3 EXPERIMENTAL PROCEDURES

3.1 Preparation of Grain Refiners

Seven grain refiners were prepared using commercial purity aluminium, boron oxide (B₂O₃) and aluminium-titanium alloy (Al-43%Ti) obtained by aluminothermic reduction of titanium oxide (TiO₂), commercial purity aluminium and aluminium-titanium-boron alloys (Al-42%Ti-11%B) obtained by aluminothermic reduction of boron oxide (B₂O₃) and titanium oxide (TiO₂). The compositions of these materials are given in Table 3.1. In this work, grain refiner is also referred to as master alloy.

_**Table 3.1:** Composition of materials used for the preparation of grain refiners_

<table>
<thead>
<tr>
<th>Feed materials</th>
<th>Element, mass %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ti</td>
</tr>
<tr>
<td>Al (CP)</td>
<td>0.01</td>
</tr>
<tr>
<td>Al-42%Ti-11%B</td>
<td>41.9</td>
</tr>
<tr>
<td>Al-43%Ti</td>
<td>42.7</td>
</tr>
<tr>
<td>B₂O₃</td>
<td>-</td>
</tr>
</tbody>
</table>

CP: Commercial Purity

The grain refiners were prepared in different furnaces and were identified according to the furnace used: Elec, Ind and Arc for grain refiners prepared in an electric resistance furnace, an induction furnace and a button arc furnace respectively. The materials and procedures used for the preparation of the aluminium-based grain refiners are outlined in Table 3.2.

Alloy Elec in Table 3.2 was prepared by mixing commercial purity aluminium in granular form (granules of about 10mm in size) with crushed Al-42%Ti-11%B compound, melting the mixture and holding at 950°C for 1h. The temperature was then reduced to 850°C and held for one more hour. The grain refiner was then cast into a cast iron mould to form a short cylinder which was later sawed into small sections for use in the metallographic examination and grain refining experiments. Alloy Ind in Table 3.2 was prepared in a fashion similar to that described for alloy Elec with the melting being carried out in an induction furnace. The temperature of the melt was raised to 1000±50°C and held at that level for 2 hours. Alloy Arc in Table 3.2 was prepared from
granulated aluminium, crushed Al-43%Ti compound and B₂O₃ with the melting being carried out in an arc furnace. The alloy was heated to a temperature between 1500 and 1600°C, it was then allowed to cool down to 850°C before casting in a cast iron mould as described earlier. By use of these procedures 7 different grain refiner compositions were produced.

3.2 Determination of Chemical Composition

The chemical compositions of the grain refiners were determined by mass spectrometry for all the elements except for C and N, which were determined by combustion spectrometry (Leco method). Commercial grain refiners (KBM Al-5Ti-1B) manufactured by the salt route were also analysed for comparison.

Table 3.2: Conditions for the preparation of the grain refiners

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Feed material</th>
<th>Furnace</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elec</td>
<td>Al Al-42Ti-11B</td>
<td>Electric resistance</td>
<td>850°C for 1h, 950°C for 1h</td>
</tr>
<tr>
<td>Ind</td>
<td>Al Al-42Ti-11B</td>
<td>Induction</td>
<td>1000°C for 2h</td>
</tr>
<tr>
<td>Arc</td>
<td>Al Al-43Ti B₂O₃</td>
<td>Button Arc</td>
<td>1500-1600°C</td>
</tr>
</tbody>
</table>

3.3 Microstructural Examination

Samples for optical microscopy were cut from the cast cylinders, ground and polished using standard methods and examined in the unetched condition. Samples for SEM were deep etched using an iodine-ethanol solution (90ml ethanol + 10ml iodine). They were then repolished and etched using the modified Keller’s reagent (10ml HNO₃ + 1.5ml HCl + 1.0ml HF + 87.5 ml water).

3.4 X-Ray Diffraction and EDS Analyses

Powder X-ray diffraction and EDS analyses were performed on grain refiner powders obtained by electrolysis. Plates of grain refiner alloys, 27 mm long, 20 mm wide and 5 mm thick were used as soluble anodes in a solution of hydrochloric acid of pH=1.0 - 1.5, with a maximum potential of 1.5V in an electrolysis cell at room temperature for 240 hours. This condition allowed
the release of intermetallic compounds (TiAl₃ and TiB₂) which sank to the bottom of the cell as the aluminium matrix dissolved according to the chemical reaction:

\[
\text{Al} \rightarrow \text{Al}^{3+} + 3e \quad \text{(anodic reaction)}
\]

The falling intermetallic compounds led to the formation of anodic slurry which was dried to obtain a powder of aluminium grains and intermetallic compounds.

The X-ray diffraction analyses were performed using a Philips (PW 1710 generator fitted with a Philips PW 1820 vertical goniometer) diffractometer. The EDS analyses were performed using two scanning electron microscopes namely a LEO 906A and a LEO 1525 FE.

3.4 Thermal and Mechanical Treatments of Grain Refiners

Samples of four of the grain refiners were subjected to cold rolling at room temperature and reduced by 20, 40, 60 and 80% in each case. After cold rolling, the samples were examined in the electron microscope to see the effects of cold deformation on microstructure. Longitudinal specimens from the cold worked materials were investigated. One half of each of the rolled samples was heated in an electric resistance furnace at 625°C for 4 hours and allowed to cool in the furnace. After heat treatment the samples were cut, ground and polished for optical and scanning electron microscopy.

3.5 Hardness Tests

The samples were tested for hardness in the as-cast condition, after cold rolling and after cold rolling and heat treatment. The tests were carried out with the Vickers hardness testing machine and a load of 5kg. Ten measurements were carried out per sample.

3.6 Measurements of Precipitate Particle Sizes in Grain Refiners

The precipitate sizes were determined by the linear intercept method using the semi-automatic image analysis (Winster Software). These measurements were carried out on as cast and rolled samples in order to quantify changes in particle size due to mechanical and thermal treatments.

3.7 Measurements of Grain Size in Inoculated Aluminium : TP-1 Test

The grain sizes of the inoculated alloys were determined by the Heyn linear intercept method as per ASTM Standard Specification E112⁵¹. Measurements were carried out on samples prepared and sectioned according to the TP-1 test standard⁵². In order to evaluate the grain refining performance of the experimental grain refiners and the influence of mechanical and thermal
treatments on their performance, the TP-1 test was performed on aluminium inoculated with grain refiners in different conditions as follows:

- Inoculation of aluminium melts with as cast grain refiners
- Inoculation of aluminium melts with cold rolled grain refiners.
- Inoculation of aluminium melts with cold rolled and heat treated grain refiners.

The following materials and equipment were used:

- Commercial purity aluminium.
- Experimental grain refiners of different compositions.
- Electric resistance furnace (Figure 3.1)
- Silicon-carbide crucible (Figure 3.1)
- Thermocouple and controller indicator
- Two conical ladles in mild steel coated with graphite spray (Figure 3.2)
- Wood stirrer
- Quench tank (Figures 3.3 and 3.4)
- A gas flame for preheating the ladles to around 310°C

### 3.8 Melting and Casting Procedures

A series of castings were produced using commercial purity aluminium as base metal. The chemical analysis of the aluminium used is given in Table 3.3. For each casting 5kg of aluminium was melted in an electric resistance furnace (Figure 3.1) heated to 950°C and held at this temperature for about 1 hour for homogenisation and then allowed to cool down to 720±5°C. Mild steel ladles coated with graphite (Figure 3.2) were preheated in gas flame and used for sampling. The first sample of aluminium was taken after stirring the melt and before the addition of grain refiner. This sample was termed the 0-minute sample. Following the addition of grain refiners, further samples were taken after 2, 5, 10, 20 and 30 minutes after 10 seconds of stirring of the melt in each case. In this work the addition rate of grain refiner in the melt was 0.01% Ti in all cases.

*Table 3.3: Composition of aluminium used as feed material in the TP-1 test*

<table>
<thead>
<tr>
<th>Element</th>
<th>Cu</th>
<th>Mg</th>
<th>Si</th>
<th>Fe</th>
<th>Mn</th>
<th>Ni</th>
<th>Zn</th>
<th>Pb</th>
<th>Sn</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content (Wt %)</td>
<td>0.001</td>
<td>0.001</td>
<td>0.04</td>
<td>0.08</td>
<td>0.001</td>
<td>0.004</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001</td>
<td>99.85</td>
</tr>
</tbody>
</table>
The weight of grain refiner to be added was determined as follows:

$$\text{Weight of grain refiner to be added} = (%\text{Ti or B desired}) \times (\text{Weight of the Melt}) \times \frac{\%\text{Ti or B in Grain Refiner}}{100}$$

A conical aluminium ingot was obtained after solidification as shown schematically in Figure 3.5. For metallographic examination, a transverse section 38mm from the base (as measured along the sloping side) was cut as specified in the TP-1 standard.

The microstructure of the alloys was revealed by electrolytic etching in fluoroboric acid (1228ml water+ 22ml acid). A voltage of 40V was applied for 2 minutes without stirring followed by 2 minutes with stirring at a voltage of 50 V. Contrast between grains was revealed with polarized light. Figure 3.6 shows the equipment used in the electrolytic etching and Figure 7 shows the specimen holder.

The velocity of the solidification front was estimated by assuming solidification in the conical ladle to be unidirectional. The rate was calculated by measuring the time taken for the solidification front to move from the bottom to the top of the ladle in contact with the running water.

*Figure 3.1: Electric resistance furnace*
Figure 3.2: Schematic representation of ladle for TP-1 Test

Material: 0.125 in. (3 mm) Thick Mild Steel

Figure 3.3: Mould quench
Figure 3.4: Schematic figure of a mould tank
Figure 3.5: Details of the cast samples

Figure 3.6: Equipment for electropolishing
Figure 3.7: Specimen holder for electrolytic etching