of the population, recalescence-limited efficiency is high and decreases for a large population of small particles. This was the case of alloy Ind2A where TiB$_2$ particles smaller than 1$\mu$m represented more than 55% of the population. This alloy achieved the best grain refinement (236$\mu$m). The other alloys with finer TiB$_2$ particles representing less than 50% of the population gave poor results (352, 332 and 345 $\mu$m for alloys Elec1A, Elec1B and Ind1B respectively). However, alloys Ind2B which showed the same size distribution of TiB$_2$ particles as alloys Elec1A, Elec1B and Ind1B gave a smaller ultimate grain size (275$\mu$m). The main reason of the small improvement appears to be the high titanium-to-boron ratio combined with low titanium and boron contents in Ind2B (Table 4.). The presence of TiC particles next to TiB$_2$ particles may
have also made a contribution by acting simultaneously as nuclei in the aluminium melt and increasing the number of possible nucleation sites. TiC particles present in Ind2B could not improve the performance to a level below 220µm because of their size and morphology in the aluminium matrix of the grain refiner. In commercial Al-Ti-C grain refiners where the nucleating potency is high, TiC particles appear as very small particles, submicron in size and dispersed in the matrix.\textsuperscript{6,54} Agglomerates of TiC particles give poor refining performance. In Ind2B and Arc2B, TiC particles were agglomerated in huge particles as big as 20µm, in some cases. Further more, Arc2B which also showed the presence of TiC particles did not give the same performance as Ind2B in term of ultimate grain size (301µm). TiC particles could not lead to highly improved grain refining performance due to agglomeration.

Silicon was not responsible for the poor refining performance of the experimental grain refiners. Although silicon particles were present in the aluminium matrix of the grain refiners, the overall content of silicon in the melt was far below the upper limit of 0.2% beyond which poisoning by silicon starts.\textsuperscript{55} Within this limit, silicon is not deleterious to the performance of grain refiners. At an addition level of 0.01%Ti in the melt, the corresponding level of silicon introduced in the melt was even smaller and did not represent any threat to the refining performance of the experimental grain refiners (Table 4.11).

The analysis of size distribution of TiB\textsubscript{2} particles and the grain size achieved shows that there was a relation between the microstructure of the grain refiners and the grain size achieved in the inoculated aluminium. The tendency to achieve grain refinement increases with increase of population of fine particles.

5.8 Influence of Mechanical and Thermal Treatments on the Performance of the Grain Refiners

Cold rolling improved the nucleation potency of TiB\textsubscript{2} particles by redistributing TiAl\textsubscript{3} particles and probably introducing defects which would be a favourable state in the nucleation stage. When the experimental grain refiners were used cold rolled, grain refiners showed better performance than as-cast one. The improvement in performance was lost after heat treatment of the materials. This observation showed that cold rolling would improve the grain refining performance of the experimental grain refiners.

During the inoculation of the aluminium with the experimental grain refiners, the titanium aluminide particles dissolved at the operating temperatures. As a result, the only added nucleation sites in the melts for heterogeneous nucleation were the TiB\textsubscript{2} particles and possibly the TiC
particles. At this stage, the role of the titanium in the melt appeared to be the formation of a titanium aluminide layer on the TiB₂ particles. TiAl₃ lattice is known to be coherent with that of aluminium and therefore facilitates the nucleation of aluminium²³. Another role played by the dissolved titanium is to promote the constitutional undercooling ahead of the advancing solid/liquid interface during solidification. But at the concentration of 0.01 % in the present work, this role was of minor influence on the grain size of the solidified aluminium. The key factor remains the size and size distribution of the titanium diboride particles. Since there was no change in this factor before and after mechanical and thermal treatments of grain refiners, no significant change could be expected in the grain refining performance of the grain refiners. This was the case in the present work.