Thermodynamics and Kinetics of Transition Metal Borides Formation in Molten Aluminium

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Declaration

The author declares that this thesis on the “Thermodynamics and Kinetics of Transition Metal Borides Formation in Molten aluminium”;

- Contains no material which has been accepted for the award to the candidate of any other degree or diploma, except where due reference is made in the text of the thesis.
- To the best of the candidate’s knowledge, this thesis contains no material previously published or written by another person except where due reference is made in the text of this thesis.
- This thesis also disclosed the relative contributions of the respective workers or authors in the case of any joint research or publication.
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Abstract

Aluminium is widely used for overhead cables for power transmission due to its good electrical conductivity and light weight properties. Smelter grade aluminium needs to be further processed to meet the low impurity level for the manufacturing of electrical grade conductors. The presence of transition metal impurities especially vanadium (V), titanium (Ti), zirconium (Zr) and chromium (Cr) deteriorate the electrical conductivity of aluminium. Transition metal impurities come from raw materials such as alumina and petroleum coke. Literature investigation showed that the level of V is rising in petroleum coke that is used for consumable anodes in Hall-Heroult process and end up in the potline metal.

Industrially, transition metal impurities are removed by the addition of boron bearing substances called boron treatment. Mostly, aluminium boron master alloys containing AlB\textsubscript{12} or AlB\textsubscript{2} phases are added to remove transition metal impurities from solution into their borides. The transition metal borides are stable and heavy that are removed from aluminium by gravity settling or filtration. Although boron treatment of aluminium has been used in industry, the fundamental understanding of reaction mechanism of boron and transition metal impurities is not well documented. Thermodynamics and kinetics of boron treatment process are partially investigated. The purpose of this study is to investigate the thermodynamics and kinetics of V removal and elucidate the mechanism of vanadium diborides (VB\textsubscript{2}) formation in molten aluminium. Further aim is to identify the opportunities to enhance the kinetics of the process that can improve the quality of alloys and economy of the current industrial boron treatment process.

First stage of this study focused on the thermodynamic modelling of transition metal borides formation in molten aluminium. The Gibbs free energy minimisation method was used for the prediction of stable phases. Thermodynamic modelling predicted that diborides (VB\textsubscript{2}, ZrB\textsubscript{2}, TiB\textsubscript{2}, AlB\textsubscript{2} and CrB\textsubscript{2}) of V, Zr, Ti, Al and Cr are more stable compared to their other possible borides (AlB\textsubscript{12}, TiB, VB, V\textsubscript{3}B\textsubscript{4}, V\textsubscript{5}B\textsubscript{6}, CrB, Cr\textsubscript{3}B\textsubscript{4} and Cr\textsubscript{5}B\textsubscript{3}). It was shown from thermodynamic perspective that only V, Zr and Ti can be removed from molten aluminium by the addition of Al-B master alloys.
Thermodynamic prediction revealed that Cr cannot be removed in the form of CrB$_2$ from molten aluminium because AlB$_2$ is more stable compared to CrB$_2$. Stoichiometry and 75wt% excess boron was modelled and predicted that excess boron is beneficial for the removal of transition metals from molten aluminium.

Second stage of this study was composed of thermodynamics and kinetics experiments. Thermodynamic of systems such as Al-1wt%V-0.412wt%B and Al-1wt%V-0.720wt%B was studied using induction melting and vertical tube furnaces. The results showed the reaction between AlB$_{12}$ or B and V was quick and VB$_2$ reaction product ring was formed in the early minutes, encapsulating the initially added AlB$_{12}$. The presence of black phase after an extended holding of alloy suggested slow dissolution of Al-borides (AlB$_{12}$) that was due to boron saturation of aluminium melt inside the VB$_2$ ring. The evidence from electron back scattered diffraction (EBSD) analysis suggested that the reaction product ring was composed of pure VB$_2$ that do not form mixed borides with Al/AlB$_{12}$. Comparative analysis of thermodynamic predictions and experimental results showed the alloys were for from equilibrium.

The kinetics of V removal and formation of VB$_2$ in molten aluminium were investigated using Al-1wt%V-0.412wt%B alloy. It was shown during the analysis that reaction kinetics was first order with respect to V in molten aluminium. The kinetics of VB$_2$ was divided into two stages. First stage was fast and controlled by the mass transfer of V in molten aluminium. It was found that the activation energy and mass transfer coefficient were 25.94 kJ/mol and of 2.15 x 10$^{-3}$ m/sec respectively. The reaction rate in the second stage was slower and controlled by the diffusion of B through VB$_2$ ring. Experimental data fit with Jander and Ginstling-Brounshtein diffusion models that provided strong evidence of B diffusion through solid VB$_2$ layer that controlled the kinetics in the second stage of reaction. Stirring of melt using gas injection revealed that kinetics of V removal was enhanced by increasing mass transfer and breaking of VB$_2$ rings formed in the early stage of reaction. A mechanism of VB$_2$ formation in molten aluminium was also proposed based on experimental results.

The analyses of Al-Zr-B and Al-V-Zr-B alloys were also carried out in this study. Similar to the case of Al-V-B systems, the results showed the formation of ZrB$_2$ ring
encapsulating the initially added AlB₁₂ in the Al-1wt%Zr-0.223wt%B alloy. However, the particles of ZrB₂ were needle like and less dense compared to VB₂. It was also shown that ZrB₂ formed in preference to VB₂ in the Al-0.50wt%Zr-0.50wt%V-0.115wt%B alloy.

Finally, industrial trials on boron treatment of smelter grade aluminium were critically investigated. Trials were performed at one of the high purity aluminium producers in Australasia. The analysis showed a linear decrease between V and Ti during the boron treatment at 750°C. Mass balance analysis showed that more than 85 wt% V and Ti were removed by the addition of Al-8wt%B (AlB₁₂) master alloy for holding time of 793 minutes. It was recommended to industry that better economy of the process may be achieved by tailoring the source of boron, addition of Al-B in multiple stages, better stirring and optimising the melt holding time.
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To my beloved parents, wife and daughter
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Chapter 1
Introduction

1.1 Research motivation

Smelter grade aluminium is used for electrical grade applications after the removal of transition metal impurities. Impurities such as vanadium (V), titanium (Ti), zirconium (Zr) and chromium (Cr) reduce the electrical conductivity of aluminium when present in aluminium solid solution (Gauthier, 1936, Dean, 1967). Transition metal impurities in the potline metal come from raw materials (alumina and coke) used in the Hall-Heroult process (Grjotheim et al., 1982, Metson et al., 2013, Lindsay, 2013).

Recently, it was reported that the level of V in the potline metal is increasing due to the supply of low grade coke to the aluminium smelters from petroleum refineries (Grandfield and Taylor, 2009, Sweet et al., 2013, Coney et al., 2013). This increase of V in the petroleum coke has been reported in the literature (Vogt et al., 2004, Bartholomew, 2013, Lindsay, 2013). Once impurities such as V become a part of potline metal, they are controlled in the cast houses to meet alloy specifications. Methods of controlling melt quality and the management of impurities in cast houses has been reported (Grandfield et al., 2011, Rhamdhani et al., 2013) and different strategies have been proposed to control the melt quality in the cast houses to meet the alloy specifications. The removal of V and other transition metal impurities in the petroleum coke has been the focus of many investigations in the past but these have received limited applications for the petroleum industry (McCorriston, 1983, Queneau, 1984, Schemel, 1985, McCorriston, 1985, Thornhill, 1994, Malone, 2001). Another option is V removal from the crude oil and people have looked at this but so far that has received limited commercial application. Due to these reasons, it is imperative to develop new or improve existing cast house refining processes as the concentration increases.
Industrially, impurities such as V, Ti, Zr and Cr are removed in cast house through the addition of boron bearing substances to the molten aluminium, known as boron treatment (Dube, 1983, Stiller and Ingenlath, 1984, Setzer and Boone, 1991, Cooper and Kearns, 1996, Cooper et al., 1997, Cook et al., 1997, Karabay and Uzman, 2005a, Karabay and Uzman, 2005b, Gao et al., 2007a, Gao et al., 2009a, Gao et al., 2009b, Khaliq et al., 2011b). In the boron treatment of molten aluminium, Al-B master alloys are added in the form of waffles, ingots or rods, depending on the process requirement and the required quality of the end product. Al-B master alloys containing AlB\(_2\) or AlB\(_{12}\) phases are commonly used in the industry. Impurities such as V, Ti, Zr and Cr combine with B and form their borides. The borides of transition metal impurities are stable and do not dissolve back into the melt once they form during the boron treatment of molten aluminium (Khaliq et al., 2011a). The heavy borides formed during boron treatment are separated using ceramic foam filters or gravity settling (Dube, 1983). Boride settling time can be many hours depending on the desired purity of the final aluminium alloy.

Although the boron treatment of molten aluminium is used commercially, details of the mechanism of boride formation are not well understood. Fundamental questions still remain, for example: what is the order of the formation of the transition metal borides in molten aluminium during boron treatment? Thermodynamically, what transition metal borides are stable and in what form do they exist in molten aluminium? What is the mechanism of boron by which transition metal impurities form their borides? Although, Cooper and Kearns (1996) proposed a reaction mechanism for AlB\(_{12}\)/AlB\(_2\) with Ti and V during the boron treatment of molten aluminium, no further theoretical nor experimental evidences were reported to verify this theory. What is the kinetics of V removal from molten aluminium, and what is the overall rate-controlling step during boron treatment? Is there any effect as a result of liquid phase stirring that enhances the overall rate of the reaction that forms VB\(_2\) in molten aluminium? There is limited information on the kinetics of V removal and the formation of borides in the literature. These fundamental questions need to be addressed to obtain a complete understanding.
of boron treatment in order to optimise the process for better quality and economy and to be better placed to handle the increasing V levels.

1.2 Aim of the thesis

The aim of this research is to determine the mechanism of VB$_2$ formation in molten aluminium under typical processing conditions. It was further aimed to critically analyse and optimise current industrial practice for the removal of transition metals from smelter grade aluminium.

1.3 Objectives of the research

This research was composed of a mixture of thermodynamic modelling, experimental study and industrial trials of aluminium boron treatment. Thermodynamic modelling was carried out using FactSage 6.2 and HSC Chemistry 7.0 packages to predict the solute and boride concentrations in the molten aluminium in the temperature range of 675°C to 900°C. Thermodynamics and kinetics experimental investigations of Al-1wt%V-0.412wt%B and Al-1wt%V-0.720wt%B alloys were carried out at 700°C, 750°C and 800°C using induction and resistant pot furnaces. The effect of melt stirring was also analysed using mechanical, gas and induction stirring.

Specifically, the objectives of this doctoral study are:

- To predict the transition metal solute and boride concentrations in molten aluminium under process conditions using thermodynamic packages
- To analyse the effect of the addition of stoichiometric and excess boron on the removal of V during the boron treatment of aluminium
- To elucidate the formation of the solid solution between VB$_2$ and AlB$_2$/AlB$_{12}$
- To determine the reaction rate between V and B during the boron treatment of aluminium
- To determine the rate-controlling step during the formation of VB$_2$ in molten aluminium
- To elucidate the mechanism of VB$_2$ formation during the boron treatment of aluminium melt
To analyse industrial boron treatment process and suggest recommendations to aluminium industry for the better quality and economy of electrical grade aluminium.

1.4 About this thesis

This thesis consists of nine chapters. Chapter 1 explains the background of the research as well as the aims and objectives of the study. A literature review is given in Chapter 2 to provide the basic knowledge and understanding of this research area. This includes brief information of aluminium production technology, common impurities and their impact on the properties of aluminium, as well as current technologies to remove impurities. In the literature review, details of boron treatment for the removal of V, Ti, Zr, Cr and Fe are explained. Moreover, basic thermodynamic modelling theories and phase diagram analysis of Al-B, Al-V and V-B are presented. The final section of the literature review explains the basics of metallurgical kinetics, the liquid phase and diffusion through the solid product layer control models that are used for the kinetics analysis in this study. The experimental methodology used for this investigation is given in Chapter 3, which explains the thermodynamic modelling approach, the preparation of master and Al-V-B alloys for thermodynamic and kinetic investigations using induction and resistant pot furnaces, different methods of melt stirring, boride settling practices and, finally, industrial trials carried out at one of the major electrical and high purity grade aluminium producers in Australasia.

Thermodynamic modelling of Al-V-B, Al-V-Ti-B, Al-V-Zr-B, Al-V-Cr-B, Al-V-Ti-Zr-B and Al-V-Zr-Ti-Cr-B systems is given in Chapter 4. This chapter also explains the comparative analysis of Gibbs free energy formation of V, Ti, Zr, Cr and Al borides in the temperature range of 650°C to 900°C. The effect of the addition of stoichiometric and excess boron was also analysed thermodynamically and is explained in Chapter 4. Chapter 4 also outlines the thermodynamic predictions of solute and boride concentrations in molten aluminium in the temperature range of 675°C to 900°C. An experimental study of Al-1wt%V-0.412wt%B and Al-1wt%V-0.720wt%B was carried out based on the thermodynamic predictions as described in Chapter 5. The formation
of a VB$_2$ shell in the early stage of process was observed, indicating that the reaction between V and B was very fast. The characterisation of Al-V-B alloy samples was carried out using scanning electron microscope (SEM), energy dispersive x-ray (EDX), electron back scattered diffraction (EBSD), electron probe micro analysis (EPMA) and inductively coupled plasma atomic emission electron spectroscopy (ICP-AES) tools, and these are also presented in Chapter 5. The aim of boron treatment is to remove V and other transition metal impurities from molten aluminium to produce electrical conductors. The kinetics of the removal of transition metal impurities has been described in terms of an increase in the electrical conductivity by previous investigators (Stiller and Ingenlath, 1984, Cooper et al., 1997). The kinetics of V removal and the mechanism of VB$_2$ formation in molten aluminium are important in optimising the current industrial boron treatment processes. Fundamentally, such processes deal with a fluid solid reaction and the formation of a reaction product, both of which play an important role in the reaction kinetics of VB$_2$ formation. The kinetics of V removal, the reaction rate and the SEM images of settled boride sludge are explained in Chapter 6. This chapter also contains the kinetics analysis of the early and later stages of reaction using liquid phase and diffusion through solid layer control models. The effect of stirring and fluid flow patterns are also explained briefly in this chapter.

Based on thermodynamic predictions, experiments were conducted on the Al-Zr-B and Al-Zr-V-B alloys. The boron was added stoichiometric to Zr only in both alloys to compare the experimental results with thermodynamic predictions. Previously it was reported that ZrB$_2$ will form in preference to VB$_2$ and is more stable in the temperature $(750^\circ\text{C})$ of aluminium refining (Khaliq et al., 2011a). The analysis of Al-1wt% Zr-0.23wt% B and Al-0.5wt% Zr-0.5wt%V-0.115wt%B alloy systems is given in Chapter 7. The industrial boron treatment of smelter grade aluminium was critically investigated, based on the industrial trials in Australasia, and is described in Chapter 8. Selective results of the removal of transition metal impurities from molten aluminium are presented. At the end of this chapter, recommendations are proposed for the optimisation of the current boron treatment process to improve the quality of the product and the economics of the current process. Finally, a summary of the work and
my conclusions are given in Chapter 9. To enhance the flow of thesis, most of the raw and supplementary data is given in several appendices that include:

A: Temperature profiles in vertical tube furnace

B: Melting facilities

C: Thermodynamic modelling results

D: Kinetics of V removal from molten aluminium
   
   D1: Reaction order analysis

   D2: Liquid phase control model

   D3: Estimation of AlB$_{12}$ surface area

   D4: Stirring of molten metal (induction, mechanical and gas)

E: Industrial trials

F: Error analysis
Chapter 2

Literature Review

2.1 Aluminium production

It is estimated that 7.5% of the earth’s crust is composed of aluminium, one of the most abundant elements on earth after iron and silicon. Aluminium is very reactive with other elements and is always found as a chemical compound, mostly as aluminium oxide (Al₂O₃).

![Figure 2.1. History of aluminium production in the world since 1950](http://www.alueurope.eu/, 2012)

It is shown in Figure 2.1 that aluminium production has raised dramatically over the last few decades. In 2010, China was main producer of aluminium, sharing 41% of the total world production. Aluminium has a wide range of applications in daily life, including engineering sectors (aeronautical and electrical; heat resistant cables and construction) to design, household and leisure products. Aluminium replaced copper for overhead and underground power transmission and electrical cables after 1945, due to its superior mechanical, lightweight and corrosion properties. The weight of aluminium is one-third

Charles Martin Hall (USA) and Paul L.T Heroult (France), in 1886, simultaneously developed the electrolytic process currently used for the production of aluminium from alumina. The Hall-Heroult process was recognised as the most economical process for industrial production of aluminium. Since its invention, the Hall-Heroult process had various modifications. In this process, liquid aluminium is produced by the electrolytic reduction of the alumina (Al₂O₃) that is dissolved in the electrolytic bath of cryolite (Na₃AlF₆). Alumina is separated from bauxite ore using the Bayer process that was developed by Karl Joseph Bayer in 1888.

Figure 2.2. Flow diagram of aluminium production

Industrially, aluminium is produced in two stages. These involve the separation of alumina (Al₂O₃) from raw bauxite ore using the Bayer process. The alumina is subsequently reduced electrolytically using the Hall-Heroult process. Generally, in order to produce one tonne of aluminium, two tonnes of alumina, 0.5 tonne petroleum
coke and 13 – 15 MWh of electrical energy are consumed. A flow sheet showing the process is given in Figure 2.2. It shows the different steps required for the production of aluminium using the Hall-Heroult process.

The components of alumina reduction cell in the Hall-Heroult process consist of anodes, an electrolytic bath, sidewall materials and cathodes. Alumina is dissolved in a cryolite (Na$_3$AlF$_6$) electrolytic bath and carbon anodes are used as electrodes. During the reduction of alumina, carbon anodes are dipped into the bath and oxygen is liberated from the alumina electrolytically. The discharged oxygen then reacts with the carbon in the anodes to form CO$_2$, consequently consuming electrodes during the process. A molten aluminium pool is located below the electrolyte in preformed carbon linings that also act as an insulator and which are contained in a steel shell, as shown in Figure 2.3. Aluminium is produced at the bath and metal interface, which also acts as a cathode during the reduction process. The overall reaction during the reduction of alumina in the Hall-Heroult process can be written as Eq. (2.1) (Grjotheim, 1993).

$$2\text{Al}_2\text{O}_3(dissolved) + 3\text{C}(s) = 4\text{Al}(l) + 3\text{CO}_2(g)$$  \hspace{1cm} (2.1)

![Figure 2.3. Schematic cross section of an industrial electrolytic cell (Grjotheim, 1993)](image-url)

The electrolytic bath in the Hall-Heroult process is mainly composed of cryolite (Na$_3$AlF$_6$), which has the unique quality of acting as solvent for the alumina (Al$_2$O$_3$).
Other ingredients in bath are aluminium fluoride AlF$_3$ (8 to 13 wt%), calcium fluoride CaF$_2$ (4 to 6 wt%), alumina Al$_2$O$_3$ (2 to 4 wt%), and lithium LiF or magnesium fluoride MgF$_2$ (2 to 4 wt%), depending on the cell operation and process requirements. All additives tend to decrease the cell working temperature (940°C to 970°C) but have an adverse effect on the solubility of the cryolite. In the presence of all these additives in cryolite, the concentration of alumina should be in the range of 2 to 4 wt% for an efficient cell operation.

Anodes are consumable materials in a typical Hall-Heroult process. Anodes are made from petroleum coke and a coal tar pitch binder that are moulded into the required shapes. Two kinds of anodes are widely used in aluminium production, namely prebaked and Soderberg. Prebaked anodes are replaced at regular intervals (usually 22 to 26 days), typically when they become only one third or one fourth of their original size. Prebaked anodes give a better melt quality than Soderberg because less coal tar pitch (13 to 18 wt%) is added. The carbon lining and block are made of anthracite or semi graphite joined with carbonaceous materials. The outer carbon side walls are protected with a frozen layer of cryolite to produce the right heat balance in the cell (Grjotheim, 1993).

### 2.2 Aluminium impurities

Impurities in aluminium produced using the Hall-Heroult process come from raw materials (bauxite and petroleum coke), cell materials (carbon cathodes, linings) and other melt handling equipment (furnaces, ladles and launders linings) that come into contact with the melt during different stages of the treatment (Grjotheim et al., 1982).

Impurities in aluminium can be classified into four common groups, namely volatile, reactive, or non-reactive elements and inclusions. Elements with high vapour pressure i.e hydrogen and sodium are volatile. The elements that can be removed from a melt through the addition of oxygen, water, chlorides, salts, boron or other chemicals are reactive. Common examples of reactive impurities are lithium, calcium, vanadium, zirconium and titanium. Elements that are very difficult to remove through the ordinary refining processes are called non-reactive elements i.e iron and nickel. Melt inclusions
may be in the form of liquids or solids, and include oxides, silicates and borides. The general classifications of dissolved impurities and solid inclusions in molten aluminium are given in Table 2.1. Mostly, the dissolved impurities consist of sodium, lithium, calcium, magnesium, vanadium, nickel and zirconium that come from raw materials for the production of aluminium. Some other impurities like iron, silicon, manganese and copper come from recycled aluminium that contains different grade of aluminium alloys. Inclusions in the molten aluminium could be exogenous and endogenous that comes from refractories and electrolysis as given in Table 2.1.

Dissolved impurities come from the raw materials used for the electrolysis and during remelting. The supply of low-grade coke to the aluminium industry means that the level of primary metal impurities is increasing gradually.

Table 2.1. Impurities classification in aluminium melts

<table>
<thead>
<tr>
<th>Dissolved impurities</th>
<th>Solid inclusions</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>Metals</td>
</tr>
<tr>
<td>Sodium</td>
<td>Iron</td>
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<tr>
<td>Lithium</td>
<td>Silicon</td>
</tr>
<tr>
<td>Calcium</td>
<td>Manganese</td>
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<tr>
<td>Magnesium</td>
<td>Copper</td>
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Solid inclusions such as Al₄C₃ and TiB₂ may form during electrolysis and also from other melting environments (refractory linings of the furnaces, ladles, reactors or launders etc) that remained in the downstream molten metal (Simensen and Berg, 1980, Friedrich et al., 2005, Grandfield and Taylor, 2009).
The primary aluminium produced using the Hall-Heroult process contains a number of impurities, which are summarised in Table 2.2. Their concentration and level in the metal produced depends upon the cell operation, the composition of feed materials, and the construction of the cell’s materials that are in contact with metal. Excessive impurity concentrations that cause a loss of properties are undesirable. Wherever specific properties are required, some alloying additions are used to meet requirements (Grandfield and Taylor, 2009).

Table 2.2. Impurities in smelter grade aluminium melts (Engh, 1992, Grandfield and Taylor, 2009, Simensen and Berg, 1980, Willey, 1967, Bell and Davis, 2003)

<table>
<thead>
<tr>
<th>Element</th>
<th>Conc. range (ppm)</th>
<th>State in molten Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vanadium</td>
<td>10- 200</td>
<td>Solution/Borides(VB₂)</td>
</tr>
<tr>
<td>Zirconium</td>
<td>10-40</td>
<td>Solution/Borides(ZrB₂)</td>
</tr>
<tr>
<td>Chromium</td>
<td>2-50</td>
<td>Solution/Borides(CrB₂)</td>
</tr>
<tr>
<td>Titanium</td>
<td>10-100</td>
<td>Solution/Borides(TiB₂)</td>
</tr>
<tr>
<td>Boron</td>
<td>&lt;2-60</td>
<td>Borides</td>
</tr>
<tr>
<td>Nickel</td>
<td>1-80</td>
<td>Solution/Al₃Ni</td>
</tr>
<tr>
<td>Iron</td>
<td>400-3000</td>
<td>Oxides</td>
</tr>
<tr>
<td>Silicon</td>
<td>200-1500</td>
<td>K/Ca- Silicates/SiO₂</td>
</tr>
<tr>
<td>Potassium</td>
<td>-</td>
<td>K/Ca- Silicates</td>
</tr>
<tr>
<td>Calcium</td>
<td>&lt;1- 50</td>
<td>K/Ca- Silicates</td>
</tr>
<tr>
<td>Sodium</td>
<td>&lt;1- 500</td>
<td>Oxides(Na,K,Ca,O)/Na₃AlF₆</td>
</tr>
<tr>
<td>Lithium</td>
<td>1-10</td>
<td>Solution/chlorides</td>
</tr>
<tr>
<td>Zinc</td>
<td>10- 200</td>
<td>Solution</td>
</tr>
<tr>
<td>Magnesium</td>
<td>5-60</td>
<td>Al₂MgO₄/MgO</td>
</tr>
<tr>
<td>Copper</td>
<td>5- 100</td>
<td>Solution</td>
</tr>
<tr>
<td>Manganese</td>
<td>5- 50</td>
<td>Solution</td>
</tr>
<tr>
<td>Chlorine</td>
<td>-</td>
<td>Chlorides (Al,Mg,K)</td>
</tr>
<tr>
<td>Fluorine</td>
<td>-</td>
<td>Fluorides (Al,Mg,K)</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>1-60</td>
<td>AlN/Nitrides</td>
</tr>
<tr>
<td>Oxygen</td>
<td>1-100</td>
<td>Oxides/Al₂O₃/Fe-oxides/SiO₂</td>
</tr>
<tr>
<td>Lead</td>
<td>1-50</td>
<td>Solution</td>
</tr>
<tr>
<td>Bismuth</td>
<td>0-10</td>
<td>Solution</td>
</tr>
<tr>
<td>Barium</td>
<td>&lt;1- 10</td>
<td>-</td>
</tr>
<tr>
<td>Carbon</td>
<td>&lt;1- 100</td>
<td>Carbides/Al₄C₃/Al₄C₄</td>
</tr>
<tr>
<td>Phosphorous</td>
<td>1- 30</td>
<td>-</td>
</tr>
<tr>
<td>Sulphur</td>
<td>&lt;1- 20</td>
<td>-</td>
</tr>
<tr>
<td>Tin</td>
<td>&lt;1- 30</td>
<td>-</td>
</tr>
<tr>
<td>Lanthanum</td>
<td>&lt;1- 10</td>
<td>-</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>0.2- 0.5</td>
<td>H/H₂O</td>
</tr>
</tbody>
</table>
2.3 Impact of impurities on aluminium properties

Impurities dissolved in the solution with the aluminium tend to reduce the electrical conductivity by electron scattering via thermal vibration of the crystal lattice (Karabay and Uzman, 2005b). The effects of impurity elements on the electrical conductivity were investigated by Gauthier in 1936. The presence of impurities has a strong effect in reducing electrical conductivity. The change in electrical resistivity of aluminium in the presence of a small amount of impurities in the solution can be determined by the relationship given in Eq. (2.2).

\[ \rho_o = \sum K_j [\% J] \]  

(2.2)

Where \( \rho_o \) is the resistivity of the pure metal, \( K_j \) is the change of electrical resistivity in the presence of 1% of element j and [\% J] is the concentration of element j. Nordheim’s rules state that in a dilute case, the residual resistivity of aluminium is proportional to the impurity concentration (Gauthier, 1936). The effects of impurities elements on the electrical conductivity of aluminium in solution and as a precipitate are given in Table 2.3.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Max. solubility in Al wt. %</th>
<th>Ave increase in resistivity per wt.% in solid solution</th>
<th>Out of Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chromium</td>
<td>0.77</td>
<td>4.00</td>
<td>0.18</td>
</tr>
<tr>
<td>Copper</td>
<td>5.65</td>
<td>0.344</td>
<td>0.030</td>
</tr>
<tr>
<td>Iron</td>
<td>0.052</td>
<td>2.56</td>
<td>0.058</td>
</tr>
<tr>
<td>Lithium</td>
<td>4.0</td>
<td>3.31</td>
<td>0.68</td>
</tr>
<tr>
<td>Magnesium</td>
<td>14.9</td>
<td>0.54</td>
<td>0.22</td>
</tr>
<tr>
<td>Manganese</td>
<td>1.82</td>
<td>2.94</td>
<td>0.34</td>
</tr>
<tr>
<td>Nickel</td>
<td>0.05</td>
<td>0.81</td>
<td>0.061</td>
</tr>
<tr>
<td>Silicon</td>
<td>1.65</td>
<td>1.02</td>
<td>0.088</td>
</tr>
<tr>
<td>Titanium</td>
<td>1.0</td>
<td>2.88</td>
<td>0.12</td>
</tr>
<tr>
<td>Vanadium</td>
<td>0.5</td>
<td>3.58</td>
<td>0.28</td>
</tr>
<tr>
<td>Zinc</td>
<td>82.8</td>
<td>0.094</td>
<td>0.023</td>
</tr>
<tr>
<td>Zirconium</td>
<td>0.28</td>
<td>1.74</td>
<td>0.044</td>
</tr>
</tbody>
</table>
It can be seen that vanadium and chromium have the greatest effect on resistivity, and the presence of these elements in the solution increases the resistivity by a factor of 10 to 20. For the electrical conductor applications of aluminium, a high level of purity is required and this is not possible in the presence of the large amount of impurities that come from smelter and other treatment processes. Impurities elements that have an adverse effect on electrical conductivity are removed from molten aluminium in the form of stable compounds. The improvement of electrical conductivity in the industrial treatment of molten aluminium will be discussed in section 2.4.3 (Gauthier, 1936, Karabay and Uzman, 2005b). Impurities in the form of solid particles i.e oxides, carbides, nitrides, fluorides and borides cause problems during processing. They cause wearing of the die during extrusion, pinholes in thin foil, lithographic plates and sometimes failure in the service of castings (Grandfield and Taylor, 2009).

Iron and silicon have the highest concentration in smelter grade aluminium. Iron increases the corrosion susceptibility of aluminium by the formation of an Al$_3$Fe intermetallic phase, which acts as a potential site for corrosion. When such a coarse phase appears in the solid aluminium, it reduces the ductility and also causes cracking in the wrought aluminium alloys during fabrication. Iron forms insoluble compounds by combining with other impurity elements (Cu, Ni, Mn and Si). Such inclusions have a similar detrimental effect to Al$_3$Fe on aluminium during processing (Ambat et al., 2006, Willey, 1967).

Silicon generally has no detrimental effect on the aluminium in the end product. A range of Al-Si alloys is produced in the foundries. When zinc and titanium are added, they can impart specific properties and give additional benefits; but zinc over 100 ppm can be detrimental for aluminium. Master alloys of Al-Ti-B are used to produce a fine grain size in aluminium products (Grandfield and Taylor, 2009, Birol, 2009).

Vanadium, along with other transition elements, has a strong effect in reducing the electrical conductivity of aluminium, as can be seen in Table 2.3. It can act as a grain refiner but only in the absence of titanium. As little as 0.1 wt % increase in vanadium can increase the electrical resistivity of aluminium from 0.4 to 0.5 x 10$^{-8}$ $\Omega$.m in a solid
that has also similar effect in liquid. Vanadium will increase the recrystallization
temperature of aluminium, and this can create problems during rolling and other
forming processes. It tends to increase the strength of aluminium through the formation
of intermetallic phases and also by reducing the grain size (Willey, 1967, Grandfield
and Taylor, 2009).

Nickel is used as an alloying element to impart specific properties to aluminium i.e
strength, creep resistance, hardness at high temperatures and corrosion resistance in
high-pressure steam. Tensile properties of wrought Al-Cu-Mg alloys at room
temperature are reduced by the addition of 0.5 wt% nickel. This also reduces the
ductility and has an adverse effect on the castings and machining properties of
aluminium alloys. Nickel forms insoluble phases by combining with copper and iron
that increase the strength of alloys. In the Al-Mg alloys, nickel tends to accelerate the
rate of corrosion. The addition of nickel increases the Young’s modulus of aluminium
alloys (Willey, 1967, Grandfield and Taylor, 2009). Copper as an impurity causes hot
shortness and reduces the casting properties of aluminium. As the percentage of copper
increases in aluminium, the fluidity and resistance to hot cracking will be enhanced
(Ziman, 1969).

Both sulphur and phosphorus are detrimental to aluminium alloys. Sulphur in the
presence of iron, manganese and nickel can accelerate the corrosion rate. Phosphorus
can act as a poisoner to strontium and other modifiers in Al-Si alloys (Grandfield and
Taylor, 2009). Boron and its compounds are used in atomic energy applications due to
their higher neutron absorption capacity. Boron combines with aluminium to form
insoluble AlB$_2$, and AlB$_{12}$ compounds. It traps the transition metal elements in
aluminium to form their borides and, hence, electrical grade aluminium can be produced
from smelter grade aluminium. Small quantities of boron with titanium can be
employed as a grain refiner for aluminium alloys (Birol, 2009, Gauthier, 1936, Cooper
and Kearns, 1996).

Alkali and alkaline earth metals, i.e Li, Na and Ca, cause hot cracking during castings
and hot working processes. The light metal industry has defined the maximum limit for
such impurities in order to avoid these problems. In the magnesium industry, Na < 1
ppm is the optimum limit to minimise the hot cracking during castings. Lithium in even few ppm can cause surface corrosion, staining and other problems (Gariepy and Dube, 1986, Grandfield and Taylor, 2009).

2.4 Aluminium impurities control

Impurities in aluminium produced using the Hall-Heroult process mostly come from the raw material (Grjotheim et al., 1982). The best strategies to overcome this would be to control impurities at the raw material level, which are mainly in bauxite and petroleum coke. Removal of the impurities is more tedious and difficult in the later stages of processing. Transition metal impurities mainly come from carbon anodes (from petroleum coke) in the primary production of aluminium (K. Grjotheim, 1982). Although there are various proposed methods to remove transition metals (especially vanadium) from the petroleum coke (McCorriston, 1983, Queneau, 1984, Schemel, 1985, McCorriston, 1985, Thornhill, 1994, Malone, 2001, Zhang et al., 1996), their application in the petroleum industry is limited. An increasing trend of vanadium concentration in coke has been reported, and this ends up in potline aluminium (Grandfield and Taylor, 2009, Vogt et al., 2004, Bartholomew, 2013, Rhamdhani et al., 2013). In anticipation of an increase in vanadium, it is imperative that the currently available methods for the removal of these impurities from aluminium should be optimized or new methods be developed.

2.4.1 Removal of alkali and alkaline earth metals

Over the past couple of decades, many technologies have been developed for the refining of molten aluminium especially for alkali and alkaline earth metals. Impurity elements Na, Ca and Li have adverse effects on the end properties of aluminium. Na is known to cause hot shortness (cracking) and Li tends to accelerate surface corrosion (Kerr et al., 1996). The removal of alkali and alkaline earth metals is carried out in furnaces, inline fluxing, degassing units and in transfer crucibles in the cast houses. The sequential refining treatments of aluminium is summarised in Table 2.4 that summarise various treatments and their aim to remove impurities.
Originally, Cl\textsubscript{2} gas was used to remove Na, Ca and Li through the formation of their chlorides. N\textsubscript{2} or Ar was used as a carrier gas, with different proportions of Cl\textsubscript{2} used with the gas fluxing techniques (Rudolf Stary, 1979). Environmental constraints have minimised the use of Cl\textsubscript{2} gas for the removal of alkali and alkaline metals. Cl\textsubscript{2} gas based technology was also found to be inefficient because of the longer time needed to remove impurities, especially Li. The reaction efficiency of Cl\textsubscript{2} was increased with the assistance of mechanical dispensers or rotors that produce fine bubbles during melt treatment.

In-line fluxing and degassing units are widely used between the treatment furnaces and castings in the cast houses. The mechanically generated vortex disperses the fluorides and chlorides uniformly and also generates fine bubbles, which increases the reaction rate and therefore reduces treatment time. Such technologies can only achieve 50 to 70% removal of Li (Gariepy and Dube, 1986).

<table>
<thead>
<tr>
<th>Refining and Cleaning</th>
<th>Aim of Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Settling</td>
<td>Separation of H\textsubscript{2} and inclusions</td>
</tr>
<tr>
<td>Gas purging</td>
<td>Separation of H\textsubscript{2}, Li, Na, Mg, Ca and inclusions</td>
</tr>
<tr>
<td>Chlorination</td>
<td>Separation of Mg and Na</td>
</tr>
<tr>
<td>Filtration</td>
<td>Separation of inclusions</td>
</tr>
<tr>
<td>Vacuum distillation</td>
<td>Separation of Mg, Zn and Pb</td>
</tr>
<tr>
<td>Addition of primary aluminium</td>
<td>Dilution of metallic impurities as Fe, Si, Mn, Cu etc</td>
</tr>
<tr>
<td>Addition of aluminium alloys</td>
<td>Dilution of dissolved metallic impurities as Fe, Si, Mn, Zn, Cu etc</td>
</tr>
</tbody>
</table>

Alcan introduced a new process, the treatment of aluminium in a crucible, known as TAC. This technology is based on the treatment of melt in crucibles to remove alkali and alkaline earth metals to a minimum possible level. This process depends on the solid liquid reaction of AlF\textsubscript{3} with molten aluminium. The higher reaction rate is achieved by the mechanically generated vortex in the right axial and radial flow directions. The process parameters, which include AlF\textsubscript{3} additions, reaction time, stirring rate, melt temperature, presence and type of electrolytes in the crucible, need to be controlled precisely for the efficient removal of impurities. The Na level was reduced
from 35 ppm to 2 ppm in 2 minutes and Li from 15 ppm to 2 ppm in 6 minutes of melt
treatment, according to (Gariepy and Dube, 1986). Other melt treatment processes
developed by Alcan include rotary gas injection (RGI) and rotary flux injection (RFI),
which are based on injection of gas and flux through a rotary nozzle into melt. These
processes have achieved an even higher melt quality in 1000, 3000, 5000 and 6000
series alloys (Beland et al., 1998). Another technology, known as a melt treatment
station “MTS 1500”, has been used based on the degassing unit and other additional
features. It can inject two treatment agents simultaneously in the melt and is integrated
with a programmable logic controller (PLC) to ensure the optimum treatment cycle and,
hence, a high melt quality is possible. The optimum treatment cycle was estimated as 10
minutes with reasonable savings of energy and metal (less dross formation) (Pascual Jr,
2009).

In addition to the batch treatment of aluminium melt, continuous processes have also
been used industrially. These reactors are coupled with the refining and filtration of melt
to remove impurities such as H₂, Na, Ca, Li and small inclusions from the melt in a
single stage process. They are classified on the basis of reactor design and reacting
agents. The reacting agents can be gas fluxing (Cl₂, N₂ or Ar), salt injection (AlF₃,
MgCl₂, KCl) or a combination of these two coupled with filtration. The reactor design
can be based on nozzles, porous plugs, impellers or a combination of these with
filtration. Only a few technologies have been mentioned here based on different reacting
agents and reactor designs, such as Mint (gas fluxing with nozzle), MDC (degassing
multiCast processes URC-7000, a physical model to enhance the bubble size and their
effect on melt quality), Alcao processes (622, 503), RDU (rapid degassing unit, F-750,
F-1000), SNIF (spinning nozzle inert flotation process, based on gas fluxing and bubble
generation, stirring of melt and maximising flux treatment), GBF(gas bubbling
filtration) processes, etc (Saternus and Botor, 2009, Zhang et al., 2011, Ohno, 2001,
Bell and Davis, 2003, Doutre et al., 1985). The developments in the refining of molten
aluminium over the last three decades have been summarised by Zhang et al. and are
given in Figure 2.4.
The removal of alkaline metals (RAM) was developed by Hydro Norway in 1995, and this is in operation at many aluminium smelters (Sohar Aluminium, Dubal Aluminium, and Hydro Norway). Alkaline metals (Na, Ca, and Li), oxides, carbides and cryolite can be removed efficiently during the RAM process. RAM is based on the injection of AlF₃ in melt below the surface with the assistance of a specially designed rotor and argon as a carrier gas. This technology can be used for 2 to 9 tons in a crucible and has proved to be very efficient. This technology is excellent for its high melt quality, less dross formation, lower operational costs and a minimum clogging of filters (Haugen et al., 2011).

![Diagram of Aluminium melt refining developments in the last three decades](Zhang et al., 2011)

The final step in the treatment of molten aluminium is the removal of any solid inclusions formed during the different stages of processing. These inclusions can lead to a reduction in die life, pinholes in the sheets, an uneven surface finish, and other related
problems in the end product. During filtration solid inclusions are removed as they adhere to the walls of the filters and settle on deposited inclusions. The filtration of a liquid stream is achieved using cake or bed modes that involve gravity or friction, physical confinement, chemical bonds, Van der Waals forces or electrostatic forces. The types of filters used in cast houses are strainers cores, metal/fibreglass screens, beds, bonded particles, cartridges and ceramic foam filters. Selection of filter materials and types are decided on the basis of inclusions and specific process requirements (Bell and Davis, 2003, Doutre et al., 1985). Recently, a review on the removal and control of impurities in aluminium melt was carried out by Dewan et al. (2011). The main focus was to present the main methods and techniques to remove impurities and inclusions from smelter grade aluminium. Their findings showed that volatile, alkali, alkaline and transition metal impurities are managed well in the current cast house practice.

2.4.2 Removal of transition metal impurities

It was further reported that impurities such as Ni and Fe are difficult to remove due to their non-reactive nature in the aluminium melt. High purity (99.999%) aluminium production methods could be used to remove Fe and Ni. However, such methods (three-layer electrolysis, zone refining and fractional crystallisation) are not economical for commercial production of electrical grade alloys (Sarma et al., 2012). Rhamdhani et al. (2012) investigated the different possibilities to remove Ni from molten aluminium. Thermodynamic analysis and experiments were carried out using P and B to remove Ni in the form of NiP and NiB. Experimental results showed that Ni cannot be removed from molten aluminium by the addition of B and P because AlB$_2$ and AlNi were more stable than NiP and NiB (Schmidt et al., 2003). Copper and aluminium are used in the electrical industry because of their high electrical conductivity. Gauthier (1936) investigated the influence of small metallic additions on super purity aluminium. High purity aluminium (99.99%) was used in this investigation and all other elemental additions were kept within their solubility limits. Special precautions were adopted to avoid unwanted contamination during the alloy melting. A graphite crucible was used for melting alloys of the required composition, which were then chill cast into shallow ingots to avoid any segregation. The samples for chemical analysis were taken by
drilling the ingots. The experiments were repeated to ensure reliable outcomes and minimum error. The conductivity tests were carried out on annealed and quench samples. The 64 mm billets were extruded, and then drawn to 7.975 mm diameter and 1.15 m length to use in a Kelvin double bridge. Gauthier measured the conductivity (65.45% of copper) of super pure annealed aluminium (Fe = 0.0011%, Si = 0.0015%, Cu = 0.005% and rest Al = 99.997%) and obtained the highest measurements ever quoted. Prior to that, the highest observed values had been 64.6% of copper for 99.971% Al as measured by Edwards, and 63.4% of copper for 99.968% Al as given by Edwards and the Bureau of Standards respectively. The metallic additions were carried out from 0.005% to more than 1.50% in the high purity aluminium to quantify the reduction in conductivity. In the first batch of experiments, single metallic additions of Fe, Si, Cu, Zn, Ni, Mn, V, Ti and Cr were added into the high purity aluminium. Afterwards, more than one element was added simultaneously to find any additive effects on the conductivity of the aluminium. Gauthier divided the investigated metallic additions into three categories on the basis of their impact on reducing the electrical conductivity of super purity aluminium. According to his investigation, Au, Ga, Ni, Si, Fe and Zn had little effect compared to Cu, Ag and Mg. The elements Ti, V, Mn and Cr in the third group were more deleterious to the conductivity of the aluminium. The addition of 0.005% to 0.025% vanadium to the high purity aluminium reduced its conductivity from 64.25% to 60.00% of copper, which is not acceptable for electrical grade applications (Gauthier, 1936).

Dean (1967) investigated the effects of alloying elements and impurities on the properties of aluminium. Several properties of aluminium, including electrical conductivity and resistivity, were discussed in his work. Dean presented the work of Willey (Dean, 1967) on the effect of impurities in reducing the electrical conductivity of aluminium, and this is summarized in Table 2.3. It was demonstrated that the transition metals vanadium, titanium, zirconium, chromium and iron have a greater detrimental impact on the electrical conductivity of aluminium in comparison with copper, nickel and zinc. Metals in solution have a greater influence than their intermetallic compounds that are out of solution with aluminium. The effect of more than one elements was
additive when they went into solution without forming any compounds with each other. In the case of an interaction between the elements, their impact was reduced and the compounds themselves may have some solubility in aluminium. Quenching of aluminium alloys will reduce electrical conductivity because impurities are trapped in the solid solution. Electrical grade aluminium has a limitation of the presence of impurities and its purity should be 99.60% minimum. Willey reported that the addition of 0.01% total of titanium and vanadium reduced the electrical conductivity by 0.8% IACS (International Annealed Copper Standard). It was further reported that the addition of boron half the weight of titanium and vanadium formed TiB₂ and VB₂ insoluble compounds in the melt. Most of the formed compounds settle down in the melt and the remainder will have no significant influence on the electrical conductivity of aluminium (Dean, 1967).

Super pure aluminium for electronic and electrical super conductor applications can be produced using three layer refining or horizontal zone refining processes. However, such super pure aluminium production processes are not cost effective due to their cell operation and maintenance (Kammer, 1999a). Smelter grade aluminium can be used as an electrical conductor more economically if the level of impurities is controlled precisely, especially the concentration of the transition metals Ti, Zr, V, and Cr. The industrial treatment of molten aluminium to remove transition metal impurities is given in next section.

2.4.3 Boron treatment of aluminium melt

From the above it is clear that the impact of impurities, especially transition metals, on electrical conductivity is enormous and should be minimised by taking them out of the solution, as shown in Table 2.3. Transition metal impurities are reactive and can be removed from a solution by the addition of some potential reactive elements. Industrially, the boron treatment of aluminium melt is carried out to remove transition metals. Dube (1983) developed a process to remove transition metals, especially Ti and V, through the addition of boron bearing substances. The mechanical agitation of melt promotes the dispersion of the chlorides or fluorides flux which that acts as a carrier for the (Ti,V)B₂ complex particles. It has also been claimed that alkali metals can be
removed in this process using agitation in the vortex and dispersed fluxes. It was further claimed that the alkali metals fluoro-aluminates, assist in fluxing the boride particles. Boron treatment of molten aluminium was carried out in batches where Al-B master alloys containing AlB₂ or AlB₁₂ boride particles were introduced into the furnace. The borides of the transition metals formed were heavy and readily insoluble in the working process conditions. The particles settled in the furnace by gravity and required the cleaning of furnaces regularly. The process was time and energy intensive, which had a direct effect on the economics of the end product. The fine particles took a longer time to settle, and remained in the melt. The presence of fine particles is deleterious in the later stages of forming and drawing. Fine particles of TiB₂ are added into the aluminium alloys to provide potent nuclei for grain refinement. Usually, the particles generated during boron treatment are too large to act as a grain refiner. The particles of (Ti,V)B₂ were in the size range of 10 µm but few particles were more than 50 µm, and this was also found in the current research. Dube (1983) adopted the approach of adding boron bearing substances such borax directly into an electrolytic cell. This technique has its own limitations due to the settling of the transition metal boride sludge at the bottom of the cell. This approach is relatively more time consuming, and requires the cleaning and closing of electrolytic cells. Other methods reported include the addition of KBF₄ salts into molten aluminium. In this method, boron first reacts with aluminium to form AlB₂/AlB₁₂ particles, which then react with transition metals to form their borides. The direct addition of a boron-bearing rod into the molten stream in the casting mould has also been reported. The removal of impurities is achievable in this process but the formed fine borides cannot be separated from the molten aluminium and solidified within the ingots.

Bearing in mind the limitations of these approaches for transition metal removal, (Dube, 1983) claimed that the addition of boron bearing substances with chloride or fluoride fluxes in a mechanically generated vortex in the melt is most economic and efficient. The removal rate of Ti and V is increased due to agitation. The fluxing material acts as a collector to isolate the fine borides from the molten aluminium. Dube recommended adding sufficient boron bearing substances to remove a major proportion of the Ti and
V. The agitation time needs to be sufficient for the fluxing materials to collect a reasonable amount of the (Ti,V)B$_2$ particles (Dube, 1983). It was further reported that the treatment time of the melt used to reduce the Ti and V (100 ppm each) should be short and consistent. The time needed for the removal of Ti and V was reported as 10 minutes for Al-B alloys addition more than the stoichiometry requirement of Ti and V to form their diborides. The addition of boron should be controlled because of economic factors and the poisoning effect of titanium based grain refiner. The recommended level of boron after the removal of Ti and V is less than 100 ppm. Trials were carried out using different levels of Al-4wt% B, the addition of aluminium fluoride, and a vortex generated by a mechanical rotator for 10 minutes. Temperature variation during the treatment was recorded and the composition was analysed with spectrometer techniques. The details of these tests and their results are shown in Table 2.5 (Dube, 1983). The residual complex boride particle (Ti, V)B$_2$ size distribution in the treated product and compared with other conventional processes for the removal of Ti and V impurities was reported. The addition of fluxes such as AlF$_3$ in the above mentioned process promotes the removal of transition metal borides particles, and hence improves melt cleanliness. The number of different size particles in a square centimetre was reported in Dube’s work and are presented in Table 2.6.

Table 2.5. Details of aluminium boron treatment trials in 4800 kg crucible for 10 minutes (Dube, 1983)

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Temperature (°C)</th>
<th>% B addition</th>
<th>AlF$_3$ kg/tonne</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Before</td>
<td>After</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>822</td>
<td>793</td>
<td>0.014</td>
</tr>
<tr>
<td>2</td>
<td>757</td>
<td>736</td>
<td>0.007</td>
</tr>
<tr>
<td>3</td>
<td>888</td>
<td>869</td>
<td>0.010</td>
</tr>
<tr>
<td>4</td>
<td>843</td>
<td>-</td>
<td>0.010</td>
</tr>
<tr>
<td>5</td>
<td>820</td>
<td>795</td>
<td>0.014</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Ti (ppm)</th>
<th>V (ppm)</th>
<th>B (ppm)</th>
<th>Ratio B addition/Stoic Req.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>X</td>
<td>√</td>
<td>X</td>
<td>√</td>
</tr>
<tr>
<td>1</td>
<td>34</td>
<td>&lt; 10</td>
<td>28</td>
<td>&lt; 10</td>
</tr>
<tr>
<td>2</td>
<td>42</td>
<td>10</td>
<td>55</td>
<td>&lt; 10</td>
</tr>
<tr>
<td>3</td>
<td>42</td>
<td>&lt; 10</td>
<td>52</td>
<td>&lt; 10</td>
</tr>
<tr>
<td>4</td>
<td>46</td>
<td>&lt; 10</td>
<td>59</td>
<td>&lt; 10</td>
</tr>
<tr>
<td>5</td>
<td>41</td>
<td>&lt; 10</td>
<td>60</td>
<td>&lt; 10</td>
</tr>
</tbody>
</table>

*X- Before boron addition

*√- After boron addition
The claims of Dube’s investigation also included the removal of Ti, V, Li, Na and Ca in the same process. The shorter (5 to 10 minutes) melt treatment time has economic advantages and the final product has minimum borides inclusions.

Table 2.6. (Ti,V)B\textsubscript{2} complex-size (µm) distribution (No/cm\textsuperscript{2}) (Dube, 1983)

<table>
<thead>
<tr>
<th>Test No.</th>
<th>&lt;5</th>
<th>6 - 10</th>
<th>11 - 20</th>
<th>21 - 30</th>
<th>31 - 50</th>
<th>&gt;50</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>18</td>
<td>15</td>
<td>4</td>
<td>1</td>
<td>2</td>
<td>0.1</td>
<td>40.1</td>
</tr>
<tr>
<td>3</td>
<td>9</td>
<td>6</td>
<td>2</td>
<td>0.2</td>
<td>0.2</td>
<td>0.06</td>
<td>17.5</td>
</tr>
<tr>
<td>4</td>
<td>25</td>
<td>12</td>
<td>3</td>
<td>1</td>
<td>1</td>
<td>0.4</td>
<td>42.4</td>
</tr>
<tr>
<td>5</td>
<td>42</td>
<td>11</td>
<td>4</td>
<td>2</td>
<td>0.5</td>
<td>0.4</td>
<td>59.9</td>
</tr>
<tr>
<td>Furnace settled, using Al-4%B, 90 ppm boron</td>
<td>145</td>
<td>35</td>
<td>40</td>
<td>20</td>
<td>7</td>
<td>1</td>
<td>248</td>
</tr>
<tr>
<td>Through addition Al-3%B rod, 90 ppm boron</td>
<td>160</td>
<td>90</td>
<td>51</td>
<td>16</td>
<td>2</td>
<td>1</td>
<td>320</td>
</tr>
</tbody>
</table>

Stiller and Ingenlath (1984) investigated the removal of Ti, V, Zr, Cr and Mn on an industrial scale and the effect of boron treatment on the grain refinement of electrical grade aluminium alloys. It was reported that boron treatment of aluminium melt depends upon the specific working conditions but the adequate removal of transition metals could only be achieved by the addition of boron excess to stoichiometry requirement. The excess boron addition exceeds by several times the actual stoichiometry of combining transition metals into their insoluble borides. A formula was proposed to calculate the boron required, based on the proportion of Ti, V, Zr and Cr in the smelter grade aluminium. The stoichiometry requirement of boron can be calculated by the summation of Ti, Zr, V and Cr (on weight basis) in the melt using the formula given in Eq. (2.3).

\[
Ti + V + Zr + Cr : B = 2.3 : 1
\]  
(2.3)
The concept of boron deficiency and excess was also introduced in mathematical form in their research. Dube, (1983) also reported the need for excess boron but gave no further details in his patent. Boron deficit and excess can be calculated using Eq. (2.4). A negative sign represents the boron deficit, thus more boron is required to achieve the stoichiometry needs of transition metals.

\[
B - \frac{Ti + V + Zr + Cr}{2.3} = 0
\]  
(2.4)

A quick reference is given in Figure 2.5 to determine any boron deficit or excess in the case of known melt chemistry. A required boron quantity, based on the summation formula and the chemical analysis of molten aluminium, is given in Figure 2.6.

![Figure 2.5](image)

**Figure 2.5.** Reference chart to determine boron excess or deficit based on total concentration of transition impurities in molten aluminium (Stiller and Ingenlath, 1984)

The exact addition of boron in a tonne can be calculated by considering the boron content in the Al-B master alloy \(B_v\) given in Eq. (2.5).

\[
\frac{(Ti + V + Zr + Cr)}{2.3} \cdot \frac{1000}{B_v}
\]  
(2.5)
In the above calculations, the most stable boride phases TiB$_2$, VB$_2$, ZrB$_2$ and CrB$_2$ of Ti, V, Zr and Cr were assumed. It was further assumed that the proportion of Ti, V, Zr and Cr in the melt was 50%, 45%, 3% and 2% respectively.

In the batch processes, boron left in the aluminium at the end is not representative of the total addition because, during treatment, boron in the form of transition metal borides will settle at the bottom of the furnace or ladle. Al-B addition in the inline processes is carried out just before solidification and the boride particles formed do not have sufficient time to settle and separate from the main molten pool. In such processes, the boron left in the metal at the end of process will represent the actual boron addition. Chemical analysis will not reveal any reduction in transition metal content but the boron present will represent the added quantity. The summation formula given in Eq.2.3 is limited in its use because it will not give any boron deficit or excess in the metal at the end of treatment. Moreover, in the inline boron treatment processes, the effectiveness of impurity removal cannot be quantified.

![Figure 2.6. Estimation of boron quantity required from chemical analysis of aluminium melt (Stiller and Ingenlath, 1984)](image)

Usually grain refinement of electrical grade aluminium is carried out after boron treatment. The addition of boron during the treatment will determine the quantity of grain refiner, which is usually an AlTi5B alloy. If there is excess boron in the melt,
more grain refiner will be required to achieve the required grain refinement. Moreover, it has been observed that wire grain refinement has no adverse effect on the electrical conductivity of aluminium. It was reported that the Al$_3$Ti intermetallic phase in the AlTi$_5$B grain refiner has a limited time for dissolution during the wire addition in the launder and titanium will not be released and form solution with the aluminium (Stiller and Ingenlath, 1984).

Setzer and Boone, (1991) investigated the use of Al-4wt% B (AlB$_{12}$) and Al-5wt% B (AlB$_2$) master alloys from KB Alloys. The reaction rate of AlB$_2$ and AlB$_{12}$ phases with transition metals was experimentally studied in a 10 kg resistant furnace. Commercial purity aluminium (99.7%) was melted in an induction furnace able to carry 70 kg of melt, then argon gas was flushed, and 10 kg melt was then transferred to a resistant furnace. The temperature was stabilized at 677°C in the resistant furnace. The chemical composition was determined by optical emission spectroscopy which revealed the presence of 0.0054% Ti, 0.013% V and 0.0042% Cr in the melt. The boron additions were made 0.013% and 0.052% in the first series of experiments. Ingots of Al-4wt% B (AlB$_{12}$) and Al-5wt% B (AlB$_2$) were used and the melt was stirred for 30 seconds (no more details of stirring were reported). Samples were taken at intervals of 0.5, 1, 2, 3, 4, 5, 10, 15, 30, 60, 120 and 208 minutes and were cast into analytical disc specimens. The first level of boron addition (0.013%) was in a 20% nominal safety factor ensuring excess boron. Another level of boron addition 0.052% was 5 times higher than the total requirement of Ti + V + Cr contents (0.0226%) in the melt. Electrical conductivity was measured using the eddy current technique in this study.

The results of the electrical conductivity measurements of melt treated with Al-5wt% B (AlB$_2$) are shown in Figure 2.7. From Figure 2.7, it can be seen that the increase in electrical conductivity is dramatic and represents the removal of Ti, V and Cr from the aluminium solution into their borides. The rate of the AlB$_2$ reactions with Ti, and V were very fast and completed within 1 minute of the addition of Al-5wt% B (AlB$_2$) ingots into the melt. The increase in electrical conductivity in the melt was observed from 60.9% IACS (International Annealed Copper Standard) to 61.9 IACS in the first minute of boron addition. It was reported that the addition of 0.0138% V, 0.0175% Ti
and 0.0126% Cr to the solution decreased the electrical conductivity by 1.0% IACS, that makes commercial purity aluminium unacceptable for electrical grade applications. A slow settling rate of transition metal borides was observed, which was determined by the percentage of Ti + V + Cr originally present in the melt. The settling of borides particles continued over a period of several hours, as shown in Figure 2.7.

The comparative analyses of AlB\(_2\) and AlB\(_{12}\) reactions and their settling rates are given in Figure 2.8 and 2.9. It was assumed that dispersion of aluminium borides would take 15 to 30 seconds and then a reaction would take place with the transition metals. The reaction of AlB\(_{12}\) was delayed although completed in 3 to 4 minutes, but the reaction of AlB\(_2\) was immediate and completed within 1 minute. Setzer and Boone reported the addition of boron in excess to the stoichiometry requirement of Ti, V and Cr has no significant effect on increasing the electrical conductivity of aluminium, as can also be seen in Figure 2.8. This argument was supported by the fact that boron has limited solubility in liquid aluminium (0.022% at eutectic) and solid solubility is negligible. Moreover, the boron effect on the reduction of electrical conductivity in the aluminium
is small compared with transition metals. An excess of 0.4% boron will reduce the electrical conductivity of aluminium by 1% IACS.

![Figure 2.8. Comparative analysis of AlB$_2$ and AlB$_{12}$ phase reaction rate with Ti, V and Cr in aluminium melt (Setzer and Boone, 1991)](image)

The settling rate of borides generated by AlB$_{12}$ was reported to be faster, compared to the AlB$_2$ phase, as can be seen in Figure 2.9. The same settling trend was observed in both the laboratory and industrial trials, which confirmed the faster settling of AlB$_{12}$ generated borides. In the case of aluminium melt treated with AlB$_2$, 25% of the boride particles settled in 10 minutes and 40% in 30 minutes, which is much less than the 42% in 10 minutes and 75% in 30 minutes for the AlB$_{12}$ phase. The morphology of AlB$_2$ particles was observed as equiaxed or hexagonal with occasional platelet structures. The AlB$_{12}$ phase predominantly consisted of platelet structured that exhibited clustering among the particles. TiB$_2$ and other borides were pushed to the grain boundaries due to their inertness towards solidification of aluminium. More borides formed by AlB$_2$ were found in the specimen, as compared to AlB$_{12}$ due to their dense, coarse particle size. It was concluded that AlB$_2$ and AlB$_{12}$ are effective agents for the removal of transition metals from molten aluminium and the reaction of AlB$_2$ was relatively faster than in the case of AlB$_{12}$ phase. The settling rate of AlB$_{12}$ generated borides was faster compared to
AlB$_2$ and the addition of only a little excess boron had no significant effect on the electrical conductivity of aluminium (Setzer and Boone, 1991).

![Graph](image)

**Figure 2.9.** Settling rate of borides generated by AlB$_2$ and AlB$_{12}$ phase (Setzer and Boone, 1991)

Cooper and Kearns (1996) studied boron treatment in more detail and reported on the action mechanism of boron with impurities. The events taking place during the process were explained in terms of impurity diffusion, mass transfer and the settling of boride particles. It was reported that transition metal boride formation depends upon the availability of aluminium boride surfaces for reaction and impurity diffusion rather than on the thermodynamics of relative borides. In this research, experiments were conducted in a resistance-heated furnace using 12 kg aluminium melt. Commercial purity (99.7%) aluminium (V < 30 ppm and (Ti, Cr and Zr) all < 20 ppm) was used in all the experiments, and was inoculated with Ti and V master alloys to raise their concentration level to 100 ppm. Boron was added at 25, 50, 75 and 100% excess to the stoichiometry requirement of transition metal diborides formation. Stirring of melt was carried out, followed by sampling with minimal disturbance just below the melt surface. Aluminium boron master alloys Al-3wt% B and Al-5wt% B having an AlB$_2$ predominant phase, and Al-4wt% B and Al-5wt% B having an AlB$_{12}$ phase were employed as the source of boron.
The results of this investigation suggested a logarithmic decay of impurities elements caused by the addition of aluminium boron master alloys. The boride particles observed had different settling rates due to their density, size and shape. The sludge formed by the AlB$_2$ phase was found to be thicker than that formed with AlB$_{12}$ which was highly enriched with Ti (45%) and V (33%) and significantly enriched with Cr (> 10%) and Zr (> 5%). The microstructure of the borides showed that aluminium borides were present for the first 5 minutes and totally dissolved after 120 minutes of the treatment. Moreover, it was reported that boride core was enriched in aluminium and depleted in Ti and V. An increase in the conductivity was observed in the first 2 minutes of boron treatment, which corresponded to a 70% increase where only 10% boride particles had settled. Different levels of boron addition (25, 50, 75 and 100 % excess) revealed that a maximum increase in conductivity was achieved at 75% excess. The required addition of boron was dependant on the boron treatment time, for instance a shorter time (30 minute), and 50 to 75% excess was recommended.

Setzer and Boone (1991) suggested that AlB$_2$ reacts faster than AlB$_{12}$ but Cooper and Kearns (1996) reported that it has no practical significance. The particle size of AlB$_2$ and AlB$_{12}$ is the main factor determining the reaction with transition metals. As the particle size of AlB$_2$ is smaller it will react faster and will settle more slowly than the larger particles of AlB$_{12}$ which react more slowly and settle faster. The density of AlB$_2$ (3.19 g/cm$^3$) is more than that of AlB$_{12}$ (2.55 g/cm$^3$), which is, in turn, comparable with aluminium melt (2.35 g/cm$^3$) (Cooper and Kearns, 1996). However, AlB$_{12}$ settles faster because its density increases rapidly when reacting with impurities elements. The extent of the reaction between AlB$_2$, AlB$_{12}$ and transition metal impurities is not completely known but some SEM/EDX and SIMS analyses suggest that it is incomplete. This hypothesis is supported by the coring of borides, which are enriched in aluminium and depleted in transition metals. The diffusion of impurities to the aluminium boride surfaces took place in a few seconds (assuming melt diffusion coefficient D = 3 x 10$^{-5}$ cm$^2$/s) as they react to nucleate transition metal borides followed by clustering. The clusters settle faster, leaving the melt with fewer impurities in the solution and possessing greater electrical conductivity (Cooper and Kearns, 1996). Cooper and
Kearns (1997) extended their investigation to the effect of residual V on different grain refiners and electrical conductivity. It was reported that V contents should be below a certain threshold level to give adequate grain refinement without compromising electrical conductivity. Moreover, it was found during experiments that residual V had no effect on the grain refiners. The borides of Ti formed in preference to V so that the excess boron present in the melt formed TiB₂ rather than VB₂. Grain refiners of TiBAL are composed of TiB₂ particles covered by TiAl₃, which provide a potent site for the nucleation of α-Al during solidification. The TiAl₃ particles also dissolved to release Ti, which provided constitutional supercooling and promoted grain refinement. The constitutional supercooling phenomenon is absent when there is excess boron. The best balance between electrical conductivity and grain refinement was suggested as being 10 to 50 ppm excess boron (Cooper et al., 1997).

The action mechanism of boron with transition metal impurities was explained by Wang et al. (2002). Commercial purity aluminium (99.7%) containing 0.196% Fe, 0.005% Ti, 0.10% V, 0.002 % Zr, 0.004% Cr and 0.004% Mn was melted in a graphite crucible in a resistance heated furnace. Two crucibles were used each containing 2 kg aluminium melt held at a temperature of 700 ± 10 °C. Boron was added to one crucible only in the proportion of 0.06% B using an Al-B (AlB₂) master alloy containing 3.35% B. The melt was stirred for 30 seconds and held at the same temperature for 2 hours followed by solidification outside the furnace in air. The dimensions of the crucible used are shown in Figure 2.10. Sections made from boron treated and boron free ingots were analysed using SEM, EDX and XRD. The concentration of boron was analysed by ICP analysis. The extraction of borides from the settled residue was carried out by dissolving fine chips in methanol containing iodine and tartaric acid. Electrical resistivity was measured using a 2.28 mm diameter rod according to IEC 468 standards.

SEM results showed a similar morphology in the upper part in both cases. They observed two kinds of insoluble borides in the residue of decanted aluminium melt. The bottom sections contained different phases, which were observed as α-aluminium matrix, hexagonal and lath shapes, and fine clusters. The particles in a hexagonal shape were detected as borides of AlB₂ having 78.59% B, 14.97 % Al and 2.56 % (mole
fraction) transition elements. The lath shape, after deep etching, was identified as FeAl$_3$, which is normally found in aluminium alloys due to the high content of Fe in the initial material. The fine cluster compounds were composed of 54.42 % B, 13.70 % Al and 23.39 % (mole fraction) transition elements Ti, V, Zr and Fe. Using EDX analysis, Cr and Mn were not detected in any phase. X-ray diffraction of the residue that settled at the bottom of the settling ingots confirmed the presence of AlB$_2$, TiB$_2$ and FeAl$_3$ phases formed by a reaction between the boron and transition metals.

![Figure 2.10. Dimensions of the settling ingots and cross section investigated (Wang et al., 2002)](image)

Wang et al. (2002) was reported on the formation of iron boride in this investigation. Previous researchers detected the borides of Ti, V, Zr and Cr but not Fe. Wang et al. detected Fe in the residue of borides and explained that the presence of Fe is higher than its solubility (0.04%) in aluminium.

Usually, excess Fe is observed as FeAl$_3$ in aluminium alloys and is converted from one intermetallic into another (boride). Once boron is introduced into the melt in the form of Al-B master alloys, boron in excess of the solubility (0.022%) will remain as AlB$_2$ or AlB$_{12}$ phase. The boron in solution will react with trace element impurities and form fine boride particles that have a tendency to cluster. The presence of transition impurities in the hexagonal AlB$_2$ phase (possessing similar lattice parameters to other
borides) gives an indication of a solid solution of diborides, which has been reported by earlier investigators (Dube, 1983, Setzer and Boone, 1991, Cooper and Kearns, 1996). Moreover, Wang et al. assumed that the reaction of aluminium borides with transition metals was incomplete and that there was no evidence of Zr removal, which contradicted the results of previous investigators (Stiller and Ingenlath, 1984, Cooper et al., 1997). The decrease in electrical resistivity was suggested as 86.2% of what can be achieved by the complete removal of impurities from the aluminium melt (Wang et al., 2002).

Most of the previous investigations were carried out on a laboratory scale and the results were found to be quite consistent except for the removal of Zr, Cr and Fe. Karabay and Uzman (2005) inoculated transition elements by adding AlB₂ and AlB₁₂ to 99.6% pure aluminium in a CCL (continuous casting line) to manufacture conductors. Industrial trials were carried out on commercial grade aluminium (99.6%) containing 0.013% Ti, 0.011% V and 0.006% Cr impurities by employing Al-5wt%B (AlB₁₂), Al-4wt%B (AlB₁₂) and Al-3wt%B (AlB₂) master alloys in the form of rods, waffles and ingots. Spectral analysis of impure, EC grade aluminium and the standard requirements can be seen in Table 2.7.
The samples taken from the initial untreated aluminium, the inoculated aluminium and the electrical grade (EC) aluminium (99.7%) were investigated under SEM/EDX. The industrial set up of the CCL is shown in Figure 2.11. It consists of a melting furnace (2.5 tonne capacity), two holding furnaces, a CCL wheel and rolling machines. Trials were conducted in three stages. In stage one, Al-5wt% B (AlB$_{12}$) waffles were introduced in the holding furnace and the melt was gently stirred then held for 2 hours at 850°C. Inoculation in stage 2 and 3 was carried out in a launder to a feed casting wheel in the form of Al-4wt% B (AlB$_{12}$) and Al-3wt% B (AlB$_{2}$) wires. Stage 1 experiments were reported to be unsuccessful due to the batch processes that caused capacity loss. The clogging of the launder due to excessive melt oxidation interrupted the CCL unit, was and therefore not economically viable.

Table 2.7. Spectral analysis of impure and commercial EC grade aluminium with standard limits for EC grade impurities (Karabay and Uzman, 2005a, ASTM, 2005)

<table>
<thead>
<tr>
<th>Element</th>
<th>Impure Al 99.6% (wt %)</th>
<th>Commercial EC-grade 99.7%</th>
<th>Specification limits of EC grade Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon</td>
<td>0.08</td>
<td>0.06</td>
<td>Max. 0.07</td>
</tr>
<tr>
<td>Iron</td>
<td>0.20</td>
<td>0.14</td>
<td>0.13 – 0.20</td>
</tr>
<tr>
<td>Copper</td>
<td>0.001</td>
<td>-</td>
<td>Max.0.01</td>
</tr>
<tr>
<td>Zinc</td>
<td>0.030</td>
<td>0.02</td>
<td>Max.0.02</td>
</tr>
<tr>
<td>Magnesium</td>
<td>-</td>
<td>0.003</td>
<td>Max.0.01</td>
</tr>
<tr>
<td>Titanium</td>
<td>0.013</td>
<td>0.003</td>
<td>Max.0.005</td>
</tr>
<tr>
<td>Vanadium</td>
<td>0.011</td>
<td>0.002</td>
<td>Max.0.005</td>
</tr>
<tr>
<td>Chromium</td>
<td>0.006</td>
<td>0.003</td>
<td>Max.0.005</td>
</tr>
<tr>
<td>Manganese</td>
<td>0.021</td>
<td>0.001</td>
<td>Max.0.005</td>
</tr>
<tr>
<td>Other elements</td>
<td>0.003</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Aluminium</td>
<td>99.63</td>
<td>99.76</td>
<td>99.7</td>
</tr>
</tbody>
</table>

The trials carried out in stage 3 using Al-3wt% B (AlB$_{2}$) were found to be successful operationally, economically and in meeting the electrical conductivity (61.5% IACS) requirement. A cross section of the launder used to transfer the metal to the casting wheel is shown in Figure 2.12. The borides of the transition metal formed in the stage 2 and 3 trials could not be separated and hence remained inside the metal as inclusions.
Previous researchers recommended the use of an AlB$_2$ phase where the melt treatment time was short and a high reaction rate was required (Dube, 1983, Setzer and Boone, 1991). The findings of Karabay and Uzman (2005) support the arguments made by earlier investigators. The SEM/EDX analysis of samples revealed the formation of Ca-aluminate/phosphate, dross and an intermetallic of FeAl$_3$. The fine particles of the transition metals diborides TiB$_2$, VB$_2$, ZrB$_2$ and CrB$_2$ were not detected in his research, probably because of the short reaction time and the limitation of the SEM resolution. An increase in the electrical conductivity was the main evidence of the removal of the transition metal impurities from the solution into their fine borides. All phases observed were in oxides and silicates. During EDX analysis, weak peaks of Si, Ti and B were detected in the oxides, providing further evidence of the formation of transition metal borides (Karabay and Uzman, 2005a, Karabay and Uzman, 2005b).

The removal of Fe from commercial purity aluminium using Na$_2$B$_4$O$_7$ with NaCl and KCl salts was investigated more recently by Gao et al. (2007, 2009). Their starting material was composed of 0.3304% Fe, 0.0019% Mn, 0.0122% Ca, 0.0060% Cu, 0.0076% Na, 0.0136% B, and 0.0066% Zn and balanced aluminium. Experiments were conducted in a resistance furnace using a ceramic crucible at 993 K. The samples were analysed using SEM, OM, XRD and ICP-AES material characterizing techniques. It
was reported that the Fe contents dropped from 0.3304% to 0.1805% during purification with the $\text{Na}_2\text{B}_4\text{O}_7$ compound. Thermodynamic calculations were based on the assumption of an ideal solution, where the activities of the elements were exchanged with their mole fractions, although this is not the case in actual solutions. The calculated Gibbs free energy of the entire reaction involved in Eq. (2.6) was negative, which supported their assumption of $\text{Fe}_2\text{B}$ formation.

$$
\text{Na}_2\text{B}_4\text{O}_7(s) + \frac{14}{3} \text{Al}_l(l) + 8\text{Fe}_l(l) = \frac{7}{3} \text{Al}_2\text{O}_3(s) + 4\text{Fe}_2\text{B}(s) + 2\text{Na}_l(l) \quad (2.6)
$$

$$
\Delta G_{993K} = -51473087 \, j/\text{mol} \quad (2.7)
$$

The x-ray diffraction pattern also detected mullite, $\text{Al}_2\text{O}_3$ and $\text{Fe}_2\text{B}$ phases in the melting sludge, which is shown in Figure 2.13.

![X-ray diffraction pattern of aluminium melting sludge](image)

Figure 2.13. X-ray diffraction pattern of aluminium melting sludge (Gao et al., 2007b, Gao et al., 2009b)

It was further reported that the needle like FeAl$_3$ phases at the grain boundaries became thinner after treatment with $\text{Na}_2\text{B}_4\text{O}_7$. The apparent grain refinement was observed after purification that may due to the heterogeneous nucleation of residual boride particles and therefore it can act as a grain refiner. An optical image of the purified aluminium showing the difference between the FeAl$_3$ phases is provided in Figure 2.14. Kinetic
analyses revealed that the Fe removal increased with holding time, and this follows the first order exponential decay law.

![Image](image.jpg)

Figure 2.14. Optical micrographs of the aluminium samples: (a) before purification and (b) after purification (Gao et al., 2007b, Gao et al., 2009b)

The effect of boron on the removal of Fe in the presence of Ti and V from aluminium melt was investigated by the Gao et al. (2009), using a treatment similar to boron treatment. This was discussed previously, in detail. Results showed that Fe could not be removed from molten aluminium by the addition of Al-B master alloys. Thermodynamic calculations based on assumptions of an ideal solution revealed that Ti could reduce AlB$_2$ to form TiB$_2$. Thermodynamically V also reacted with B to form stable borides. Theoretically, Fe cannot reduce AlB$_2$ directly or react with B to form their borides in the given conditions.

There was no evidence of any formation of Fe borides in the SEM micro-structural analysis. EDX analyses revealed the presence of Ti, V and Al in the sediment particles. Borides of Ti, V and Al were detected during XRD analyses. It has been suggested that the lowest Fe concentration that can be purified by boron, as with other transition metals, was approximately 11.7 wt% (Gao et al., 2009a). The detection of FeB$_2$ in previous work of Gao et al. was assumed to be due to a reaction of B$_2$O$_3$ with Fe, which purified the aluminium melt (Gao et al., 2009a). Zhang et al. (2012), in their review article, briefly discussed the detrimental effect of Fe intermetallic phases on the mechanical properties of aluminium alloys. They reviewed the removal of iron from
aluminium melts in the form of sludge, frictional solidification, electro refining and the addition of fluxes (Zhang et al., 2012). Removal of Fe from aluminium of commercial purity further increases conductivity, as was previously discussed in detail.

### 2.5 Metallurgical thermodynamics

According to Thomson and Berthelot, the tendency for a reaction to take place is determined by the heat of the reaction. For a spontaneous reaction to occur, heat must be given off by the system and signed as negative. The enthalpy term is a heat absorbed or evolved during a reaction at constant pressure, and is given by Eq. (2.8).

\[ H = E + PV \quad (2.8) \]

The enthalpy change of a system while going from temperature T (298.15 K) to T is given by Eq. (2.9).

\[ \Delta H_T = \Delta H_{298.15} + \int_{298.15}^{T} \Delta C_P dT \quad (2.9) \]

Where \( \Delta C_P \) the changes in heat capacities of reactants and products, \( \Delta H_T \) is the enthalpy of formation at temperature T and \( \Delta H_{298.15} \) is the enthalpy of formation at 298.15 K. According to the second law “the entropy of a closed system will always increase (in a reversible process) or stay constant (in equilibrium)”. For a spontaneous process to occur \( \Delta G \) must be negative and the change in the Gibbs free energy at constant pressure is given by;

\[ \Delta G = \Delta H - T \Delta S \quad (2.10) \]

Heat capacity can be used to determine a change in Gibbs free energy and the entropy of a system, which has been given by Eq. (2.11) and Eq. (2.12).

\[ S_T = S_{298.15} + \int_{298.15}^{T} \frac{C_P}{T} dT \quad (2.11) \]

\[ G_T = H_{298.15} + \int_{298.15}^{T} C_P dT - T(S_{298.15} + \int_{298.15}^{T} \frac{C_P}{T} dT) \quad (2.12) \]
Where \( S_{298.15} \) is the entropy of a substance at 298.15 K. By using Eq. (2.12), the total Gibbs free energy of a substance, with the help of heat capacity, can be calculated. The Gibbs free energy of a phase with a fixed composition can be written as an empirical relation similar to heat of capacity, if the pressure and magnetic dependence are ignored,

\[
G = A + BT + CT \ln T + DT^2 + ET^{-1} + FT^{-3} + \ldots
\]  

(2.13)

In equilibrium, reactants and products will be in equilibrium and will have the same Gibbs free energy \( (G = 0) \). In such a situation, product activities will be equal to the equilibrium constant, and then the standard Gibbs energy of reaction will be equal to;

\[
G_o = -RT \ln K_a
\]  

(2.14)

This relationship is very useful for the reactions of oxidation and reduction of metals, as has been given on the Ellingham diagram for various metals (Saunders and Miodownic, 1997).

### 2.5.1 Gibbs free energy minimisation

Experimental techniques are not the only methods to construct phase diagrams. The determination of thermodynamic properties (heat capacities, enthalpy, excess energy) are also useful in phase equilibria, hence the construction of phase diagrams of various systems. A simple system is given in Figure 2.15(a), which shows a single-phase (\( \alpha \)) field at higher temperatures. At a low temperature (critical), this phase becomes unstable due to repulsive interaction between the constituent components (\( A, B \)) and transforms into two separate phases (\( \alpha_1, \alpha_2 \)). The associated Gibbs energy vs mole fraction (\( G/X \)) diagram is given in Figure 2.15 (b), which shows a single minimum at high temperatures, while at low temperatures it shows a central hump and two separate minima by further lowering the Gibbs energy of the system (Saunders and Miodownic, 1997).

A stable phase at a high temperature will lower its Gibbs free energy with a decrease in temperature, and at a critical temperature it will become unstable. At this critical temperature, the Gibbs free energy will be lowered through the formation of two
separate phases. The mixture will keep on decreasing in energy until no more change in phases can take place. This will be a state of equilibrium, when the phases in the system will have a minimum of Gibbs free energy. That is components \( A \) and \( B \) have the same chemical potential in both \( \alpha_1 \) and \( \alpha_2 \) phases. Mostly, phase diagrams are constructed by performing Gibbs free energy minimisation with respect to the composition of component \( A \) or \( B \) in a system. Another method is to minimise difference in the chemical potential of components \( A \) and \( B \) in the phases.

![Phase diagram](image)

**Figure 2.15.** (a) Phase diagram for A-B binary system showing a miscibility gap, (b) respective (G/X) diagram at different temperatures

2.5.2 Solution thermodynamics

In practice, real systems have solubility of species in each other, and are hence called a solution. The species making a solution are defined as components. The total Gibbs energy of a binary solution is composed of three parts.

\[
\Delta G^{\text{sol}} = \Delta G^{\text{reference}} + \Delta G^{\text{ideal}} + \Delta G^{\text{excess}}
\]  

(2.15)

Where \( \Delta G^{\text{reference}} \) the standard Gibbs energy of pure components making a solution is given by

\[
\Delta G^{\text{reference}} = \sum x_i G_i^o
\]  

(2.16)
2.5.3 Activity and activity coefficient

If the chemical potential in a unary or multi-component is known as a function of temperature, pressure and composition for one component, then all other thermodynamic properties of that system can be computed. The change in the partial chemical potential \( d\Delta \mu_k \) of a component \( k \) in a system is equal to the change in partial Gibbs free energy \( \Delta \tilde{G}_k \). Experimental determination of thermodynamic properties is not based on the measurements of chemical potential, but rather using another property of component \( k \), known as activity. The activity in terms of chemical potential will be,

\[
\mu_k - \mu_k^0 = \Delta \mu_k = \Delta \tilde{G}_k = RT \ln a_k
\]

Where \( a_k \) is the activity of a component at a given temperature, pressure and composition and \( R \) and \( T \) are gas constant and temperature. It is a unit less quantity. Another convenient measure of solution behaviour is the measure of activity coefficient of component \( k \) and is given by,

\[
a_k = \gamma_k X_k
\]

Now change in the chemical potential of a component in a multi-component system can be written in the form of the activity coefficient, which is usually measured experiment.

\[
\mu_k - \mu_k^0 = \Delta \mu_k = RT \ln a_k = RT \ln \gamma_k X_k
\]

If \( \gamma_k = 1 \), the activity of component \( k \) is equal to its mole fraction in that system and the behaviour of the solution will be determined by its composition only. This gives the conditions of an ideal solution. If \( \gamma_k < 1 \) then \( a_k < X_k \), which suggests that there are less components of \( k \) given by the composition, and that the solution deviates negatively from an ideal behaviour. If \( \gamma_k > 1 \) means the activity of a component \( k \) is more than its composition and the solution deviates positively from an ideal behaviour. The graphical representation of ideal and real solution with positive and negative deviation is given in Figure 2.16 (DeHoff, 1993).
2.5.4 Ideal solutions

It is assumed, in an ideal solution, that components have no interaction between each other, and hence the heat of mixing $H_{mx} = 0$ will be zero. Excess energy contribution will be due only to their random mixing (configuration entropy of mixing). The total energy of an ideal solution will be the sum of the change in standard Gibbs energy and the ideal mixing energy and can be written as;

$$G_{ideal}^{sol} = \sum x_i G_i^o + RT \ln(x_i \ln x_i)$$  \hspace{1cm} (2.20)

Ideal mixing is usually assumed for gases where it predicts thermodynamic properties very well. For condensed phases it is not reasonable to assume ideal mixing as there is always some interaction between atoms (Saunders and Miodownic, 1997, DeHoff, 1993).

2.5.5 Real solutions

In real solutions, the heat of mixing $H_{mx}$ is not zero as is the case in an ideal solution. The heat of mixing will be a function of composition, although entropy will be similar to that of an ideal solution, which is a random mixing $S_{mx} = -R \ln(x_i \ln x_i)$.

The simplest form of a real solution is a regular solution where interaction between components is incorporated in the solution excess energy of mixing. The interaction energies between atoms $A-A$, $B-B$, $A-B$ are given by $E_{AA}$, $E_{BB}$ and $E_{AB}$ that are assessed and then a solution interaction parameter is introduced to incorporate interaction energies. The excess energy of a real solution will be,

$$\Delta G^{excess} = x_a x_b L_{a,b}$$  \hspace{1cm} (2.21)

In Eq. 2.21, $L$ is a solution interaction parameter, which is a function of temperature in a regular solution. It is determined by the interaction energies of an atom. Now the change in the total Gibbs free energy of a regular solution can be written as Eq. (2.22),

$$G^{sol} = \sum x_i G_i^o + RT \ln(x_i \ln x_i) + \sum \sum x_i x_j L_{i,j}$$  \hspace{1cm} (2.22)
In a sub-regular solution, the interaction energy varies linearly with composition and the expression for $G^{\text{excess}}_{\text{mix}}$ will become,

$$G^{\text{excess}}_{\text{mix}} = x_i x_j (L_{i,j} x_i + L'_{i,j} x_j)$$  \hspace{1cm} (2.23)

The generalized expression using the Redlich - Kister polynomial for the excess energy from mixing can be written as,

$$G^{\text{sol}} = \sum x_i G^0_i + RT \ln(x_i \ln x_i) + \sum \sum_{i,j} x_i x_j \sum L_{i,j}^\nu (x_i - x_j)^\nu$$  \hspace{1cm} (2.24)

Where $L_{i,j}$ is a binary interaction parameter on the value of $\nu$ and $G^{\text{excess}}_{\text{mix}}$ will become regular when $\nu = 0$ and sub-regular when $\nu = 1$. In the FactSage thermodynamic package, the excess component of Gibbs free energy is calculated using the Redlich-Kister polynomial for liquid phases. The extrapolation of excess Gibbs energy to a multi-component is based on the summation of binary and ternary excess components. For sub-regular solutions, the most widely used equations are given by Muggianu’s, Kohler’s and Toop’s, but the selection should be made with care, taking into account the system under investigation (Saunders and Miodownic, 1997, DeHoff, 1993).

### 2.5.6 Dilute solutions

Consider a pure component $A$ when the addition of a few atoms of component $B$ will form a dilute solution. The few atoms of $B$ will only reduce small numbers of $A$. They will have little effect on its properties because only a fraction of the atoms $A$ and $B$ will be next to each other. In such a situation, solvent atoms act as if they are in an ideal solution where activity is equal to their concentration. This behaviour of a solution is known as Raoult’s law for solvents, and for component $A$ it can be written as,

$$\lim_{x_i \to x_i} a_A = x_A$$  \hspace{1cm} (2.25)

In the same dilute range, solute atoms $B$ will be completely surrounded by the solvent atoms until sufficient solute atoms are added that their spheres of influence will begin to interact. In that dilute range, each solute atom added will have the same influence on the properties of the solution and hence the average properties of solute atoms will be proportional to their concentration. This behaviour is different for different solutes.
added in the same solvent. This behaviour of solution is known as *Henry’s law for solutes* and is given by,

$$ \lim_{X \to 0} a_B = \gamma^o X_B \quad \text{(2.26)} $$

Here, $\gamma^o$ is the Henry's constant and is independent of the solute concentration in solution. It depends upon temperature and pressure. It can be concluded that Henry’s Law will be obeyed if the activity of the solute is proportional to its concentration in that solution. The mole fraction is not convenient for metallic solutions, hence wt% solute with a standard state of 1 wt% in relevant solvent metal is assumed. Then Henry’s Law for component “$i$” will become,

$$ a_i = X_i \quad \text{(2.27)} $$

Now the proportionality constant has disappeared and hence Eq. (2.27) says the activity of a component in a dilute solution is simply equal to its concentration. Activity may deviate from this unit activity and, indeed, it happens in many real solutions. When deviation occurs, it can be written in terms of a concentration multiplied by an activity coefficient, and is given in Eq. (2.28) (DeHoff, 1993, Engh, 1992)

$$ a_i = f_i [%] \quad \text{(2.28)} $$

![Figure 2.16. Activities in liquid mixtures of copper and iron at 1550°C with Henry’s Law tangent for Cu dissolved in Fe and Fe dissolved in Cu (Engh, 1992)](image-url)
In Figure 2.16, activity is given as a function of composition at a constant temperature and pressure. In the Henry’s law, the activity changes linearly following slope at infinite dilution and the activity is represented in terms of [wt%] that is given in Eq. (2.28). The ratio between Henrian and Raoultian activities for dilute solutions is given as,

\[
\frac{a_2^H}{a_2^R} = \frac{[\text{%}B]}{\gamma_2^0 X_2} = \frac{100 M_2}{\gamma_2^0 M_1}
\]

(2.29)

Where \(M_1\) and \(M_2\) are the molecular weights of component \(A\) and \(B\), and \(X_1, X_2\) are mole fractions and in the case of an infinite dilution \(X_1 \sim 0\). In Eq. (2.29), \(\gamma_2^0\) is a Raoultian activity coefficient for a component \(B\) at infinite dilution, which is similar to the tangent slope of Henry’s law at \(X_2 = 0\).

In an ideal solution, it has been considered that a solution contains only two components that have no interaction between each other. In reality, solutions are composed of more than one element and there are many other dilute impurities that react with solvent as well as between each other. When atoms \(i\) interact with \(j\) atoms, the enthalpy, entropy and structure around \(i\) atoms will change. Such interaction between solvents and the atoms of impurities can be incorporated by considering their interaction parameters. The first order interaction coefficient between atoms can be written as,

\[
\frac{\Delta \mu_i}{RT \Delta x_i} = \varepsilon_{ij}
\]

(2.30)

It has been recognised that \(\varepsilon_{ij} = \varepsilon_{ji}\) and the Raoultian activity in the case of solute interaction can be written as,

\[
\ln \gamma_i = \ln \gamma_i^0 + \sum_{j=1}^{k} \varepsilon_{ij} x_i
\]

(2.31)

The interaction coefficients \(\varepsilon_{ij}\) while considering the mass per cent and corresponding activity coefficient is given by Eq. (2.32) (Engh, 1992, DeHoff, 1993).

\[
\log f_i = \sum_{j=1}^{k} \varepsilon_{ij} [\text{wt%} j]
\]

(2.32)
2.5.7 Sub-lattice model

Solid solution phases (metal diborides) in Al-V-M systems have been modelled using a sub-lattice model in the FactSage thermodynamic package used in the current study. It is assumed that a phase is composed of interlocking sub-lattices where components can mix to make a solution. Sub-lattice models are mostly applied to crystalline phases where crystallographic information is used to calculate the Gibbs energy of a solution. Let us consider two sub-lattice models for a solid phase $\Phi$, which are represented by $(A,B)_a,(C,D)_b$ where $a$, and $b$ are the number of sites on the first and second sub-lattices. Components $A$ and $B$ occupy sites on the 1st and $C$ and $D$ on the 2nd sub-lattice in a phase $\Phi$. After normalization, usually $a + c = 1$ and the Gibbs energy of phase $\Phi$ will be given by,

$$G_m^\Phi = \sum_i y_i \ln y_i + \sum_{i<j} y_i y_j G_{ij} + aRT \sum_i y_i \ln y_i + cRT \sum_j y_j \ln y_j$$

The energy in Eq. (2.33) is called compound energy model.

A sub-lattice model can be used for line compounds (borides, carbides, silicides). Such phases have sub-lattice occupation because of certain combinations of atomic size and electronegativity. They also possess well-defined stoichiometry with respect to components. Although these phases are considered stoichiometry, they mostly have limited solubility of other elements. In borides, carbides and silicides, mixing mostly occurs by substitution on a sub-lattice occupied by metal components. Such compounds can have the following kind of sub-lattice occupation,

$$(A,B,C,D,\ldots)_a,(Z)_b$$

Where $A, B, C, D$ are metallic components that are variable on a metallic sub-lattice and $Z$ has a fixed stoichiometry of compounds i.e boron in borides in the current investigation. The Gibbs energy of such compounds can be written using two sub-lattice models:

$$G_m = \sum_i y_i G_i + aRT \sum_i y_i \ln y_i + \sum_{i<j} y_i y_j \sum_{k} L_{ij}^k (y_i - y_j)^k$$

(2.35)
Where $i$ and $j$ are components mixing on sub-lattice 1, $Z$ is a component with fixed stoichiometry and $a$ will be the molar number of sites on sub-lattice 1 in the line compounds. The mixing will only occur at sub-lattice 1 where components have limited solubility in each other and excess energy will only be associated with this mixing process. Interstitial compounds can also be modelled using sub-lattice model, where sub-lattice 1 will be occupied by metallic components and interstitial and a vacancy will be on sub-lattice 2. Compounds with a complex crystal structure and having variation in stoichiometry can also be modelled using the Sub-lattice model (Saunders and Miodownic, 1997).

2.5.8 Modified quasichemical model

Ionic liquids can be modelled using cellular, modified quasichemical, sub-lattice or associated solution models. A modified quasichemical model will be explained briefly in this section. It was developed by Pelton et.al. where they assumed that components in liquid have a strong tendency to come closer around specific compositions due to some physical or chemical phenomena (Pelton et al., 2000, Pelton and Blander, 1984). This model has been used for higher orders efficiently and can be applied to a wide range of systems. It is assumed that $A$ and $B$ atoms mix substitutionally on a quasi-lattice with coordination number $Z$. There is possible that $A-B$ pairs can make pairs of $A-A$ and $B-B$ on same quasi-lattice in the following way,

\[ A - A + B - B = 2(A - B) \]  

(2.36)

Pelton and Blander defined the molar enthalpy ($\omega$) and entropy ($\eta$) of the above reaction, by ($\omega - \eta T$). The mixing will be ideal if $\omega - \eta T = 0$ and will order a mixture with a 50:50 composition when the values are negative. The enthalpy and entropy of such solutions will show distinct minima in an $AB$ composition. The mole fractions are replaced with equivalent fractions $y_a$ and $y_b$ because minima does not always occur with the $AB$ composition,
\[ y_a = \frac{\beta_a x_a}{\beta_a x_a + \beta_b x_b} \]  
\[ y_b = \frac{\beta_b x_b}{\beta_a x_a + \beta_b x_b} \]  

(2.37)

(2.38)

Where \( \beta_a \) and \( \beta_b \) are chosen for \( y_a = y_b = 0.50 \) at in a composition of maximum ordering in a solution on a quasi-lattice. Enthalpy, entropy and excess entropy in the mixing of a solution that contains \( x_{AA}, x_{BB}, x_{AB} \) moles fractions of \( A-A, B-B \) and \( A-B \) pairs respectively are given by,

\[ H_{\text{mix}} = (\beta_A x_A + \beta_B x_B) \left( \frac{x_{AB}}{2} \right) \omega \]  

(2.39)

\[ S_{\text{mix}}^{\text{config}} = -\frac{RT}{2} \left( \beta_A x_A + \beta_B x_B \right) \left[ x_A \ln \frac{x_{AA}}{y_a} + x_B \ln \frac{x_{BB}}{y_b} + x_{AB} \ln \frac{x_{AB}}{2 y_a y_b} \right] - R(x_a \ln x_a + x_b \ln x_b) \]  

(2.40)

\[ S_{\text{mix}}^{\text{excess}} = (\beta_A x_A + \beta_B x_B) \left( \frac{x_{AB}}{2} \right) \eta \]  

(2.41)

The mass balance equations for \( A \) and \( B \) components in a binary system are given as,

\[ 2y_a = 2x_{AA} + x_{BB} \]  

(2.42)

\[ 2y_b = 2x_{BB} + x_{AA} \]  

(2.43)

The quasichemical equilibrium can be calculated with the help of Gibbs free energy minimisation of the solution on a quasi-lattice,

\[ \frac{x_{AA}^2}{x_{AA} x_{BB}} = 4 \exp \left( \frac{-2(\omega - \eta T)}{zRT} \right) \]  

(2.44)

Equation (2.44) can be solved to calculate \( \omega \) and \( \eta \) which can be used to calculate \( x_{AA}, x_{BB} \) that \( x_{AB} \) required for the enthalpy and entropy of mixing on a quasi-lattice in a binary system. The values of \( \beta_A \) and \( \beta_B \) are calculated from following Eq. (2.45).

\[ (1 - r) \ln(1 - r) + r \ln r = 2 \beta_B r \ln 0.5 \]  

(2.45)
Where \( r = \frac{\beta_A}{\beta_A + \beta_B} \) and other dependences of enthalpy and entropy on the composition are calculated from following relationships,

\[
\omega = \sum_{n=0}^{\infty} \omega^n y^n_b \quad \text{and} \quad \eta = \sum_{n=0}^{\infty} \eta^n y^n_b \quad (2.46)
\]

The modified quasichemical model has been used in a variety of applications including for oxides, salts, and silicate slags and metallic systems showing short range ordering. This approach can be efficiently extended to a multi-component system (Saunders and Miodownik, 1997).

### 2.6 Kinetics of metallurgical reactions

Knowledge of thermodynamics and kinetics is important for an understanding of the reactions that take place in metallurgical processes. Thermodynamics provide information relating to chemical equilibrium and the possible direction of reactions in particular working conditions. Thermodynamics also guide engineers about the heat liberated or absorbed by different reactions during processes. This knowledge, however, cannot provide any information relating to the rate of reaction. A reaction can be thermodynamically favourable but not kinetically under given conditions. Under such conditions, a reaction may take place or be too slow to reach equilibrium and, hence, will require more processing time. Chemical reactions that occur during metallurgical processes involve the rearrangement or redistribution of chemical species (reactants) to make new molecules (products). Knowledge of chemical kinetics is required to understand the various steps, rates and mechanisms of the reactions. It also searches for factors that influence the reaction rate, and which will ultimately determine the processing time in metallurgical processes.

Metallurgical reactions are mainly heterogeneous and involve more than one phase in a multi-component system, for example, the roasting of ores, solid dissolution in acids, smelting processes, and gas-slag-metal reactions in steel making. The rate of reaction is influenced by temperature, pressure, composition and rate of mass transfer between different phases. The overall reaction rate in a multiphase system will depend on three major steps. The first is the transport of reacting species, together or at the interface.
The second is the rate of the chemical reaction at the interface and last is the transport of the reaction product away from the reaction interface. The slowest step will determine the overall reaction rate of the process, and hence named the rate limiting step. The overall reaction rate is very important in designing the reactor and for the economy of a process. A fast overall reaction rate is always desirable and is achieved by increasing the interfacial areas and mass transfers of the species in the metallurgical processes. The rate of reaction for a component “i” based on the unit mass of solid in a solid-fluid system can be defined as,

\[
\frac{dN_i}{dt} = \frac{\text{moles formed}}{(\text{mass of solid})(\text{time})}
\]  

(2.47)

Different rate equations are interchangeable by manipulating their constant of proportionality and dimensions. The rate sign will be positive for products and negative for the reactants consumed during a reaction. The rate of reaction is a state function and depends upon temperature and concentration (Levenspiel, 1972).

### 2.6.1 Chemical reaction controlled kinetics

Most metallurgical reactions are controlled by either a slow chemical reaction or by the rate of mass transfer of reactants or products. Consider a single molecule \(A\) colliding or interacting with \(B\) to give product \(C\) and \(D\). The rate of reaction will be equal to the number of collisions but the number of collisions at a given temperature will be proportional to the concentration of reactants \(A\) and \(B\) in the system. A general reaction is given in Eq. (2.48).

\[
aA + bB \rightarrow cC + dD
\]

(2.48)

The rate of forward reaction can be written as,

\[
\text{Rate} = k_1 C_A^a C_B^b
\]

(2.49)

For a first order heterogeneous reaction, the relationship can be written as given in Eq. (2.50).

\[
\text{Rate} = k_1 C_A
\]

(2.50)
For a second order reaction, the rate equations will become,

\[ \text{Rate} = k_1 C_A^2 \text{ or } k_1 C_A C_B \]  \hspace{1cm} (2.51)

In the above relationships, the rate and order of rates are given for irreversible reactions. For example, the formation of borides in molten aluminium, which are relatively stable in the working conditions. There could be reversible reactions in high temperature systems, for example in the oxygen steel making, where the rate will depend on both forward and reverse reactions. The reaction rate for reversible metallurgical reactions can be written as,

\[ \text{Rate} = k_1 C_A - k_2 C_c \]  \hspace{1cm} (2.52)

Here \( k_1 \) and \( k_2 \) are the forward and reverse reaction constants and their units depend upon the order of reaction. For a first order reaction, the units of rate constant will be \( \text{ms}^{-1} \). The determination of reaction order and rate constant will provide important information regarding the slowest reaction step, and hence the rate limiting step in the process. The plots of reaction rates and the composition of the reacting component will determine the order of reaction. Metallurgical reactions are usually first order but plots will determine the exact order of the reaction.

The Arrhenius equation will determine the temperature dependency of any chemical reaction and it is established that chemical reaction control reactions are strongly affected by temperature. It can be written as Eq. (2.53).

\[ k = k_o e^{-E/RT} \text{ or } \ln k = \ln k_o - \frac{E}{RT} \]  \hspace{1cm} (2.53)

Where \( k \) and \( k_o \) are the rate constant and frequency factor respectively. \( E \) is the activation energy required for a species to react in given conditions. The semi-log plot of the reaction rate and 1/T in a fixed composition will give the activation energy of a reaction, which is useful in differentiating between chemical and diffusion control reactions. The activation energy of chemically controlled reactions is 2400 to 3600 kJ/mol and for diffusion control reactions it lies in the range of 20 to 80 kJ/mol. The fluid flow or stirring of the mixture will have little effect on the reaction rate of

2.6.2 Diffusion and mass transfer controlled kinetics

The temperature in metallurgical reaction is usually higher than the melting point of the reactants and, therefore, chemical control mechanisms are not usually found in such reactions. The transport of reactants and products plays an important role in the metallurgical processes and this is usually the rate limiting step. The diffusion control reactions involve molecular diffusion or convective diffusion, which usually affected by fluid turbulence or laminar flow.

Mass transfer in bulk liquids and gases is mainly as a result of forced or natural convection, but molecular diffusion is the main mode for mass transport within a thin (δ) film at the interface. The liquid flow is laminar in this small boundary layer, which is tangent to the concentration profile that intersects the distance axis at δ, i.e. the thickness of the boundary layer. In weakly agitated melts, the concentration of the boundary layer determines the mass transfer, and this will decrease with increased melt velocity. Within a thin boundary layer, mass transfer occurs due to molecular diffusion, which is proportional to the concentration gradient. According to Fick’s Law it can be written as Eq. (2.54),

\[ J_{D_{m}} = -D_{m}(\frac{\Delta C}{\Delta x}) \]  

(2.54)

Where \( J_{D_{m}} \) is a diffusive flux (number of moles per unit time per unit area) and can also be written as \( \frac{dm}{dt} \), \( D_{m} \) is an atomic or molecular diffusion constant, \( \frac{\Delta C}{\Delta x} \) is the concentration gradient over a fractional distance. In the case of turbulence or convection in liquids or gases, mass transport will not just due to the molecular diffusion. In such complex systems, the concept of a mass transfer coefficient is used instead of molecular diffusion. The simplest form of flux, replacing the molecular diffusion coefficient with a mass transfer coefficient, \( \Delta C \) with \( (C_{m}^{b} - C_{m}^{<}) \) and \( \delta = \Delta x \) can be written as,
\[ J_{Dm} = k_m^D(C_m^b - C_m^i) \]  

(2.55)

Where, \( k_m^D = \frac{D_m}{\delta} \) is a diffusion mass transfer coefficient (m/s) in the metal phase, \( C_m^b \) and \( C_m^i \) are the concentration at bulk and interface (k mole/m\(^3\)). The value of mass transfer coefficient will be influenced by factors affecting the molecular diffusion coefficient, the agitation intensity and geometry of the reactor. At the interface of immiscible liquid like slag-metal systems, in the absence of turbulence, the flux will be equal to,

\[ J_D = J_{Dm} = k_m^D(C_m^b - C_m^i) \]  

(2.56)

Generally, it is assumed that diffusion and turbulent mass transfer are taking place at the same time so, on average, the overall mass transfer coefficient \( k_m \) can be written as,

\[ k_m = A_D k_m^D + (1 - A_D) k_m^E \]  

(2.57)

Where \( A_D \) is the fractional contribution of diffusional mass transfer and \( k_m^E \) is a turbulent mass transfer. Experimentally, it has been established that turbulent mass transfer is proportional to the velocity of fluid normal to the interface. It can be observed that the diffusion flux \( J_D \) is similar to the first order chemical reaction, which can be written as,

\[ J_D = \frac{dn}{dt} A = \frac{dC}{dt} V = k_m(C_m^b - C_m^i) \]  

(2.58)

By rearranging

\[ \frac{dC}{dt} = \frac{k_m A}{V}(C_m^b - C_m^i) \]  

(2.59)

In the above Eq. (2.58), \( n \) is the number of the mole of the reacting species, \( A \) is the surface area of the interface and \( V \) is the volume of metal. It is not easy to calculate the surface area at the interface, hence the use of volume. So the mass transfer coefficient can be written in another form known as the mass transfer capacity coefficient \( k \). This is given in Eq. (2.60).

55
\[ k = k_m \frac{A}{V} \quad (2.60) \]

As the turbulent mass transfer coefficient is directly proportional to the stirring of fluid, then the mass transfer capacity coefficient will be,

\[ k \propto \varepsilon^n \quad (2.61) \]

Where, \( \varepsilon \) is the mixing power density (W/ton) and \( n \) is the mixing exponent whose values range from 1/2 to 1/3, near to 0.50 (viscous forces) in most cases. The values of 0.25 represent mildly agitated melt and for 2 or 3, the melt droplet will eject showing a high mass transfer capacity factor. There are three major models that describe inter-phase mass transfer in a multiphase system and these are given in the next sections.

2.6.2.1 Two film model

This is the simplest model of mass transfer between phases and assumes the existence of a thin film in each phase at the interface where the mass transfer of species takes place. No hydrodynamic interactions between phases exist and the equilibrium conditions prevail at the interface. A steady state mass transfer occurs through these thin films across the interface, as explained in section 2.6.2.

2.6.2.2 Boundary layer model

In this model, a boundary layer of thickness \( \delta \) is assumed at the interface. The mass transfer takes place from this boundary layer by molecular diffusion where turbulent diffusion is ignored. With bulk, turbulence diffusion plays an important role for mass transfer as compared with molecular diffusion. The effective boundary layer thickness for liquid flowing over a solid body can be calculated using Eq. (2.62),

\[ \delta = D_m^{1/3} \nu^{1/6} \sqrt[3]{\frac{z}{u}} \quad (2.62) \]

Where \( \nu \) is the kinematic viscosity, \( u \) is flow velocity of bulk liquid and \( z \) is the distance where liquid flows over the solid particles. The thickness of the boundary layer is a function of mixing, geometry and physical properties. Boundary thickness is very difficult to measure in practice in the agitated fluids.
2.6.2.3 Surface renewal model

This is also known as the Higbie model and is based on moving film theory. It is assumed that a certain fluid volume is carried by eddies and will spend some time at the interface on some paths. During the time \( t_i \) at the interface, elements are assumed to be stagnant, where mass transfer can occur through unsteady state diffusion or penetration between phases. According to this theory, the diffusional mass transfer can be calculated as,

\[
\frac{i}{m}D \frac{m}{t} \frac{D}{k} \times 2
\]

(2.63)

It is difficult to determine a small volume element residence time \( t_i \) at the interface, but it has been shown for several systems that this relationship \( k_m^D \propto \sqrt{D_m} \) will hold very well (Deo and Boom, 1993, Rhamdhani, 2005).

The models discussed in this section cannot be used for further modifications. It is assumed in these models that the concentration gradient and mass transfer coefficient do not change from one section of reaction to another. It is further assumed that the surface area remains constant, which is definitely not the case in metallurgical reactions where it increases some times, up to 300% to 500% beyond its original value (Rhamdhani et al., 2006). The surface areas also shrink during the reactions of solids with liquids or gases. A consideration of these variables is important in evaluating the mass transfer controlled mechanism of metallurgical reactions (Rhamdhani, 2005).

2.6.3 Fluid solid particles kinetics

There are many metallurgical heterogeneous reactions that involve the interaction of fluid with solid particles to transform them into product. The reaction product of such interactions could be fluid, solid or fluid solid particles, for example, the roasting of sulphide ores, smelting processes, the nitrogenation of calcium carbide and the burning of coal. The initial solid particle after a reaction may remain solid. It may remain the same size or shrink during the process. The behaviour of such a solid particle is shown in Figure 2.17 (Levenspiel, 1972).
Figure 2.17. Different behaviours of reacting particles in fluids (Levenspiel, 1972)

The major limitations in chemical kinetics have already been explained as the concentration of the reacting species, the temperature, pressure, heat and mass transfer. In a solid liquid reaction, the rate of process is mainly limited by mass transfer rather than heat transfer, as most metallurgical processes involve a high temperature. The limitation of external mass transfer could be overcome by applying agitation to the fluid phase. Internal mass transfer only exists in porous particles and can be practically investigated through experiments using different particle sizes. The rate of diffusion in a system is composed of bulk and Knudsen diffusion. The mass transport in porous layer will depend upon the pores size and mean free path (Smith, 1981). The fluid-solid systems that have the phenomenon of product layer, Knudsen diffusion could also be a rate controlling step in the overall kinetics.

Usually, the progress of a chemical reaction in a solid liquid system is investigated by observing the change in weight of the solid phase or by measuring product concentration in the liquid phase. One important difference between homogenous and heterogeneous reactions is that the former depends upon the concentration of the reacting species but this is not the case later. Heterogeneous systems, such as solid liquid reactions, depend on the active surface area of the solid phase. Two-fold increases in the surface area will double the reaction rate in such systems. Moreover, the
active surface will not be uniform throughout a particle as some crystals may be more reactive than others, which further complicates the kinetics of solid liquid systems in metallurgical and other industrial processes (Grénman et al., 2011).

Kinetic modelling of solid liquid reactions is not a simple task due to the challenges discussed in the last section. All the models used are based on geometrical assumptions and their rate expressions have been developed to analyse real situations. If a model is selected for a particular real situation, its rate expression has to be taken into consideration; otherwise the kinetic predictions will not be reliable. There are two broad categories of non-catalytic liquid solid systems, namely progressive conversion and an un-reacted (shrinking) core.

2.6.3.1 Progressive conversion models

It is assumed in this model that liquid or gases enter the solid particle and react all over the surface area. Thus reaction rate may be variable at various locations of the particle but it converts into product progressively during the process. The schematic representation of such models is given in Figure 2.18.

2.6.3.2 Shrinking (un-reacted) core models

It is visualized in the shrinking core model that fluid reacts at the outer boundary of the solid phase first and then progresses into the core, leaving behind reacted product that is solid and chemically inert. The outer product formed is called ash and the un-reacted core can be observed during an examination of such systems. It has been observed that the shrinking core situation represents the real situation for the most part, so kinetic equations for such systems have been established. Yagi and Kunii (1955) visualise five different possible steps during the reaction of gas with a solid particle, and these are given below:

1- Diffusion of reacting gas through the film surrounding the surface of the particle.
2- Diffusion of reacting gas through the reacted solid layer, or ash, which covers the un-reacted core of a solid particle.
3- Chemical reaction at the reactive surface between the reacting gas and solid particle.
4- Diffusion of the gaseous product through the ash layer back into the exterior surface of the solid particle

5- Diffusion of gaseous products through the gas film back into the bulk fluid phase

Figure 2.18. Progressive conversion model for solid fluid reactions (Levenspiel, 1972)

These steps may not all exist at all times during the reaction, and different steps will also have variable resistances. The step with the highest resistance among all the possible steps will be the rate-controlling in such systems.

2.6.3.3 Diffusion through ash (product) layer controls

Consider the reaction of a spherical particle, with gas and diffusion through the ash or product layer, to be the rate-controlling step. Two-step analyses are required to develop an expression between the time and radius of the solid particle. The partially reacted particle for this situation is given in Figure 2.19. It is assumed in such systems that both reactant A (in this case gas but it could be liquid) and the un-reacted core move inward towards the centre of the spherical particle. It can be observed in such situations that the shrinking of the core is much slower than the diffusion of the reactant A towards the un-reacted core. It is logical to consider the concentration gradient of reactant A from the ash layer to the surface of the un-reacted core at any time and the steady state conditions.
In the steady state condition, the rate of reaction of \( A \) at any time will depend on its diffusion rate to the reacting solid surface and will be given as,

\[
\frac{dN_A}{dt} = 4\pi r^2 Q_A = 4\pi R^2 Q_{AS} = 4\pi r_C^2 Q_{AC} = \text{constant} \tag{2.64}
\]

Figure 2.19. Representation of diffusion through product layer model (Levenspiel, 1972)

The flux of reactant \( A \) can be expressed by Fick’s Law, where \( Q_A \) and \( \frac{C_A}{dr} \) are both positive due to diffusion inside the ash layer. The flux will then be,

\[
Q_A = D_e \frac{dC_A}{dr} \tag{2.65}
\]

Where \( D_e \) is the effective diffusion coefficient of a reactant species through the ash layer and where it is difficult to assign a value due to impurities in the solids, and also a variable environment of particles in the fluid. By rearranging for \( r \) and integrating for the ash layer from \( R \) to \( r_c \), one can obtain the condition of particle at any given time,

\[
-\frac{dN_A}{dt} \int_{r_c}^{r} dr = 4\pi D_e \int_{C_{As}}^{C_{Ac}} dC_A = -\frac{dN_A}{dt} \left( \frac{1}{r_C} - \frac{1}{R} \right) = 4\pi D_e C_{Ag} \tag{2.66}
\]

61
This relationship expresses that the size of the un-reacted core changes with time and, for a given size of un-reacted core, \( \frac{dN_A}{dt} \) will be constant. With the passage of time, a reaction will proceed and the layer thickness will increase, which will decrease the diffusion of A. Replacing \( N_A \) (moles of fluid reactant) in terms of \( r_c \) and integrating between times for complete conversion will yield,

\[
- \rho_b \int_{r_c=0}^{r_c} \left( \frac{1}{r_c} - \frac{1}{R} \right) r_c^2 dr_c = bD_c C_{Ag} \int_0^t dt
\]

\[2.67\]

\[t = \frac{\rho_b R^2}{6bD_c C_{Ag}} \left[ 1 - 3\left( \frac{r_c}{R} \right)^2 + 2\left( \frac{r_c}{R} \right)^3 \right]\]

\[2.68\]

Time required for complete conversion of particle \( r_c = 0 \) will be given by Eq. (2.69),

\[\tau = \frac{\rho_b R^2}{6bD_c C_{Ag}} \]

\[2.69\]

Progression of the reaction in terms of the time required for complete conversion can be written as dividing Eq. (2.70) and Eq. (2.71).

\[\frac{t}{\tau} = 1 - \left( \frac{r_c}{R} \right)^2 + 2\left( \frac{r_c}{R} \right)^3\]

\[2.70\]

In terms of a fractional conversion, the relationship can be rearranged as,

\[\frac{t}{\tau} = 1 - 3(1 - X_A)^{2/3} + 2(1 - X_B)\]

\[2.71\]

This relationship given in Eq. (2.71) can be used to determine the reaction kinetics of a solid liquid reaction where the diffusion through the ash or product layer is the main rate-controlling step. If the experimental data fits well into the Eq. (2.71) rate expression, then it could be suggested that diffusion of the reacting species through the product layer is hindering the progress of the reaction (Levenspiel, 1972).

Table 2.8. Solid liquid kinetic Models (Grénman et al., 2011, Órfão and Martins, 2002, Dickinson and Heal, 1999)
<table>
<thead>
<tr>
<th>No</th>
<th>Integral forms of models</th>
<th>Model description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$kt = \alpha$</td>
<td>Zero order kinetics; one dimensional advance of reaction interface</td>
</tr>
<tr>
<td>2</td>
<td>$kt = -\ln(1 - \alpha)$</td>
<td>First order kinetics</td>
</tr>
<tr>
<td>3</td>
<td>$kt = \ln(1 - \alpha)^{-1}$</td>
<td>Second order kinetics</td>
</tr>
<tr>
<td>4</td>
<td>$kt = 2 \left[ -\alpha^{-1/2} - 1 \right]$</td>
<td>Three-halves order kinetics</td>
</tr>
<tr>
<td>5</td>
<td>$kt = 2 \left[ -\alpha^{-2} \right]$</td>
<td>One-half order kinetics; two dimensional advance of reaction interface</td>
</tr>
<tr>
<td>6</td>
<td>$kt = 3 \left[ -\alpha^{-3} \right]$</td>
<td>Two-third order kinetics; three dimensional advance of interface</td>
</tr>
<tr>
<td>7</td>
<td>$kt = 1 - \alpha^{-3}$</td>
<td>One third order reaction kinetics</td>
</tr>
<tr>
<td>8</td>
<td>$kt = 3/2 \left[ -\alpha^{-3/2} \right]$</td>
<td>Jander; Three dimensional</td>
</tr>
<tr>
<td>9</td>
<td>$kt = 3/2 \left[ 1 + \alpha^{7/3} - 1 \right]$</td>
<td>Komatsu-Uemura Eq. (Anti – Jander Eq)</td>
</tr>
<tr>
<td>10</td>
<td>$kt = 3/2 \left[ 1 - \frac{2\alpha}{3} - \alpha^{-2/3} \right]$</td>
<td>Ginstling–Brounshtein (Mass transfer across nonporous product layer)</td>
</tr>
<tr>
<td>11</td>
<td>$kt = \left[ \frac{1}{1 - \alpha^{-3/2}} - 1 \right]^2$</td>
<td>Zhuravlev-Lesokhin-Tempelman (conc. Of diffusing species varies with $\alpha$)</td>
</tr>
<tr>
<td>12</td>
<td>$kt = \frac{1}{\alpha^{-3/2} - 1}$</td>
<td>Dickinson, Heal, transfer across the contacting area</td>
</tr>
<tr>
<td>13</td>
<td>$kt = 1 - 3\alpha^{-3} + 2\alpha^{-2}$</td>
<td>Shrinking core, product layer (different form of Crank-Ginstling-Brounshtein)</td>
</tr>
</tbody>
</table>

Similar rate expressions for fluid solid reactions have been developed for diffusion through gas film and chemical reactions controls, and are given in Eq. (2.72) and (2.73),

$$\frac{t}{\tau} = 1 - \left( \frac{r_c}{R} \right)^3 = X_b \quad \text{(Gas film controls)} \quad (2.72)$$

$$\frac{t}{\tau} = 1 - \frac{r_c}{R} = 1 - (1 - X_b)^{1/3} \quad \text{(Chemical reaction controls kinetics)} \quad (2.73)$$
2.7 Previous thermodynamic studies on Al-B, V-B systems

The literature shows that a large number of researchers have investigated transition metal borides. A thorough literature review has revealed different opinions between researchers. Some researchers have claimed that transition metal borides are pure compounds and others have claimed that they make a solid solution. Previous work on transition metal borides can be divided into two arguments, namely pure and solid solution existence, and are discussed in the next section.

2.7.1 Borides of transition metals as pure compound

The existence and formation of borides during boron treatment has not yet been completely explained and still requires more research. Post (1952), prepared the borides of W, Ti and Zr by heating with boron followed by phase detection with X-ray diffraction. The borides identified were WB (orthorhombic), Ti$_2$B$_5$ (hexagonal), TiB (tetragonal), TiB and ZrB$_2$ (hexagonal). These phases were reported as pure solid compounds made of W, Ti and Zr with boron in the given experimental conditions (Post and Glaser, 1952). The stability of various borides with graphite and N$_2$ were investigated and it was found that most of them were stable. The most stable borides were of Ti, Zr, Nb and Ta as compared with other borides (Brewer and Haraldsen, 1955). Jones and Pearson reported TiB$_2$ phase to be a pure compound that does not have any solubility with aluminium. They were investigating the grain refinement of aluminium with Ti and B additives (Jones and Pearson, 1976). During the investigation of inclusions in aluminium, borides (AlB$_2$, AlB$_{12}$, TiB$_2$, VB$_2$ and ZrB$_2$) were detected which were hexagonal. These borides exist mostly in the form of clusters or rectangular discs. The morphology of AlB$_2$ particles in aluminium is shown in Figure 2.20 (polarized light). Figure 2.20 reveals that AlB$_2$ borides have a high aspect ratio and a tendency to form clusters. The individual borides are 0.1 to 10 µm in diameter and are found in more than 50 µm clusters.

Borides are difficult to detect under a light microscope although VB$_2$ were reported to be darker than TiB$_2$ particles. The AlB$_{12}$ boride of aluminium was reported as irregular, porous lumps or polyhedral grey particles under light microscopy (Simensen and Berg,
The presence of TiAl₃ on the TiB₂ particles was investigated but the results were not clear as to whether both were making a solid solution or retained their identity during the grain refinement of aluminium alloys (Bunn, 1997).

Figure 2.20. AlB₂ particle under polarized light in aluminium at x200 magnification (Simensen and Berg, 1980)

The stability of (Al,Ti)B₂ in the Al-rich Al-B and Al-Ti-B alloys was investigated by Fjellstedt et al. (1999) using optical microscopy, EDX and XRD techniques. Samples were prepared from pure aluminium, and powders of Ti, TiB₂, AlB₂ and boron bearing substances. The powders were melted at 1800 K and simultaneous rotation was applied at an angle of 270° for one hour. The samples were heat treated at different temperatures (1073, 1173K) for 1 and 2 weeks for further analysis. Clusters of AlB₂ surrounded by TiB₂ particles were detected and can be seen in Figure 2.21. Figure 2.21 shows that a reaction between AlB₂ and Ti produced a reaction product composed of a TiB₂ ring. It was reported that AlB₂ and TiB₂ particles are stable and exist separately in all samples treated at different temperatures. There was no evidence of mutual solubility among them in any case investigated. It was further reported that Ti showed a limited solubility in the AlB₁₂ metastable phase of aluminium boron master alloys (Fjellstedt et al., 1999). Otani (2000), while investigating the hardness of TiB₂, VB₂ and CrB₂, reported them as pure borides. No further details regarding the solution was reported except for boride
manufacturing and hardness measurement procedures (Otani, 2000). Recently, Yeh and Wang (2011) produced borides of V and reported that VB and VB$_2$ are the only borides that form in a pure or nearly pure form. Other borides (V$_3$B$_2$, V$_3$B$_6$, V$_2$B$_3$) were not detected, possibly because of their complex crystalline structure (Yeh and Wang, 2011).

![Image of AlB$_2$ clusters surrounded by TiB$_2$ particles](image)

Figure 2.21. The clusters of AlB$_2$ surrounded by TiB$_2$ particles

### 2.7.2 Borides of transition metals as solid solutions

Other investigators reported that borides form solid solutions. Higashi et al. (1976) studied the solubility of aluminium in various metal borides, including TiB$_2$, ZrB$_2$, HfB$_2$, VB, V$_3$B$_4$, NbB$_2$, TaB and W$_2$B$_5$, by growing their crystals from molten aluminium at 1300°C to 1550°C. They reported that the maximum solubility of aluminium in borides was 0.1wt% at temperature of 1300°C to 1550°C. This was interpreted that AlB$_2$ do not form mixed crystals with the above borides, having little solubility in aluminium (Higashi et al., 1976).

The solid solution of (Al,Ti)B$_2$ was reported in the literature as being in the Al-Ti-B system. It was assumed that (Al,Ti)B$_2$ is a metastable phase that formed with other stable phases (AlB$_2$, TiB$_2$, TiAl$_3$) and that might play a role in the grain refinement of aluminium alloys (Sigworth, 1984, Easton and StJohn, 1999b, Quested, 2004, Easton and StJohn, 2005). Similar arguments regarding the existence and stability of (Al,Ti)B$_2$
were reported by other investigators of aluminium grain refiners (McCartney, 1989, Easton and Stjohn, 1999a). The interaction of boron fibres with aluminium melt revealed the formation of AlB$_2$, AlB$_{12}$ and a solid solution of boron and aluminium (Chernyshova et al., 1988).

Lee et al. (1993), during the investigation of interfacial phenomena in the reactions of Al-Ti-B and Al-Zr-B with KF-AlF$_3$ and NaF-AlF$_3$, reported the presence of K and F in TiB$_2$ particles during EDX analysis. It was not confirmed that TiB$_2$ formed a solid solution or that K and F came from base material during EDX analysis (Lee et al., 1993). Single crystals of V$_2$B$_3$, using a high temperature aluminium solution, was prepared by Okada and Lundstrom (1993) using high purity vanadium chips and boron. The optimum conditions to obtain large crystals required a holding time of 5 hours at 1600°C. Electron micro probe analysis (EPMA) revealed the presence of Fe, Ca, Si and Al impurities in the grown crystals but the solubility of aluminium was comparatively less (Okada and Lundström, 1993).

Cizek et al. (2003) detected a (Al,Ti)B$_2$ phase during the EDX analyses of the Al-Ti-B grain refiner and explained that it was difficult to detect AlB$_2$ and TiB$_2$ under TEM diffraction due to their similar hexagonal structure, space group (196-Pmmm) and lattice parameters (Cizek et al., 2004). It was further reported that borides were free from any coated layer of TiAl$_3$ which was proposed by Bunn (Cizek et al., 2004). The findings of Suarez (2004) are similar to Cizek et al. who reported the presence of ternary phases (Al$_x$Ti$_{1-x}$B$_2$) or (Al,V) B$_2$ during the EDX analysis of samples. According to the argument of Suarez, TiB$_2$ may dissolve and provide B for TiAl$_3$ solid solution, but which is beyond the detectable limits of the EDX technique. Moreover, it was supported that a ternary phase (Al,Ti)B$_2$ could be considered a thermodynamically stable phase (Suarez, 2004). These findings support the assumptions of Sigworth and McCartney but contradict Fjellstedt et al., as explained earlier. A continuous solid solution of NbB$_2$ and TiB$_2$ borides was also reported in the literature. The EPMA analysis revealed the presence of 23 mol% and 15 mol% of Nb in TiB and Ti in NbB respectively. Similarly, the solubility of Ti in Nb$_3$B$_4$ was reported as approximately 7 mol% and that of Nb in Ti$_3$B$_4$ was 2 mol% (Nakama et al., 2009).
Figure 2.22. Lattice parameters and peaks width of different solid solution of ZrB₂ with other refractory borides (a) Zr₁₋ₓNbₓB₂, (b) Zr₁₋ₓTaxB₂, (c) Zr₁₋ₓTaxB₂ and (d) Zr₁₋ₓHfxB₂ systems (Otani et al., 2009)

Otani et al. (2009) investigated the solid solution ranges of ZrB₂ with refractory diborides (HfB₂, TiB₂, TaB₂, NbB₂, VB₂ and CrB₂). Mixed-boride samples were melted using an arc-melting furnace in an Ar atmosphere at 1600°C. The samples were analysed using x-ray diffraction and inductively-coupled plasma techniques. Their study showed that ZrB₂ formed a perfect solution with NbB₂, HfB₂ and TaB₂. In the case of a ZrB₂-TiB₂ system, they observed two phases, i.e. ZrB₂-rich (Zr₀.₇₆Ti₀.₂₄B₂) and TiB₂-rich (Zr₀.₁₁Ti₀.₈₉B₂) phases. It was also reported that ZrB₂ made a solid solution with VB₂ and CrB₂ but that the solubility was very low i.e. < 3 mol% and < 1 mol%, respectively at 1600°C (Otani et al., 2009). The lattice parameter values of different solid solutions are given in Figure 2.22.

Hamdad et al. (2010) also reported a solid solution of Nb and Ti boride as a ternary phase (Ti₀.₅Nb₀.₅B₂) and calculated the electronic structure, bonding and chemical stability by using first principle calculation. In the literature, the chemical stability of
refractory borides has been given in decreasing order from TiB$_2$ > VB$_2$ > CrB$_2$ > MnB$_2$ to FeB$_2$ in the 3d transition metals, in the 4d series ZrB$_2$ > TiB$_2$ > NbB$_2$ > MoB$_2$ and in the 5d series HfB$_2$ > TaB$_2$, which is the work of Vajeeston as reported by Hamdad et al. (Hamdad et al., 2010).

2.7.3 Al-B binary system

Knowledge of the Al-B binary system is important in understanding solution thermodynamics and the mechanism of transition metal removal from molten aluminium. As discussed earlier, boron is added in the form of Al-B master alloys to combine vanadium into their stable, heavy and insoluble borides. Aluminium boron master alloys Al-10wt.% B (AlB$_{12}$), Al-6wt.% B (AlB$_{12}$), Al-5wt.% B (AlB$_2$) and Al-4wt.% B (AlB$_{12}$) are commonly used for the boron treatment of aluminium melt in cast houses (Khaliq et al., 2011b, Cooper and Kearns, 1996, Setzer and Boone, 1991). The Al-B system is also an integral part of the Al-Ti-B ternary system, which is important due to its grain refinement, precipitation hardening and the mechanical reinforcement of aluminium alloys. A thermodynamic investigation of the Al-B binary system is important to understand boron treatment and transition metal borides formation in molten aluminium.

Jones and Pearson (1975) investigated the solution behaviour of boron in an Al rich solution during the grain refinement of aluminium alloys using titanium and boron additives. The thermodynamic properties were taken from “MTDATA” bank of the National Physical Laboratory. Ideal mixing was assumed for the modelling of solute elements (B, Ti) in the solvent of aluminium. Moreover, it was assumed that solute elements have no interaction in solution with aluminium (although this is not the case in real solutions). The solubility (mole fraction) of different solutes was calculated on the basis of Eq. (2.74), which is given below.

$$\log_{10} X_{\text{Al}} = a + b \cdot 10^3 T^{-1} K$$  \hspace{1cm} (2.74)

The values of constant $a$ and $b$ are 0.870 and -3.500 for the AlB$_2$ separating phase from a solution with a lower temperature limit of 934 K. The given values are applicable up to 0.050 mole fraction and 1500 K temperature. It was further argued that the exchange
of Al and Ti in Eq. (2.75) will be substitutional when kinetics is slow and a reverse reaction will not completed throughout the systems.

\[ TiB_2 + [Al] \rightarrow AlB_2 + [Ti] \]  

(2.75)

This argument may be valid in the case of vanadium borides in molten aluminium by reaction of V with AlB\(_2\) or AlB\(_{12}\) (Jones and Pearson, 1976). Cisse et al. (1972) hypothesised about the dissolution of TiB\(_2\) particles in aluminium during grain refinement. They assumed that the product layer at the interface between particle and melt would hinder mass transfer, a part of which is controlled by very slow diffusion. This diffusion flux across the interface will take a finite time to reach equilibrium. The assumption of 9% dissolution TiB\(_2\) in Ti-B-Al master alloys was ruled out on the basis of the diffusion barrier hypothesis (Cissé et al., 1972, Jones and Pearson, 1976).

The reported solubility of boron is limited that is less than 100 ppm in solid aluminium. The literature states that a eutectic reaction (Eq. 2.76) takes place at 0.022 wt% boron and 659.7°C in an Al-B binary system. The liquid solubility of boron is not well documented. Molten aluminium dissolves about eight times more boron compared with solid (Sigworth, 1984). The x-ray diffraction patterns were reported by Serebryanskii et al. (1967), who observed broadening of (420) reflections, which they assigned to mechanical stresses in the powders (used as starting material). There was no reasonable evidence for the solid solubility of boron in aluminium (Serebryanskii et al., 1967).

\[ liquid \rightarrow Solid + AlB_2 \] (Eutectic at 0.022 wt% B and at 659.7°C)  

(2.76)
Serebryanskii *et al.* (1967) constructed an Al-B phase diagram and compared their findings with previous investigators. A high temperature thermal analysis technique was used in these experiments with the different weight ratios of aluminium and boron. The phases detected were pure aluminium, AlB$_2$, α-AlB$_{12}$, AlB$_{10}$, β-AlB$_{12}$ and β-B. A few phases (AlB$_{10}$ and β-AlB$_{12}$) were also observed during the quenching of samples from a high temperature on brass cooled by dry ice. The phases were detected by the x-ray diffraction technique. The phase diagram of Al-B binary system showing thermal arrests is given in Figure 2.23.

A detailed investigation of the Al-B system was carried out by Carlson (1990). The solubility, stable phases, reaction temperatures, lattice parameters and thermodynamic properties of the Al-B system were reported. The assessed phase diagram of Al-B system is shown in Figure 2.24. The next section is devoted to elaborating on the possible phases in the Al-B binary system.
2.7.3.1 Boron

The existence of boron has been reported in three crystalline forms, namely α-B (rhombohedral), tetragonal and β-B (complex rhombohedral). The β-B phase is considered to be the most stable because it formed on cooling in a crystalline form and remained stable at room temperature. Thermodynamically, β-B rhombohedral is the most stable phase at room temperature, and the lattice parameters are given in Table 2.9.

2.7.3.2 AlB$_2$

The AlB$_2$ phase of the Al-B binary system form peritectically at 980°C and has a melting temperature of 1655 ± 50°C. The stability of AlB$_2$ was confirmed by Serebryanskii et al. during their thermal arrest experiments at 980, 1450, 1550, 1600, 1850 and 2070°C in beryllium oxide crucible in a purified helium environment. The AlB$_4$ stoichiometric phase was also reported during x-ray diffraction analysis, but later it was omitted by Serebryanskii et al. AlB$_2$ exists in a hexagonal crystal structure with a C32 crystal type and having a = 0.3006 nm and c = 0.32562 nm lattice parameters.
Table 2.9. Al-B binary system crystal structure data (Villars, 1997, Carlson, 1990, Kohn and Eckart, 1960)

<table>
<thead>
<tr>
<th>Phase</th>
<th>Comp. at.% B</th>
<th>Pearson Symbol</th>
<th>Space group</th>
<th>Prototype</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>0</td>
<td>cF4</td>
<td>Fm3m</td>
<td>Cu</td>
</tr>
<tr>
<td>AlB₂</td>
<td>66.7</td>
<td>hP3</td>
<td>P63/mmm</td>
<td>AlB₂</td>
</tr>
<tr>
<td>α-AlB₁₂</td>
<td>92.3</td>
<td>oC88</td>
<td>Cmcm</td>
<td>AlB₁₂</td>
</tr>
<tr>
<td>β-AlB₁₂</td>
<td>92.3</td>
<td>tP216</td>
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<td>AlB₁₂</td>
</tr>
<tr>
<td>AlB₁₀</td>
<td>90.9</td>
<td>Orthorhombic</td>
<td>Ima</td>
<td>AlB₁₀</td>
</tr>
<tr>
<td>β-B</td>
<td>100</td>
<td>hR105</td>
<td>R₃m</td>
<td>β-B</td>
</tr>
<tr>
<td>γ-AlB₁₂</td>
<td>92.3</td>
<td>oP384</td>
<td>P₂₁₂₂₁</td>
<td>AlB₁₂</td>
</tr>
<tr>
<td>α-B</td>
<td>100</td>
<td>hR12</td>
<td>R₃m</td>
<td>α-B</td>
</tr>
<tr>
<td>γ-B</td>
<td>100</td>
<td>tP50</td>
<td>P₄₂/mmm</td>
<td>γ-B</td>
</tr>
<tr>
<td>B(Tetragonal)</td>
<td>100</td>
<td>tP196</td>
<td>P₄₁</td>
<td>B(Tetragonal)</td>
</tr>
</tbody>
</table>

**Metastable Phases**

<table>
<thead>
<tr>
<th>Phase</th>
<th>Comp. at.% B</th>
<th>Pearson Symbol</th>
<th>Space group</th>
<th>Prototype</th>
</tr>
</thead>
<tbody>
<tr>
<td>γ-AlB₁₂</td>
<td>92.3</td>
<td>oP384</td>
<td>P₂₁₂₂₁</td>
<td>AlB₁₂</td>
</tr>
<tr>
<td>α-B</td>
<td>100</td>
<td>hR12</td>
<td>R₃m</td>
<td>α-B</td>
</tr>
<tr>
<td>γ-B</td>
<td>100</td>
<td>tP50</td>
<td>P₄₂/mmm</td>
<td>γ-B</td>
</tr>
<tr>
<td>B(Tetragonal)</td>
<td>100</td>
<td>tP196</td>
<td>P₄₁</td>
<td>B(Tetragonal)</td>
</tr>
</tbody>
</table>

2.7.3.3 AlB₁₂

In the Al-B binary system, low temperature modification is α-AlB₁₂ phase. At high temperatures β-AlB₁₂ and γ-AlB₁₂ are reported but no experimental evidence was provided. The melting temperature of β-AlB₁₂ is 2150 ± 50°C. Carlson accepted α-AlB₁₂ and β-AlB₁₂ as stable phases in his construction of an Al-B phase diagram. The transformation from α →β takes place at 1550°C. AlB₁₂ is reported to exist as a tetragonal (α-AlB₁₂), body centred orthorhombic (β-AlB₁₂) and γ-AlB₁₂ with a large primitive orthorhombic cell. The lattice parameter detail is given in Table 2.9.

2.7.3.4 AlB₁₀

The AlB₁₀ has been proved as a catatectic phase that is stabilized by the impurity contents. This phase was reported as being formed from a peritectic reaction L + β-AlB₁₂ → AlB₁₀ at 1660°C. Serebryanskii et al. also identified AlB₁₀ during the quenching of samples from 1660°C and 1850°C. It was argued by other investigators that AlB₁₀ is a carbon stabilized ternary (AlB₂₄C₄) phase rather than binary. The crystal structure of AlB₁₀ was reported as an orthorhombic, pseudo-tetragonal with lattice parameters a = 0.8881 nm, b = 0.9100 nm and c = 0.5690 nm.
The solid solubility of aluminium in boron was reported from 93 wt% to 100 wt% on the basis of minor broadening of the β-B lattice parameters (dashed lines in Serebryanskii et al Al-B phase diagram). Later on, other researchers proved there was no solubility of aluminium in boron, which was accepted by Carlson for his Al-B phase diagram assessment. Mirkovic et al. suggested that β-B has 3 at% solubility of aluminium, which is in disagreement with Duschanek and Rogl (Duschanek and Rogl, 1994, Mirković et al., 2004).

The details of phase transformation reactions, their types, boron composition and temperatures are summarized in Table 2.10. The eutectic transformation in Al-B binary system takes place at 659.7°C and 0.025 at% boron that produces AlB$_2$ solid phase. The crystallographic information of all possible phases in Al-B binary system is given in Table 2.11. Duschanek and Rogl (1994) critically re-assessed Al-B system and reported that only α-AlB$_{12}$, AlB$_2$ are stable phases. The other phases, such as β-AlB$_{12}$ (Serebryanskii et al., 1967, Carlson, 1990), γ-AlB$_{12}$ (Serebryanskii et al., 1967) and AlB$_{10}$ (Serebryanskii et al., 1967, Kohn and Eckart, 1960, Carlson, 1990), reported by previous investigators, are not stable and are influenced by carbon.

An additional phase, Al$_2$B$_3$, reported by Verdiman, was accepted by Duschanek and Rogl for their assessment of Al-B binary system (Duschanek and Rogl, 1994).
Table 2.11. Al-B binary system lattice parameters (Villars, 1997, Carlson, 1990, Kohn and Eckart, 1960, Will, 1966)

<table>
<thead>
<tr>
<th>Phase</th>
<th>Comp. at% B</th>
<th>Lattice parameters (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>a</td>
</tr>
<tr>
<td>Al</td>
<td>0</td>
<td>0.4050</td>
</tr>
<tr>
<td>AlB₂</td>
<td>66.7</td>
<td>0.3006</td>
</tr>
<tr>
<td>α-AlB₁₂</td>
<td>92.3</td>
<td>1.0161</td>
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<tr>
<td>β-AlB₁₂</td>
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<td>1.017</td>
</tr>
<tr>
<td>AlB₁₀</td>
<td>90.9</td>
<td>0.881</td>
</tr>
<tr>
<td>β-B</td>
<td>100</td>
<td>1.096</td>
</tr>
<tr>
<td>γ-AlB₁₂</td>
<td>92.3</td>
<td>1.6623</td>
</tr>
<tr>
<td>α-B</td>
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<td>0.491</td>
</tr>
<tr>
<td>γ-B</td>
<td>100</td>
<td>0.8743</td>
</tr>
<tr>
<td>B(Tetragonal)</td>
<td>100</td>
<td>1.014</td>
</tr>
</tbody>
</table>

Metastable phases

<table>
<thead>
<tr>
<th>Phase</th>
<th>Comp. at% B</th>
<th>Lattice parameters (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>γ-AlB₁₂</td>
<td>92.3</td>
<td>1.6623</td>
</tr>
<tr>
<td>α-B</td>
<td>100</td>
<td>0.491</td>
</tr>
<tr>
<td>γ-B</td>
<td>100</td>
<td>0.8743</td>
</tr>
<tr>
<td>B(Tetragonal)</td>
<td>100</td>
<td>1.014</td>
</tr>
</tbody>
</table>

2.7.3.5 Peritectic transformation

Hall and Economy (2000) investigated the peritectic reaction of Al + AlB₁₂ → AlB₂ using a DSC technique. Boride particles were extracted by dissolving Al matrix in a 25% aqueous solution of HCl followed by separation through screening. It was further reported that AlB₂ was dissolved in solvent aluminium and formed AlB₁₂ after reaching the peritectic temperature (Hall and Economy, 2000).

The recorded peritectic temperature was 956 ± 5°C which contradicts the 980°C reported by (Serebryanskii et al., 1967) and the 1030 ± 5°C reported by (Duschanek and Rogl, 1994). A peritectic temperature of 975°C and a composition of 0.55 at% B was reported by Sigworth (1984) during a thermodynamic assessment of the aluminium rich corner of the Al-B system (Sigworth, 1984). This discrepancy in peritectic composition and temperature is summarised in Table 2.12.

Table 2.12. Peritectic composition and temperature discrepancy in literature (Hofmann and Jäniche, 1935, Serebryanskii et al., 1967, Sirtl and Woerner, 1972, Sigworth, 1984,
Mirkovic *et al.* (2004) re-assessed the Al-B phase diagram and calculated the enthalpy formation of AlB$_{12}$ experimentally using a DSC technique. The reported enthalpy (-2.32 ± 0.2 kJ/mol) was about three times less than that previously quoted in the literature (-7.67 kJ/mol and -11.4± 0.6 kJ/mol) (Meschel and Kleppa, 1995). Additional features related to the stability of AlB$_2$ in the Al-B phase diagram were reported in this work. The maximum stability range for AlB$_2$ was proposed as in the temperature range of 972°C to 213°C. It was further proposed that the formation of AlB$_2$ from AlB$_{12}$ on cooling was very sluggish and that peritectic transformation could not be detected during DSC experiments. Moreover it was concluded that AlB$_{12}$ melting occurs congruently rather than incongruently, reported by (Mirković et al., 2004). The findings of Duschanek and Rogl and Mirkovic were accepted by Raghavan for the calculation of Al-Ti-B and Al-B-Mg ternary systems (Raghavan, 2009, Raghavan, 2010). The latest phase diagram of Al-B binary system is given in Figure 2.25, after including above reported modifications.
There is a consensus on the eutectic temperature ($659.7^\circ$C) and composition (0.055 at%) between investigators. The aluminium rich corner of an Al-B phase diagram is shown in Figure 2.26, and has been extensively investigated by researchers interested in aluminium grain refinement.

Figure 2.25. Phase diagram of Al-B binary system by Okamoto (2006)

Figure 2.26. Aluminium rich corner of Al-B binary phase diagram (Okamoto, 2006, Carlson, 1990, Duschanek and Rogl, 1994, Mirković et al., 2004)
The Al-Ti-B master alloys used for grain refinement contain up to 3 wt% B. The aluminium rich section of the Al-B binary system is also important for the boron treatment of aluminium alloys and the current investigation on vanadium borides formation. A knowledge of the Al-B binary system helps understand the mechanism of AlB\(_2\) and AlB\(_{12}\) stability and dissolution in molten aluminium, which are directly associated with vanadium borides formation.

2.7.4 Al-V binary system

Vanadium is a minor impurity in smelter grade aluminium and usually originates from the petroleum coke and bauxite used in the Hall-Heroult process. The effect of vanadium and other transition metals on the electrical conductivity of aluminium was summarised in Section 2.3. The addition of 0.1% V within the solubility range increased the electrical resistivity of aluminium by 0.4 to 0.5 x 10\(^{-8}\) ohm.m. The vanadium addition had no substantial effect on the mechanical properties of aluminium. The small increase in strength may be due to grain refinement rather than any intrinsic strengthening mechanism. As a grain refiner of aluminium alloys, vanadium is weaker than titanium and zirconium. This section describes the phase equilibria in aluminium rich corner of Al-V binary system. The knowledge of phase equilibria can be used to predict stable phases in the boron treatment of aluminium to produce electrical grade aluminium.

Al-V binary system has been studied by a number of investigators (Murray, 1989, Rostoker W. and A., 1954, Bailey et al., 1959, Carlson et al., 1955). So far, five equilibrium phases have been reported. They are given in Table 2.13 with their crystal structure and space group. Peritectic reactions take place in the aluminium rich section of Al-V binary system where liquid and AlV\(_{10}\) transform into an aluminium vanadium solid solution. The solid solubility of vanadium decreases from 0.37% V at peritectic to less than 0.20% V at 527°C. The rapid quenching can lead to a metastable alloy with 0.5% to 2.6% V in a super saturated solution (Kazakova and Rusnyak, 2009). The Al\(_{21}\)V\(_2\) (Al\(_{10}\)V) phase, having 15.8% V exists from 15.1% to 15.9% V, forms peritectically at 677°C from liquid. An Al\(_7\)V (Al\(_{45}\)V\(_7\)) phase having 21.2% V. Al\(_7\)V is also formed peritectically from Al\(_6\)V (Al\(_{23}\)V\(_4\)), which contains 23.8% V at 687°C. An
Al$_6$V phase is also formed peritectically but at a temperature of 735°C from Al$_3$V. Phase AlV (Al$_{50.1}$V$_{46.9}$) in the Al-V binary system was also detected recently by Huber and Richter (2010).

Table 2.13. Al-V binary system stable phases with their lattice parameters, Pearson’s symbol, space group and prototype (Villars, 1997, Huber and Richter, 2010)

<table>
<thead>
<tr>
<th>Phase</th>
<th>Lattice parameters (nm)</th>
<th>Pearson’s symbol</th>
<th>Space group</th>
<th>Prototype</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>0.4050</td>
<td>---</td>
<td>cF4</td>
<td>Fm3mCu</td>
</tr>
<tr>
<td>Al$_{21}$V$<em>2$ (Al$</em>{10}$V)</td>
<td>1.4492</td>
<td>---</td>
<td>cF184</td>
<td>Fd-3mA$_{12}$V$_2$</td>
</tr>
<tr>
<td>Al$_{43}$V$_7$</td>
<td>2.5604 0.7621 1.1081</td>
<td>mC104</td>
<td>C2/mAl$_{13}$V$_7$</td>
<td></td>
</tr>
<tr>
<td>Al$_{23}$V$_4$</td>
<td>0.76928 --- 1.7040</td>
<td>hP54</td>
<td>P6$_3$/mmcAl$_2$V$_4$</td>
<td></td>
</tr>
<tr>
<td>Al$_3$V</td>
<td>0.3772</td>
<td>---</td>
<td>tB8</td>
<td>I4/mmmAl$_3$Ti</td>
</tr>
<tr>
<td>Al$_8$V$_5$</td>
<td>0.9234</td>
<td>---</td>
<td>c152</td>
<td>I45mCu$_5$Zn$_8$</td>
</tr>
<tr>
<td>V</td>
<td>0.30309</td>
<td>---</td>
<td>cI12</td>
<td>Im3mW</td>
</tr>
</tbody>
</table>

The alloy samples were prepared using arc melting in an inert environment in a water-cooled copper mould. The samples were encapsulated under vacuum in quartz tubes, followed by heating for 3 weeks at 500°C and 620°C. The samples were characterized by EPMA and x-ray powder diffraction techniques to identify the exact composition and subsequent phases.

In the Al$_{50}$V$_{50}$ sample, AlV and Al$_8$V$_5$ phases were detected by EPMA compositional analysis. The DTA analysis of a newly detected phase AlV showed no detectable change in transition temperature. The suggested temperature for the new phase formation was below 540°C. Single crystals of AlV phase have not been produced so far and tetragonal structure was suggested on the basis of diffracted peaks. A SEM image of the Al$_{50}$V$_{50}$ sample annealed at 500°C is shown in Figure 2.27.

The aluminium rich section of the Al-V system is complex and was investigated by Richter and Ipser (2000). The Al-V binary system between 0 and 50 at% V was investigated using differential thermal analysis (DTA), x-ray diffraction (XRD) and electron probe micro analysis (EPMA) on the arc melted samples in an argon
environment. The homogeneity of various peritectic temperatures and phases were determined experimentally. The constructed phase diagram shows a significant deviation from previous investigations. The peritectic reactions and temperatures are given in Table 2.14.

Figure 2.27. SEM-BSE image of Al50V50 sample showing Al8V5 and proposed AIV which is annealed at 500°C (Huber and Richter, 2010)

Table 2.14. Peritectic reactions and temperatures in Al-V binary system (Richter and Ipser, 2000)

<table>
<thead>
<tr>
<th>Phase reaction</th>
<th>Composition of phases, at% V</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L + Al₂V₂ ↔ (Al)</td>
<td>0.09</td>
<td>8.7</td>
</tr>
<tr>
<td>L + Al₄₅V₇ ↔ Al₂₁V₂</td>
<td>0.1</td>
<td>13.5</td>
</tr>
<tr>
<td>L + Al₃₅V₄ ↔ Al₄₅V₇</td>
<td>0.13</td>
<td>14.8</td>
</tr>
<tr>
<td>L + Al₃V ↔ Al₂₃V₄</td>
<td>0.22</td>
<td>25</td>
</tr>
<tr>
<td>L + Al₃V₇ ↔ Al₃V</td>
<td>14</td>
<td>38.5</td>
</tr>
<tr>
<td>L + (V) ↔ Al₈V₅</td>
<td>33</td>
<td>46</td>
</tr>
</tbody>
</table>

The findings of Richter and Ipser are in disagreement with the findings of other investigators (Carlson et al., 1955) regarding peritectic transformation temperatures and
stable compounds in the Al-V system. Carlson et al. also investigated the Al-V system using thermal, microscopic and x-ray diffraction methods and reported four stable compounds, namely Al$_{11}$V (685°C), Al$_6$V (735°C), Al$_3$V (1360°C) and Al$_8$V$_5$ (1670°C). The compound Al$_{45}$V$_4$ was not observed by Carlson et al. and the significantly higher temperatures of Al$_3$V and Al$_8$V$_5$ compounds may be due to an error in the experimental procedure. The higher temperature was measured using the pyrometric method, which is not as accurate (Carlson et al., 1955).

It has been observed that the Richter and Ipser findings are more reliable compared to those of previous investigators, due to the sophistication of the experimental procedure and samples preparation. The characterization techniques are more reliable and accurate compared to the thermal and microscopy techniques used by Carlson et al. Thermodynamic optimisation of Al-V system was carried out by other researchers using the findings of Richter and Ipser (Gong et al., 2004). A sub-lattice model was used for the Al$_8$V$_5$ phase for the final optimisation. Phases such as liquid, fcc (Al) and bcc (V) were modelled using the Redlich-Kister polynomial and others as stoichiometric compounds in the reassessment of the Al-V phase diagram. The reassessed phase diagram was consistent with experimental findings reported by previous workers. The vanadium rich section is important due to the good superconductivity of Al$_3$V phase, but is limited by the higher temperature involved in alloy making. The measurements become difficult at higher temperatures that are essential for the investigation of phase stability.

The phase equilibria information in an Al-V binary system has been used for the investigation of other ternary systems for specific applications. The ternary systems investigated include: Al-V-Nd (Mo et al., 2010), Ti-Al-V (Wang et al., 2010), Al-V-RE (RE = Gd, Ho) (Zhan et al., 2012), Al-Ti-V (Raghavan, 2005c), Al-V-Ni (Raghavan, 2005b) and quaternary systems Al-V-Ni-Ti (Raghavan, 2005a). The thermodynamic properties (activities, integral Gibbs energies of mixing and excess energy) of the Al-V binary system at high temperatures (1727°C, 1827°C and 1927°C) were calculated using the thermodynamic package, FactSage, and reported (Kostov and Živković, 2008).
latest phase equilibrium diagram for the Al-V binary system is shown in Figure 2.28. It compares the work of Murray and Richter given by (Okamoto, 2001).

![Figure 2.28. Al-V binary phase diagram (Okamoto, 2001)](image)

**2.7.5 V-B binary system**

The phase equilibria investigation of the V-B binary system is also of importance to the boron treatment of molten aluminium. The equilibrium phases and their stability are important to the future design and optimisation process parameters to avoid the dissolution of vanadium borides. As a part of the vanadium borides formation in aluminium melt, it is necessary to critically assess the current literature on the V-B binary system.

The V-B binary system has been investigated by researchers in the past (Spear et al., 1987, Spear et al., 1968). Recently, the invariant reactions of the V-B binary system were evaluated (De Lima et al., 2004). The stable phases reported in literature are $\text{V}_{ss}$(vanadium solid solution with boron), $\text{V}_3\text{B}_2$, $\text{VB}$, $\text{V}_5\text{B}_6$, $\text{V}_3\text{B}_4$, $\text{V}_2\text{B}_3$, $\text{VB}_2$ and $\text{B}_{ss}$ (boron solid solution with vanadium) (Okada and Lundström, 1993, Okada et al., 2008, De Lima et al., 2004, Yeh and Wang, 2011). The stability of the $\text{VB}_2$ phase in the Al-Si alloy revealed a barrier to the inter-diffusion and interaction of aluminium with silicon at 500°C in vacuum during the investigation of silicon integrated circuit boards (Kolawa}
et al., 1988). The stability and the formation of $V_5B_6$ in the V-B binary system was investigated on samples made by arc melting followed by heat treatment at 2000°C for 2 hours. The SEM (BSE) and XRD analysis revealed the peritectic ($L + V_3B_4 \leftrightarrow V_5B_6$) formation of $V_5B_6$ from liquid instead of peritectoid ($V_3B_4 + VB \leftrightarrow V_5B_6$) at 1727°C. It was further reported that $V_5B_6$ is stable at 2000°C, which is in disagreement with the work of previous investigators (Nunes et al., 2004). According to De Lima et al., the composition of the liquid phase in invariant reactions, reaction types and temperatures of different stability is summarised in Table 2.15.

Table 2.15. Composition of liquid phase in the invariant reactions, reaction temperature and reaction type (De Lima et al., 2004)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Composition of liquid phase at% V</th>
<th>Reaction type</th>
</tr>
</thead>
<tbody>
<tr>
<td>$L \leftrightarrow V_5B_6$</td>
<td>12</td>
<td>Eutectic</td>
</tr>
<tr>
<td>$L + VB \leftrightarrow V_3B_2$</td>
<td>19</td>
<td>Peritectic</td>
</tr>
<tr>
<td>$L \leftrightarrow VB$</td>
<td>50</td>
<td>Congruent</td>
</tr>
<tr>
<td>$L \leftrightarrow VB + V_5B_6$</td>
<td>~52</td>
<td>Eutectic</td>
</tr>
<tr>
<td>$L + V_3B_2 \leftrightarrow V_3B_6$</td>
<td>~53</td>
<td>Peritectic</td>
</tr>
<tr>
<td>$L + V_3B_4 \leftrightarrow V_3B_5$</td>
<td>56</td>
<td>Peritectic</td>
</tr>
<tr>
<td>$L + VB_2 \leftrightarrow V_2B_3$</td>
<td>57</td>
<td>Peritectic</td>
</tr>
<tr>
<td>$L \leftrightarrow VB_2$</td>
<td>67</td>
<td>Congruent</td>
</tr>
<tr>
<td>$L \leftrightarrow VB_2 + Bss$</td>
<td>95</td>
<td>Eutectic</td>
</tr>
</tbody>
</table>

Vss (vanadium solid solution with boron where vanadium is in excess)
Bss (boron solid solution with vanadium where boron is in excess)

Different composition samples of the V-B alloy were prepared by arc melting in an argon environment from pure (< 99.5%) V and B, and analysed using SEM and x-ray diffraction. The eutectic reaction in the V rich region takes place at 12 at% V instead of 15 at%, proposed by Massalski in the phase diagram given in Figure 2.29. Other findings of De Lima et al. that disagree with the previous investigators include $L + VB \leftrightarrow V_3B_2$ reaction at 19 at% instead of 25 at%, VB congruent formation instead of peritectic reaction ($L + V_3B_4 \leftrightarrow VB$), and $V_5B_6$ formation from liquid peritectically. Moreover, a new eutectic reaction was proposed, which forms VB and $V_5B_6$ from liquid at approximately 52 at% V, and a composition associated with eutectic ($L \leftrightarrow VB_2 +
Bss) was proposed approximately 95 at% in the V-B binary system (De Lima et al., 2004).

![V-B binary phase diagram by Massalski based on Rudy data (Rudy, 1969)](image)

Figure 2.29. V-B binary phase diagram by Massalski based on Rudy data (Rudy, 1969)

The information related to crystal structure, lattice parameters, space group, Pearson’s symbol and prototype is summarised in Table 2.16 (Villars, 1997, Okada and Lundström, 1993, Okada et al., 2008)

Table 2.16. The crystallographic information of stable phases in V-B binary system

<table>
<thead>
<tr>
<th>Phase</th>
<th>Lattice parameters (nm)</th>
<th>Pearson’s symbol</th>
<th>Space group</th>
<th>Prototype</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a</td>
<td>b</td>
<td>c</td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>0.30309</td>
<td>---</td>
<td>---</td>
<td>cI12</td>
</tr>
<tr>
<td>V&lt;sub&gt;3&lt;/sub&gt;B&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.5728</td>
<td>---</td>
<td>0.303</td>
<td>tP10</td>
</tr>
<tr>
<td>VB</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>V&lt;sub&gt;3&lt;/sub&gt;B&lt;sub&gt;6&lt;/sub&gt;</td>
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<td></td>
</tr>
<tr>
<td>V&lt;sub&gt;3&lt;/sub&gt;B&lt;sub&gt;4&lt;/sub&gt;</td>
<td>0.3052</td>
<td>1.335</td>
<td>0.298</td>
<td>oH4</td>
</tr>
<tr>
<td>V&lt;sub&gt;3&lt;/sub&gt;B&lt;sub&gt;3&lt;/sub&gt;</td>
<td>0.30595</td>
<td>1.844</td>
<td>0.298</td>
<td>oC8</td>
</tr>
<tr>
<td>VB&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.2998</td>
<td>---</td>
<td>0.305</td>
<td>hP3</td>
</tr>
<tr>
<td>β-B</td>
<td>1.096</td>
<td>---</td>
<td>2.389</td>
<td>hR105</td>
</tr>
<tr>
<td>1.09251</td>
<td>---</td>
<td>2.382</td>
<td>hR111</td>
<td>R3m</td>
</tr>
</tbody>
</table>
Different composition samples of V-B binary systems are shown in Figure 2.30. Vanadium solid solution (V\text{ss}) and V\textsubscript{3}B\textsubscript{2} are shown, which were produced by arc melting (De Lima et al., 2004).

![Figure 2.30. SEM-BSE image of as cast V-B alloys: a - V89B11, b- V88B12, c- V87B13, d-V81B19 (De Lima et al., 2004)](image)

Vanadium borides crystals have been produced using a high temperature aluminium solution and molten metal flux methods (Okada and Lundström, 1993, Okada et al., 2008). Recently, vanadium borides have also been produced using self-propagating high temperature synthesis (SHS) techniques. Powders of V and B after ball milling was converted into compacts, followed by self-propagating synthesis in an argon environment. The phases detected by x-ray diffraction were VB and VB\textsubscript{2}. It was reported that other phases of this V-B system were kinetically unfavourable for this method due to their complex crystal structure and the temperature of process (Yeh and Wang, 2011).
2.8 Summary

There have been a number of studies on the removal of impurities from aluminium in the last couple of decades; the main focus was on alkali and alkaline earth metals. Literature on the removal of transition metals, especially vanadium, is limited and the available work is explained in terms of industrial practice and electrical conductivity. Although boron treatment has been used in industry for the removal of transition metals from molten aluminium, the fundamental understandings relating to the thermodynamics of borides formation is not well understood. Moreover, the kinetics of vanadium removal and the mechanism of vanadium borides formation in molten aluminium have not been clearly reported by previous investigators.

Removal of vanadium in the form of borides during boron treatment requires an understanding of basic thermodynamics of different binaries (Al-B, Al-V and V-B) systems. Knowledge of thermodynamically stable phases and their transformation at given temperatures and composition is important. From the perspective of boron treatment, knowledge of the aluminium rich section of these binary systems has been critically assessed and is described in Section 2.7.3, 2.7.4 and 2.7.5.

It was concluded from literature review that the level of vanadium is increasing in the potline metal. Aluminium smelters and high purity electrical conductor producers have raised their concerns on the rising of V in petroleum coke. It is imperative to improve current industrial boron treatment or develop new methods to counter this rise of impurities in smelter grade aluminium. However, the improvement in the current boron treatment process could be achieved by the better understanding of thermodynamics and kinetics of transition metal borides formation in molten aluminium.
Chapter 3
Experimental Methodology

In the current study, a combination of thermodynamic modelling and experimental approach was adopted. Thermodynamic modelling provides useful information about the limits of the removal of impurities and the formation of borides in molten aluminium. Thermodynamic predictions were used as basis for designing experimental works. The kinetics of V removal were also investigated to establish the reaction mechanism of VB$_2$ formation in molten aluminium. The investigation of borides settling also provided useful information for the optimisation of the industrial boron treatment of molten aluminium. Both the thermodynamic and experimental approaches are given briefly in this chapter. This chapter also deals with the preparation and analysis of alloys, experimental apparatus, experimental procedures, melting practices, stirring methods and the techniques required to sample for different material characterisation.

3.1 Thermodynamic evaluation approach

Thermodynamic modelling of Al-TM-B (TM = V, Zr, Ti, Cr) systems was carried out using the thermodynamic packages FactSage 6.2 and HSC Chemistry 7.1. Equilibrium calculations were carried out for different alloy systems. The addition of boron was stoichiometric and 75wt% excess, assuming transition metal diborides formation in the molten aluminium. Each system was analysed in the temperature range of 675°C to 950°C, which covers the temperature range of industrial boron treatment. The predictions from thermodynamic analysis were used for the designing of thermodynamic experiments. The approach used in the thermodynamic modelling and results obtained are explained in more details in Chapter 4.
Figure 3.1. Summary of experimental methodology used in this study
**Source alloys**
- Pure aluminium
- Al-10%V
- Al-10%B (AlB₁₂)
- Al-4%B (AlB₁₂)
- Al-5%B (AlB₂)
- Al-15%Zr

**Master alloys**
- Al-1wt%V-0.412wt%B
- Al-1wt%V-0.720wt%B
- Al-1wt%V-1.03wt%B
- Al-1wt%Zr-0.23wt%B
- Al-0.50wt%V-0.50wt%Zr-0.115wt%B

Figure 3.2. Summary of materials used and alloys prepared

- Thermodynamic study
- Kinetics study

Figure 3.3. Details of characterization techniques used in the current study

- OM, SEM, EDX, OES
- OM, SEM, EDX, OES, ICP-AES
- OM, SEM, EDX, EBSD, EPMA, OES, ICP-AES
- OM, SEM, EDX, OES

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3.2 Experimental Study

The experiments conducted in the current study were divided into three categories which are given below,

- Experimental investigations of Al-V-B, Al-Zr-B and Al-V-Zr-B alloys
- Kinetic investigation of V removal from molten aluminium
- Analysis of borides settling in molten aluminium

Experimental investigation of Al-V-B, Al-Zr-B and Al-V-Zr-B alloys were carried out. The addition of boron was stoichiometric, sub-stoichiometric and 75 wt% excess assuming VB$_2$ and ZrB$_2$ formation in the molten aluminium. The thermodynamically stable compounds that are formed during the reaction of Al-B (AlB$_{12}$/AlB$_2$) with V and Zr in solution with molten aluminium were investigated. The summaries of experimental methodology, materials and characterisation techniques are described in Figure 3.1, 3.2 and 3.3 respectively.

3.2.1 Sample preparation

Master alloy samples were prepared for the experimental studies. The source master alloys were used for thermodynamic experiments. For the kinetics and boride settling experiments, Al-1 wt% V master alloys were prepared from Al-10 wt% V in an induction furnace. The list of source aluminium master alloys used and their characterisation is given in the next section.

3.2.2 Acquiring of source alloys and their analysis

The source alloys Al-10wt% V, Al-10wt% B (AlB$_{12}$) and Al-5wt% B (AlB$_2$) were obtained from KB Alloys USA. Other source alloys, including Al-10wt% Zr and Al-4wt% B (AlB$_{12}$), were obtained from KBM Affilips B.V. Netherlands. Aluminium master alloy ingots were prepared according to the required composition and a total mass of 1000 g was aimed at for each alloy. The balance of alloy weight was adjusted with pure aluminium (99.90 wt%) provided by CSIRO Material Science and Engineering, Melbourne. Prepared ingots were heated in an oven for a couple of
hours at 300°C to remove dirt, oil, grease and moisture. The spark emission spectrometer compositional analysis of Al-10wt% V, Al-10wt% Zr and pure aluminium is given in Table 3.1. The composition of the master alloys showed a variation between the actual and the supplier-claimed contents of V and Zr in their alloys.

Table 3.1. Spectrometer compositional analysis of pure Al, Al-V and Al-Zr source alloys

<table>
<thead>
<tr>
<th>Elements</th>
<th>Al-10wt% V</th>
<th>Al-10wt% Zr</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>V</td>
<td>9.7</td>
<td>---</td>
<td>0.0027</td>
</tr>
<tr>
<td>B</td>
<td>&lt;0.01</td>
<td>---</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td>Zr</td>
<td>&lt;0.01</td>
<td>10.2</td>
<td>&lt;0.0003</td>
</tr>
<tr>
<td>Ti</td>
<td>0.01</td>
<td>---</td>
<td>0.0032</td>
</tr>
<tr>
<td>Cr</td>
<td>N.D**</td>
<td>---</td>
<td>&lt;0.0005</td>
</tr>
<tr>
<td>Si</td>
<td>0.08</td>
<td>0.05</td>
<td>0.014</td>
</tr>
<tr>
<td>Fe</td>
<td>0.13</td>
<td>0.12</td>
<td>0.021</td>
</tr>
<tr>
<td>K</td>
<td>N.D**</td>
<td>---</td>
<td>N.D**</td>
</tr>
<tr>
<td>Na</td>
<td>&lt;0.01</td>
<td>---</td>
<td>0.0015</td>
</tr>
<tr>
<td>Cu</td>
<td>0.01</td>
<td>---</td>
<td>&lt;0.0002</td>
</tr>
<tr>
<td>Mn</td>
<td>&lt;0.01</td>
<td>---</td>
<td>&lt;0.0005</td>
</tr>
<tr>
<td>Al</td>
<td>90</td>
<td>89.2</td>
<td>99.90</td>
</tr>
</tbody>
</table>

The compositional analysis of Al-B source alloys used for this investigation is given in Table 3.2. This shows that Al-B alloys have a 2 to 10% variation in claimed and actual boron. Moreover, other major impurities were Si, Fe and K in the master alloys used that would end up in the final alloy.

For the kinetics and boride settling experiments, master alloys similar to those in the thermodynamic experiments were used. Al-1wt% V alloy was prepared in 4 kg batches from an Al-10wt% V master alloy balanced with pure aluminium in an induction furnace. Melting of the alloys was carried out in a clay bonded graphite crucible. The alloy was melted and held at 775 ± 10°C for 10 to 15 minutes and cast in a graphite mould. Finally, the aluminium master alloys Al-1wt% V, Al-10wt% B (AlB₁₂) and Al-5wt% B (AlB₂) were used for the kinetics experiments. The chemical composition of the Al-1wt%V alloy produced is given in Table 3.3.
Table 3.2. Composition of Al-B master alloys used for this study

<table>
<thead>
<tr>
<th>Elements</th>
<th>Al-10 wt% B</th>
<th>Al-4wt% B</th>
<th>Al-5wt% B</th>
<th>Al-6wt% B</th>
</tr>
</thead>
<tbody>
<tr>
<td>V</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>B</td>
<td>10.2</td>
<td>3.9</td>
<td>4.5</td>
<td>6.7</td>
</tr>
<tr>
<td>Zr</td>
<td>&lt;0.005</td>
<td>&lt;0.005</td>
<td>N.D**</td>
<td>N.D**</td>
</tr>
<tr>
<td>Ti</td>
<td>0.02</td>
<td>0.015</td>
<td>0.04</td>
<td>0.06</td>
</tr>
<tr>
<td>Cr</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>0.01</td>
<td>N.D**</td>
</tr>
<tr>
<td>Si</td>
<td>0.11</td>
<td>0.12</td>
<td>0.14</td>
<td>0.07</td>
</tr>
<tr>
<td>Fe</td>
<td>0.2</td>
<td>0.19</td>
<td>0.11</td>
<td>0.13</td>
</tr>
<tr>
<td>K</td>
<td>0.36</td>
<td>0.35</td>
<td>0.42</td>
<td>---</td>
</tr>
<tr>
<td>Na</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>0.21</td>
<td>---</td>
</tr>
<tr>
<td>Cu</td>
<td>0.01</td>
<td>0.01</td>
<td>0.02</td>
<td>---</td>
</tr>
<tr>
<td>Mn</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>0.01</td>
<td>---</td>
</tr>
<tr>
<td>Al</td>
<td>89.5</td>
<td>96</td>
<td>95</td>
<td>93.5</td>
</tr>
</tbody>
</table>

The prepared alloy contained 12 to 13% less vanadium than the composition aimed for, as given in Table 3.3. This could be due to the variation in the initial Al-V master alloy and losses during induction melting. The major impurities were Si, Fe, Cu, Mn and Ni.

Table 3.3. Spectrometer analysis of Al-1wt% V alloy prepared from Al-10wt% V and aluminium (99.90%)

<table>
<thead>
<tr>
<th>Elements</th>
<th>Batch 1</th>
<th>Batch 2</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>V</td>
<td>0.87</td>
<td>0.88</td>
<td>0.875</td>
</tr>
<tr>
<td>B</td>
<td>0.0004</td>
<td>0.003</td>
<td>0.00035</td>
</tr>
<tr>
<td>Zr</td>
<td>&lt;0.0003</td>
<td>&lt;0.0003</td>
<td>&lt;0.0003</td>
</tr>
<tr>
<td>Ti</td>
<td>&lt;0.002</td>
<td>&lt;0.002</td>
<td>&lt;0.002</td>
</tr>
<tr>
<td>Cr</td>
<td>0.0094</td>
<td>0.0111</td>
<td>0.00525</td>
</tr>
<tr>
<td>Si</td>
<td>0.033</td>
<td>0.035</td>
<td>0.034</td>
</tr>
<tr>
<td>Fe</td>
<td>0.059</td>
<td>0.1</td>
<td>0.0795</td>
</tr>
<tr>
<td>Mg</td>
<td>0.0008</td>
<td>0.011</td>
<td>0.00095</td>
</tr>
<tr>
<td>Na</td>
<td>0.0005</td>
<td>0.0008</td>
<td>0.00065</td>
</tr>
<tr>
<td>Cu</td>
<td>0.016</td>
<td>0.016</td>
<td>0.016</td>
</tr>
<tr>
<td>Mn</td>
<td>0.014</td>
<td>0.0018</td>
<td>0.0079</td>
</tr>
<tr>
<td>Ni</td>
<td>0.069</td>
<td>0.07</td>
<td>0.0695</td>
</tr>
</tbody>
</table>
Boron was added in the form of Al-10wt% B (AlB₁₂) and Al-5wt% B (AlB₂) master alloy ingots. The alloy composition aimed for consisted of stoichiometric amounts, with the addition of 75wt% and 150wt% B in excess of the requirements for vanadium (assuming VB₂ formation) during the kinetic experiments.

3.2.3 SEM and EDX analysis of aluminium source master alloys

Analysis of aluminium master alloys was important in order to understand the chemistry and morphology of the intermediate phases in the aluminium matrix and their effect on the overall kinetics of boron reaction with transition metals. It was further emphasized that the dissolution characteristics of the intermediate phases (particles) would be important from the perspective of boron treatment, hence the removal of transition metals (especially V) from the molten aluminium. The aluminium source alloys used were first analysed one by one. Most of the additions in alloy making are carried out in the form of alloys rather than their elemental forms. The dissolution kinetics of master alloys is favourable in cast houses, compared to the use of pure elements. The most important parameters in the production of aluminium master alloys include the solubility of the element, the chemistry, size and morphology of the intermetallics in the aluminium matrix and their surface properties. Aluminium master alloys are available in the form of rods, ingots, pigments, waffles and compact briquettes (Totten and MacKenzie, 2003). The master alloys used in this study are analysed in the next section.

3.2.3.1 Aluminium boron master alloy

Aluminium boron master alloys are currently used as inoculants for the production of electrical grade aluminium. They are mainly used as rods or waffles in the continuous casting lines or holding furnaces in the cast houses. As stated in Chapter 2, the Al-B binary system has two stable phases. Thermodynamically, AlB₂ will exist up to 44.6 wt% B and AlB₁₂ will be stable up to 83wt% B at room temperature. Industrially, master alloys with different boron compositions (10, 8, 6, 5, 4 and 3 wt%) are used. These alloys have, predominantly, either an AlB₁₂ or AlB₂ phase depending upon the history of the alloy making. Al-B master alloys are produced by
the reduction of KBF₄ salts directly in the molten aluminium at a specified temperature (Wang, 2005, Hall and Economy, 2000, Aly et al., 2004). The following reactions have been written for the production of either AlB₁₂ or AlB₂ phase Al-B master alloys using KBF₄ salts and aluminium.

\[
12KBF_4 + 13Al \rightarrow AlB_{12} + 12KAlF_4 \rightarrow AlB_{12} + 12KF + 12AlF_3 \\
1KBF_4 + 3Al \rightarrow AlB_2 + 2KAlF_4 \rightarrow AlB_2 + 2KF + 2AlF_3
\]  

(3.1)  

(3.2)

Aluminium borides produced are dispersed in the flux and molten aluminium. It was reported that boron recovery was less (30 to 40%) due to the entrapping of borides in flux on the top of the molten aluminium. Birol (2011) suggested an improved method where a premix of KBF₄ and Na₃AlF₆ was used instead of just KBF₄ salts. An Al-3wt% B master alloy produced by this method was free from entrapped salts. Moreover, a higher recovery (70 to 80%) of boron was achieved in the form of dispersed AlB₂ particles in the aluminium matrix (Birol, 2011). Other methods used for the production of AlB₂ particles in an aluminium matrix include the reaction of molten aluminium with borax (Na₂B₄O₇·10H₂O) or boron oxide (B₂O₃). Industrially, the thermite reaction of KBF₄ salt with aluminium is used to produce Al-B master alloys. The process temperature and the composition of the boron will determine the type of boride in the end product. A temperature higher than the peritectic temperature (980°C) is required for the formation of AlB₁₂ borides even for a composition with low boron. Master alloys (Al-10wt% B, Al-6wt% B, and Al-4wt% B and Al-3wt% B) that have AlB₁₂ as the predominant phase are produced at a higher temperature in the induction melting, which is followed by fast cooling. Master alloys (Al-5wt% B) that have AlB₂ as the predominant phase is produced at a lower temperature (850°C), which also requires less holding time at this working temperature. Al-4wt% B, which contains AlB₁₂ as the predominant phase, was used for the preparation of the Al-V-Zr-B and Al-Zr-B master alloys. Al-borides were observed as clusters having various particle sizes and shapes under an optical microscope.

Figure 3.4 shows black particles embedded in the white aluminium matrix. These particles have a wide range of particle sizes varying from a few microns to 100 μm.
Al-boride particles even bigger than 100 μm were observed under an optical microscope. These particles have irregular morphology and are mostly in clusters composed of various sizes. A scanning electron microscopic image is shown in Figure 3.5(a). The energy dispersive spectrum analysis (EDX) shows the presence of B, O, Si and F in the aluminium matrix.

Figure 3.4. Optical microscopic image of Al- 4wt% B (AlB₁₂) master alloy

Due to the low atomic element, detection of boron is only just within the detection limits of the EDX detectors used for the investigation. Although the EDX detectors can detect peaks of boron in the spectrum, they cannot quantify the content of boron. Silicon and iron were part of the starting material (molten aluminium) and F, K and O were mostly entrapped during the preparation of the Al-B master alloys shown in the EDX spectrum in Figure 3.5(b).

Figure 3.5. (a) SEM-SE image and (b) EDX analysis of borides in Al-4wt% B master alloy
In this study, an Al-10wt% V master alloy was used as the source of vanadium in the prepared alloys. The chemical composition analysis of Al-10wt% V, given in Table 3.1, shows that vanadium and some other minor elements (Si, Fe, Mn, Na and Cu) were present in the aluminium. The Al-V Phase diagram was discussed in section 2.7.4. It was shown that $\text{Al}_{21}\text{V}_{2}$ ($\text{Al}_{10}\text{V}$) and $\text{Al}_{45}\text{V}_{7}$ ($\text{Al}_{7}\text{V}$) were the stable compounds of Al and V in the Al-10wt% V master alloy, depending upon the history of the alloy making and the processing parameters. Al-V master alloys are mainly produced using the alumina-thermic reduction of vanadium oxide ($\text{V}_2\text{O}_5$ or $\text{V}_2\text{O}_3$) in the presence of fluxes. The reduction reactions are exothermic and only require initial ignition, which is self-sustainable during the process. The reduction reaction is given in Eq. (3.3).

$$3\text{V}_2\text{O}_5 + 10\text{Al} \rightarrow 6\text{V} + 5\text{Al}_2\text{O}_3 \quad \Delta H = -295 \text{ kCal.}$$

Reduced vanadium will be alloyed with molten aluminium, which is provided in excess of the requirement for vanadium oxide reduction. Different grades (10%, 40%, 60% V) of Al-V master alloys are produced through such processes. Alumina formed during the process is trapped in the flux on top of the aluminium melt. The formation of nitrides and slag voids in the aluminium master alloys when using the alumina-thermic process has also been reported in the literature (Frederick and Wyomissin, 1971, Coffer, 1957, Bobkova et al., 1981).

Optical microscopy images of the Al-10wt% V master alloy used for this investigation are given in Figure 3.6, which shows two dominant phases in the aluminium matrix. It can be seen in Figure 3.6 that the grey phase is high temperature stable and forms during the early stages of alloy solidification. The black phase solidifies at a later stage of alloy solidification, which could be observed from its morphology. The eutectics of Al, Si and Fe were also observed in the aluminium matrix in the form of concentric lines.
Slag voids reported by previous investigators were also found in the Al-10wt% V master alloys used in the alloy making. Scanning electron microscopic images and EDX analysis are shown in Figure 3.7.

It could be observed from EDX spectrum that Al and V were mainly present in the alloy. Point analysis of different areas was carried out to find the quantitative composition of the dominant phases of the Al-V master alloys, as shown in Figure 3.8(a). It was concluded from EDX analysis that the grey phase could be Al$_{10}$V and white phase could be Al$_3$V in the aluminium matrix, but further analysis is required to confirm these phases.
Compounds of Al-V (Al$_{21}$V$_2$ and Al$_{45}$V$_7$) are not thermodynamically stable at the alloy preparation temperature. If sufficient holding time is given at a higher temperature (> $736^\circ$C), then stable Al$_3$V will be formed. Rapid cooling of such an alloy will not give sufficient time for the phase transformation of Al$_3$V into Al$_{45}$V$_7$. Hence, they were only observed at room temperature in the Al-10wt% V master alloys. It must be emphasised that this investigation has been based on the EDX analysis. Further characterization will be required for the exact determination of both phases in the Al-V master alloys.

3.2.3.3 Aluminium zirconium master alloy

An Al-Zr master alloy (Al-15wt% Zr) was used as a source of Zr for the preparation of Al-Zr-B and Al-V-Zr-B alloys. A binary phase diagram of Al-Zr was used to predict a stable Al$_3$Zr phase in the aluminium matrix. Al-Zr master alloys were produced in the same way as the Al-V master alloys using alumina-thermic reduction of the oxides (Flores et al., 2012, Coffer, 1957). The overall reaction in the reduction of ZrO$_2$ can be written as,

$$3ZrO_2 + 4Al \rightarrow 3Zr + 2Al_2O_3 \quad \Delta H = -10 \text{ kCal.} \quad (3.4)$$
Master alloys are mostly produced using the induction melting due to the homogenisation of melt caused by the induction stirring. It has been reported in the literature (Flores et al., 2012) that the addition of a small amount of Mg will favour the production of Al-Zr master alloys. The alumina produced as result of reaction 3.4 will be trapped in the flux that floats on the surface of the molten aluminium. The reduced Zr will alloy with molten aluminium that is always provided in excess according to the final master alloy composition. Al-Zr alloys are used as a grain refiner in the Al-Si alloys. They are also used to manufacture heat resistant aluminium alloys. The optical microscopy image and EDX analysis of Al-15wt% Zr is shown in Figure 3.9.

It can be observed that grey particles are embedded in the white matrix. These particles are randomly distributed and observe specific elongated morphology. Black particles in the images could be inclusions from the alloy making process. Only one phase is present in the aluminium matrix shown in Figure 3.9(a).

![Image](image_url)

Figure 3.9. Optical microscopic image and EDX analysis of Al-15wt% Zr master alloy

Point analysis and elemental mapping of the alloy by EDX showed the presence of O, C and Zr in the aluminium matrix. Oxygen is uniformly distributed in the matrix and Zr is located in the Al-Zr (Al₃Zr) compounds. These are shown as white particles in the SEM image. Carbon may come from the graphite impeller dissolution that is used for the mechanical stirring of melt during alloy making. The elemental mapping of the master alloy is shown in Figure 3.10.
The grey phase shown in the SEM image was most likely Al₃Zr, based on the compositional analysis of different points through the EDX shown in Figure 3.11 (a).

<table>
<thead>
<tr>
<th>Points</th>
<th>Element (at %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Al</td>
</tr>
<tr>
<td>1</td>
<td>72.58</td>
</tr>
<tr>
<td>2</td>
<td>72.73</td>
</tr>
<tr>
<td>3</td>
<td>100</td>
</tr>
</tbody>
</table>

3.2.4 Master alloys preparation

This section is dedicated to the preparation of Al-master alloy ingots for the thermodynamic experiments. It further describes the melting practice and samples preparation for optical (OM) and scanning electron microscopy (SEM), energy
dispersive x-ray analysis (EDX), electron back scattered diffraction (EBSD), x-ray diffraction (XRD), electron micro probe analysis (EPMA), spectrometry, and inductively coupled plasma analysis (ICP).

The first batch of experiments consisted of the manufacture of 1000 g of Al-V-B systems having 1wt% V, using an induction furnace. The boron was in addition to the stoichiometry requirements, with a 75wt% boron excess assuming VB₂ formation. The second batch of experiments was involved the manufacture of 25g of Al-1wt% V-0.412wt% B and Al-1wt% V-0.72wt% B alloys sectioned from the ingots of the first batch prepared by induction melting. The weighed samples were held at 700°C, 775°C and 850°C for 12 hours in a vertical resistant heating furnace. In each trial, argon was purged in the vertical tube at the beginning and end of experiments at a flow rate of 100 l/hour for 5 minutes. At the end of each trial, the alumina crucible containing molten alloy samples was cooled in a water-cooled steel flange at the bottom of the vertical shaft.

In the third batch of experiments, a mass of 1000 g of Al-Zr-B and Al-Zr-V-B alloys was prepared from the master alloys, similar to first batch. The aimed composition of the alloys consisted of 1wt% Zr in Al-Zr-B and 0.50 wt% in the Al-Zr-V-B alloys. The alloy, Al-Zr-V-B, also contains 0.50 wt% V in addition to Zr in the aluminium. Boron was added to make stoichiometric amounts (0.23 wt%, 0.115 wt%) to Zr in both Al-Zr-B and Al-Zr-V-B alloys, assuming ZrB₂ formation.

3.2.4.1 Sample preparation for microscopy (OM, SEM), EDX and EBSD analysis

For thermodynamic experiments, a lower portion of each sample was sectioned using a Stuers (Secotom-50) cutting machine. Some samples were wire cut especially for the EBSD analysis to ensure the required dimensions. For easy handling, the sample was hot mounted in bakelite using a Buehler (Simplimet 1000) automatic mounting press. Mounted samples were mechanically polished on SiC emery papers (320, 600, 800, 1000 and 1200 grit) using water as the lubricant on a Leco (VP-150) grinding wheel. Polishing was carried out using 9, 6, 3, 1 μm diamond paste, and alcohol as the lubricant, for 3 minutes on a Buehler (Phoenix beta) polisher. Final polishing was carried out using OP-S (0.05 μm colloidal silica suspension) solution for 10 minutes.
The polished samples were cleaned using alcohol and an ultrasound stirrer (Soniclean 120T) to remove any dirt or particles. A similar polishing procedure was adopted for the preparation of aluminium master alloys. Samples for TEM observation were sliced into sheets of ~0.6 mm thick. Discs of 3 mm in diameter were punched from the alloy sheets, ground to a thickness of ~0.50 mm, and then ion milled at low-angles using a Gatan Precision Ion Polishing System (PIPS). Characterisation of the microstructures was conducted in a Philips CM20 TEM, equipped with an Oxford INCA energy dispersive spectroscopy (EDS) system. Microscopy and EDX samples from the kinetics and boride settling experiments were prepared in the same way as the thermodynamic samples. The boride sludge at the bottom of the crucible that settled during holding of the melt was collected and prepared for SEM analysis in a similar way to previous microscopy samples.

3.2.4.2 Sample preparation for ICP-AES analysis

For inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis, samples were prepared by drilling into cast ingots. The chips were then collected. A few grams of the samples were used from different locations in the main ingots, taken after different time intervals during the kinetics experiments. ICP-AES samples were analysed for V to determine whether its contents were in the solution with aluminium. Samples taken at regular intervals were dissolved in HCl for ICP-AES analysis. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was used to quantify the level of V in solution with aluminium. This analysis was conducted at Spectrometer Services Pty Ltd, Melbourne, Australia. The samples (1 to 2 g) were dissolved in HCl/HNO$_3$ solution to remove inclusions and borides. The used solution will not dissolve AlB$_{12}$, AlB$_2$ and other possible borides. It has been reported in literature that a fraction of the VB$_2$ that is dissolved in HCl solutions contain HNO$_3$ or HF (Simensen and Strand, 1981). To avoid dissolution of VB$_2$, samples were only dissolved in 50% HCl solution for the final ICP-AES analysis. For the ICP-AES analysis, both thermodynamic and kinetics samples were prepared by the above-mentioned method.
3.2.5 Thermocouple calibration and temperature profile measurements

A K-type thermocouple was used for this study and calibrated with the reference thermocouple. Both working and reference thermocouples were placed inside the vertical tube furnace at 700°C, 750°C and 850°C and the temperature recorded. It was found that the temperature difference between both thermocouples was less than 2°C at maximum. The temperature profile for the vertical tube furnace was measured and is given in Appendix A. A thermocouple was inserted at the bottom of the furnace and the temperature gradient then recorded at each 2 cm steps upward. An isothermal zone of 10 cm was located in the middle of the vertical tube furnace. It was recorded that the actual temperature in the isothermal zone was 25°C lower than the set temperature. It was assumed that the temperature gradient in the alumina crucible would be less than 1°C. The temperature profiles for each experiment conducted at 700°C, 750°C and 850°C are shown in Appendix A.

In induction melting, temperature control during the isothermal hold was maintained by careful regulation of the input power, together with manual monitoring of the temperature. The temperature of the aluminium alloys was monitored at 2 to 3 minute intervals. A K-type thermocouple, protected by an alumina sheath, was employed in these experiments. The thermocouple could not remain in aluminium melt for continuous measurement as it would have overheated in the induction field, and consequently the temperature control was not automatic. A temperature in the range of ± 10°C was maintained manually by regulating the furnace power (kV) and immersing the thermocouple at regular intervals throughout the experiments.

For the kinetics and boride settling experiments, the temperature was controlled using a K-type thermocouple sheathed with an alumina tube similar to that used for induction melting. The thermocouple was fixed with a vertical stand to the top of the furnace and immersed in the middle of the melt in a graphite crucible. The temperature controller of the furnace was connected with a working thermocouple to maintain the set temperatures of 700°C, 750°C and 800°C. A graphite crucible containing melt was placed in the middle of a resistant pot furnace and covered with a thermal insulator to avoid heat loss. The temperature variation inside the crucible from top to bottom was expected to be less than 2°C because it was completely
covered by resistant heating elements. It was assumed that the maximum temperature variation in 1000 g molten aluminium would be approximately 2 to 3°C, including any K-type thermocouple error of ~1°C in these experiments.

3.2.6 Experimental procedure

For the current study, experiments were conducted by reacting V and Zr with boron to form their insoluble borides at different temperatures and with the addition of boron in molten aluminium. For the thermodynamic experiments, the experimental procedure can be divided into two main sections, namely the melting of alloys in an induction furnace and the melting and long hold in a vertical tube furnace (resistant heating) for the purpose of equilibrium. The kinetic experiments were conducted in a resistant heating furnace to maintain better control of the temperature and stirring. Boride settling experiments were also conducted using a resistant heating furnace with a bigger (A10) graphite crucible.

3.2.6.1 Experiments using induction melting facilities

Induction melting is considered efficient for alloy making because of the melt homogenisation obtained by induction stirring. For this research, Al-V-B, Al-Zr-B and Al-V-Zr-B alloys were prepared from their master alloys in the induction furnace. A schematic representation of the induction melting facility is shown in Figure 3.12. A picture of the actual induction furnace is given in Appendix B.

Pure aluminium ingots were melted in a clay-bonded graphite crucible with a boron nitride (BN) coating using an induction furnace in air. The weighed and preheated master alloy (Al-10wt% V, Al-10wt% Zr) ingots were introduced into molten aluminium. To investigate the reaction kinetics, the melt was held at 750 ± 10°C with the stirring maintained by the induction power levels. Sampling of the melt was carried out at regular 15-minute intervals, being 0, 15, 30, 45 and 60 minutes, after the addition of the Al-B master alloys. A sample was taken before the addition of Al-B master alloy ingots into molten aluminium containing V or Zr (i.e. 0 minute). Five samples were taken from each alloys studied after the addition of Al-B master alloys. The samples taken were allowed to solidify in air.
Experiments using vertical tube furnace

For the thermodynamic experiments, 25 g ingots of each alloy were prepared from 1000 g ingots of Al-1wt% V-0.412wt% B and Al-1wt% V-0.720wt% B alloys prepared in the induction furnace. A weighed ingot of each alloy was melted in an alumina crucible and held at 700°C, 775°C and 850°C in the vertical heat resistant furnace. Alloys were held at different temperatures for 12 hours followed by rapid cooling. A vertical tube furnace equipped with molybdenum disilicide heating elements was used in these experiments. A schematic representation of the thermodynamic experimental set-up is shown in Figure 3.13. A picture of the actual vertical tube furnace is shown in Appendix B.

The lower part of the furnace was designed for the rapid quenching of molten aluminium alloys following reaction temperatures of 700°C, 775°C and 850°C. An alumina pedestal was designed with a circular disc on the top to raise and hold an alumina crucible containing molten alloys in the isothermal zone of the vertical tube furnace. A sacrificial alumina tube was used inside the main furnace tube to avoid contamination from previous experiments. The reacting chamber was flushed with high purity argon for 5 minutes at a flow rate of 100 l/hr at the start and end of each
experiment. A weighed sample of Al-V-B alloys was cleaned, dried and heated at 300°C in the oven and transferred to an alumina crucible. The crucible was slowly raised in the vertical tube furnace at a pre-set experiment temperature.

Figure 3.13. Schematic representation of the vertical tube furnace used for thermodynamic experiments

At the end of the experiment, the crucible was lowered into a stainless steel flange was cooled by circulating water in the copper coil. A cooling rate of 5 to 10°C/sec was estimated by performing separate experiments using the same cooling mechanism and melt in an alumina crucible.

3.2.6.3 Kinetics experiments using resistant pot furnace

Kinetic experiments were conducted to investigate the reaction kinetics and mechanisms of vanadium boride formation during the boron treatment of molten aluminium. Aluminium master alloys (Al-1wt% V, Al-10wt% B and Al-5wt% B) were used for the kinetic experiments. Kinetic experiments of V removal from aluminium melt were conducted by reacting V/Al-V with solid AlB₁₂/AlB₂ or B from Al-B master alloys. Experiments were performed at different temperatures (700°C,
750°C and 800°C), melt rates of stirring (no stirring, 100 rpm, 350 rpm and 550 rpm) and various amounts of added boron.

A resistant heated pot furnace was used for the kinetic experiments, giving better control of both the temperature and the stirring of the melt. A schematic representation of the apparatus is shown in Figure 3.14. A picture of the actual apparatus is provided in Appendix B.

![Figure 3.14. Resistant heating pot furnace](image)

It can be seen in Figure 3.14 that a clay bonded graphite crucible was placed in the middle of heating elements of the furnace. The pot furnace was heated using coiled tungsten wire on the ceramic holder, which was covered by a steel shell. The thermocouple was fitted on one side of the central pot where the crucible was placed, which is usually connected to an automatic temperature controller. For this study, the temperature was controlled and tracked by immersing a thermocouple in the melt. A working thermocouple was fixed to a steel stand, as shown in Figure 3.14, and connected to a temperature controller in order to maintain set temperatures of 700°C, 750°C and 800°C. A thermocouple fitted inside the furnace will have more temperature discrepancy, as it has no direct contact with either melt or crucible. This thermocouple will give a higher temperature reading than the actual temperature in
the melt because it is nearer to the heating elements and away from the crucible that contain molten aluminium alloy.

A clay bonded graphite crucible was used in these experiments. It was coated with boron nitride (BN) to avoid any contamination due to erosion and corrosion of the graphite with the aluminium. A graphite crucible (A4) was obtained from MorganMMS, which can hold 1.5 kg molten aluminium. This lift and bale out crucible has a height of 97 mm, a bottom diameter 55 mm and a top diameter 79 mm. A schematic diagram of the A4 crucible is shown in Figure 3.15.

![Figure 3.15. A bale out type clay bonded graphite crucible](image)

A resistant pot furnace is limited in the temperature achievable (>800°C), due to the dangerous possibility of the heating elements oxidising and extensive heat loss. Clearance between the crucible and furnace was insulated with ceramic fibre to avoid heat loss, and hence a high temperature (800°C) could be maintained.

In the kinetic experiments, a mass of 1000 g was prepared from Al-1wt% V and Al-10wt% B (AlB₁₂) master alloys and pure aluminium ingots. Weighed ingots were heated in the oven at 300°C to remove moisture, dirt and oil. Pure aluminium and Al-1wt% V ingots were melted in the crucible at the above-mentioned temperature in an open environment and held for some time to dissolve the Al-V compounds. An ingot of Al-10wt% B was preheated in the oven at 300°C and then introduced in the molten
Al-alloys. A temperature drop was observed due to the quenching effect of the lower temperatures (200°C to 300°C) of the Al-B master alloy ingots. The recorded temperature drop was approximately 23°C to 30°C in the case of stoichiometry boron addition and ~35°C to 45°C in 75wt% when the boron excess was added. A temperature drop of ~55°C was observed during the addition of 150wt% excess boron. The set temperature was regained in 2 to 4 minutes in stoichiometry amounts, in 6 to 8 minutes in 75wt% excess and in 8 to 9 minutes in the case of the experiments with added 150wt% boron excess.

A sample was taken before the addition of Al-B (at 0), then at 2, 4, 6, 8, 10, 10, 15, 30, 45 and 60 minutes after the addition of the Al-B ingots. A steel scope coated with boron nitride was used for sampling, which could carry 5 to 10 g of aluminium melt. A temperature drop of approximately 2 to 4°C was recorded during sampling. The steel scope and skimmer were heated above 200°C to minimise the temperature drop during sampling and the removal of dross from the top of the molten alloys. Samples were allowed to cool in air on a graphite block that was marked for recording.

The first series of kinetics experiments was carried out in the absence of melt forced convection. There was some natural stirring due to the composition and temperature gradients in the different parts of the crucible but necessary precautions were made to minimise any external turbulence. Different temperatures (700°C, 750°C and 800°C) and levels of boron addition (stoichiometry, 75% and 150% excess) were used in the kinetic experiments.

In the next series of experiments, a mechanical rotator introduced forced convection into the melt. The mechanical stirrer used consisted of an electrical motor, a chuck to grip the rotating shaft and two propellers attached at 90° to the vertical shaft. The stirrer had a mechanism to control the different stirring rates (rpm’s) applied to the molten alloys. The propellers and stainless steel shaft were covered with an alumina tube to minimise dissolution, and hence contamination of the alloys by Fe and other impurities. The stirrer was immersed in the lower part of melt for efficient mixing and stirring, as shown in Figure 3.16. Molten alloy stirring at 100 rpm, 350 rpm and 550 rpm at 750°C was carried out during the forced convection by mechanical rotation. A temperature drop of 5°C to 10°C was recorded at the start of melt stirring.
and reached the set values during the course of experiment. Samples were taken from the middle of melt at regular intervals, which has already been explained.

![Figure 3.16. Stirring of aluminium melt with mechanical stirrer](image)

Kinetic experiments were also conducted by two step addition of Al-B ingots in melt at 750°C to determine any significant effect on the removal of V from molten alloy. In these experiments, stoichiometric requirement of boron was added initially and the rest of 75wt% excess was introduced after 30 minutes. Sampling was carried out at 0, 2, 6, 10, 15, 30 (first addition), 35, 45 and 60 (second addition) minutes.

A second type of melt-forced convection was carried out by purging nitrogen (N₂) gas. An alumina tube was used for the gas purging, 10 mm in diameter, and connected to a gas cylinder through a vinyl pipe. An alumina tube was preheated to avoid thermal cracking and a gas flow rate of 1.764 l/min was used for each stirring step. The practice of melting and adding Al-B ingots was similar to previous kinetic experiments. Gas stirring was carried out for 60 seconds at 4, 9, 14, 29, 44 and 59 minutes after the addition of the Al-B ingots. Samples were taken after each stirring step (5, 10, 15, 30, 45 and 60) and allowed to cool in air. A schematic diagram of the gas stirring experimental set up is shown in Figure 3.17. During the course of the experiments, borides and other inclusions were produced by the reaction of V/Al-V
with B or AlB$_{12}$/AlB$_2$ solid particles in the melt. Borides are heavy and settle at the bottom of crucible, and were collected for the subsequent SEM and XRD analysis.

![Diagram of stirring of aluminium melt with nitrogen gas injection with top lance](image)

**Figure 3.17.** Stirring of aluminium melt with nitrogen gas injection with top lance

### 3.2.7 Details of characterisation techniques and equipment

#### 3.2.7.1 OM, SEM, EDX and EBSD analysis

The samples were subjected to optical, SEM, EDX, EBSD and EPMA analysis. Optical microscopy was conducted using Leica Microsystems (1000X Magnification) to observe any possible reaction between the solid AlB$_{12}$/AlB$_2$ particles with V/Al-V in the aluminium matrix. A SUPRA model 40VP-25-38 SEM, fitted with an energy dispersive spectrum (EDX) detector, was used for phase observation, identification and qualitative compositional analysis.

For EBSD analysis, samples with dimensions of 10 mm × 8 mm × 1 mm were wire cut from the lower section of each sample. After mechanical grinding to a 2400 grit SiC finish, the samples were carefully polished using 0.05 μm silica suspension for approximately 10 minutes and 0.05 μm alumina suspension for approximately 2 minutes. For EBSD analysis, the polished samples were examined in a JEOL JSM 7001F field emission SEM, equipped with an HKL Channel 5 EBSD system. Transmission electron microscopy characterisation of microstructures in the Al-V-B alloys was conducted in a Philips CM20 TEM, equipped with an Oxford INCA
energy dispersive spectroscopy (EDX) system at Monash Microscopy Centre, Melbourne.

3.2.7.2 EPMA analysis

The electron micro probe (EPMA) analysis of the Al-V-B alloys was carried out at The University of Queensland, Brisbane, Australia. The composition of all phases observed under SEM in the samples was measured and quantified using a JEOL 8800L Electron Probe X-ray Microanalyser (EPMA) with wavelength dispersive spectrometers (WDS). An accelerating voltage of 10 kV and a probe current of 15 nA were used. The Duncumb-Philibert ZAF correction procedure supplied with JEOL 8800L was applied. The standards used for analysis, namely Al₂O₃ for Al and O, BN for B, V for V, were from Charles M. Taylor Co. (Stanford, California). The average accuracy of the EPMA measurements was estimated to be within 1 wt% of element concentration.

3.2.7.3 ICP-AES analysis

For ICP-AES analysis, a Varian 730ES axial view inductively coupled plasma atomic emission spectrometer was used. A calibration curve was generated by pure aluminium spiked with pure vanadium; hence the quantification of samples for vanadium. The ICP-AES analysis was carried out at Spectrometer Services Pty, Coburg, Melbourne.
4.1 Modelling approach

Aluminium is widely used for overhead power cables because of its good electrical conductivity and lightweight. Metal impurities, in particular Ti, Zr, V and Cr in solution, affect the electrical conductivity of aluminium significantly. Industrially, boron treatment has been used to remove these impurities through the formation of borides, as described in Section 2.4.3. This chapter focuses on the thermodynamic modelling of transition metals (V, Ti, Zr, and Cr) borides under different temperature conditions to predict possible stable phases. The removal of transition metals (V, Ti, Zr and Cr) was analysed by different amount of boron addition. This chapter further elaborates the formation and stability of various borides in the temperature range of 675°C to 950°C. Moreover, stoichiometry amounts and the addition of excess boron are critically analysed in this chapter. Thermodynamic predictions will lead to the development and design of experiments for the removal of V and other transition metals from aluminium melt in the form of their stable borides.

Thermodynamic package HSC Chemistry 7.0 was used to predict the thermodynamic properties of pure compounds (borides) as well as developing Ellingham diagram of these borides. The thermodynamic package FactSage 6.2 was employed for the equilibrium calculations and to analyse the binary and ternary phase diagrams. The light metal database (FTlite) was used in the FactSage where a modified quasichemical model was used for the assessment of liquid phases. This model is based on the short range ordering tendency of atoms or molecules in liquid solutions (Pelton et al., 2000). The modified quasichemical model was explained briefly in Section 2.5.8. For solid boride phases (MB and MB₂), the sub-lattice model based on substitutional solution assumptions was used, which is given in Section 2.5.7. In
The sub-lattice model, it is assumed that crystalline species are formed in two or more different lattice structures (Hillert et al., 1985).

The thermodynamic analyses carried out include:

- Evaluation of Gibbs free energy formation of aluminium and transitional metal borides.
- Equilibrium calculations of different compositional systems (Al-V-B, Al-V-Ti-B, Al-V-Ti-Zr--B, and Al-Ti-Zr-V-Cr-B). The addition of boron was stoichiometry and 75wt% excess boron to the concentration transition elements (assuming the formation of their diborides).

### 4.2 Borides Gibbs free energy evaluation

The Gibbs free energy formation of various metal boride phases was evaluated using the HSC Chemistry 7.0 package in the temperature range of 650°C to 900°C. The Gibbs free energy minimisation method for predicting stable phases was used for the analysis of various compounds. The results obtained are presented in Figure 4.1. During the evaluation, it was predicted that the diboride phases (AlB$_2$, TiB$_2$, ZrB$_2$, VB$_2$, and CrB$_2$) of transitional metals were the most stable in the given conditions, as compared with their other possible phases (AlB$_{12}$, TiB, VB$_3$B$_4$, V$_3$B$_6$, CrB, Cr$_3$B$_4$, Cr$_5$B$_3$).

Figure 4.1 suggests the order of stability of pure diborides in aluminium melt from ZrB$_2$, TiB$_2$, VB$_2$, AlB$_2$, CrB$_2$ to AlB$_{12}$ in the given temperature range (650°C to 950°C). This order of stability also suggests that the elements Zr, Ti, V can be removed by the addition of Al-B master alloys through the formation of borides, as has been demonstrated experimentally by previous investigators and discussed in Section 2.4.3. Chromium diborides (CrB$_2$), however, show a lower stability compared to AlB$_2$, thus boron treatment may not be an appropriate method to remove Cr from aluminium melt. This agrees with the findings of (Wang et al., 2002), who reported that there was no evidence of the borides of Cr and Mn in the reaction products during reactions between boron and transition metals.
4.3 Equilibrium calculations

Equilibrium calculations of different Al-TM-B (TM = Ti, Zr, V, Cr) systems in aluminium melt were carried out using the FactSage 6.2 thermodynamic package in the temperature range of 675°C to 900°C. The “Equilib” module of FactSage was used for the calculations that incorporate the Gibbs free energy minimisation technique to predict the thermodynamically stable phases of different compositions and temperature conditions. Due to the lack of thermodynamic information for solutions, in these calculations it was assumed for the boride systems that:

- ZrB₂ formed an ideal solution with TiB₂, i.e. (Zr,Ti)B₂
- There was only a very small solubility of Al in (Zr,Ti)B₂ and *vice versa*
- AlB₁₂, VB₂, CrB₂ (and other borides) were pure

The total concentration of the transition metals and boron varied from 1.1 to 1.72wt% in the Al alloy-boride systems under discussion. Stoichiometry and 75wt% boron excess (assuming diboride formation) were added to the systems to investigate the boride formation preferences. It has been suggested by previous investigators (Cooper and Kearns, 1996, Stiller and Ingenlath, 1984) that excess boron may be
required for the efficient formation of transition metal borides.

When considering these diboride systems, the following reactions may occur:

\[
[M] + AlB_2(s) \rightarrow MB_2(s) + Al_{(l)} \tag{4.1}
\]

\[
[M] + [B] \rightarrow MB_{(s)} \tag{4.2}
\]

\[
[M] + 2[B] \rightarrow MB_{2(s)} \tag{4.3}
\]

\[
Al_{(l)} + 2[B] \rightarrow AlB_{2(s)} \tag{4.4}
\]

\[
[M] + AlB_{2(s)} \rightarrow (M, Al)B_{2(s)} \tag{4.5}
\]

\[
[M_1] + [M_2] + AlB_{2(s)} \rightarrow (M_1, M_2)B_{2(s)} + Al_{(l)} \tag{4.6}
\]

\[
[M_1] + [M_2] + AlB_{2(s)} \rightarrow (M_1, M_2, Al)B_{2(s)} \tag{4.7}
\]

In the above reactions M refers to transition metals (Zr, Ti, V and Cr), subscripts \( l \) and \( s \) represent liquid and solid respectively, and the \([ \ ]\) symbol refers to the associated elements in solution.

A critical review of previous work on Al-B, Al-V, V-B and Al-V-B systems was given in Section 2.7. Binary phase diagrams of the elements B, Ti, Zr, V and Cr with aluminium revealed their limited solubility at low temperatures, but solubility increases with any increase in temperature (Belov, 2005, Kammer, 1999b). Figures 4.2 and 4.3 show the solubility of selected elements in liquid and solid aluminium according to the literature. It is clear from the curves of solute elements in liquid and solid aluminium that their solubility increases with temperature, especially for Cr, Mn and Fe.

The general features of aluminium interaction with transition metals includes the formation of supersaturated solid solution, quasi-crystalline and amorphous compounds in some specific compositions, and a cooling rate during solidification (Belov, 2005). The current equilibrium calculations show that at 1.1 to 1.72wt%, boron, aluminium and transition metals (Ti, Zr, V and Cr) may possibly form AlB2, TiB2, (Ti,Zr)B2, VB2(s), CrB2(s) in the temperature range of 675°C to 900°C. The possible phases in aluminium binary and ternary alloys with boron and some transition metals are summarised in Table 4.1.

In the case of the Al-Ti-Zr-B system, mixed borides are composed in almost equal proportions of TiB2 and ZrB2. In the alloy systems containing V and Cr with B and Al, VB2(s) and CrB2(s) phases have been predicted along with AlB2 borides. It is
assumed that there is some solubility of TiB$_2$ and ZrB$_2$ in AlB$_2$ and vice versa. According to the given analysis there is no solubility of Ti, Zr or Al in CrB$_2$ and VB$_2$ as they have been predicted as separate solid phases.

Table 4.1. Thermodynamically possible stable phases in Al binary and ternary systems in the temperature range of 675$^\circ$C to 900$^\circ$C

<table>
<thead>
<tr>
<th>Alloy systems</th>
<th>Possible stable solid phases</th>
<th>Stoichiometry B</th>
<th>75 wt% B Excess</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-B</td>
<td>AlB$_2$</td>
<td></td>
<td>AlB$_2$</td>
</tr>
<tr>
<td>Al-Ti-B</td>
<td>TiB$_2$*</td>
<td>TiB$_2$*</td>
<td>AlB$_2$</td>
</tr>
<tr>
<td>Al-Zr-B</td>
<td>ZrB$_2$*</td>
<td>ZrB$_2$*</td>
<td>AlB$_2$</td>
</tr>
<tr>
<td>Al-V-B</td>
<td>VB$<em>{2\alpha}$, Al$</em>{7\alpha}$</td>
<td>VB$_{2\alpha}$, AlB$_2$</td>
<td></td>
</tr>
<tr>
<td>Al-Cr-B</td>
<td>CrB$_{2\alpha}$</td>
<td>CrB$_{2\alpha}$, AlB$_2$</td>
<td></td>
</tr>
</tbody>
</table>

*very small solubility of Al

The stability of each and every phase depends upon the temperature and composition of solute in the aluminium melt.

Figure 4.2. Solubility of some transition metals in liquid aluminium (Belov, 2005)

Under equilibrium solidification, Al$_3$Ti, AlB$_2$ and TiB$_2$ were predicted in the Al-Ti-B ternary systems as proposed by (Abdelhamid and Durand, 1985). The Al$_3$Ti phase possesses a tetragonal crystal structure but the AlB$_2$ and TiB$_2$ phases are composed of hexagonal crystal structures with only a minor difference in their lattice parameters. Hence, there are possibilities for the stability of a continuous range of (Al, Ti) B$_2$ solid solution (Belov, 2005).
In the thermodynamic analysis, complete solid solutions of ZrB$_2$ and TiB$_2$ were predicted. However, a solid solution of AlB$_2$ with TiB$_2$ and ZrB$_2$ does exist, having a limited solubility.

Previous researchers (Higashi et al., 1976), (Jones and Pearson, 1976) and (Fjellstedt et al., 1999) found that there was some solubility of Ti in AlB$_2$ and some Al in TiB$_2$ but there was no evidence of any solubility among these borides particles. Moreover, (Fjellstedt et al., 1999) explained that (Ti,Al)B$_2$ type compounds are unstable and cannot exist at room temperature. From thermodynamic modelling and previous studies, it may be assumed that TiB$_2$, ZrB$_2$ and AlB$_2$ are mixed with each other and making metal boride solid solution (MB$_2$) phases. In this chapter, different alloy systems will be modelled to predict the behaviour of V in the presence of Ti, Zr, and Cr alone and in combination with each other. Thermodynamic modelling predictions will be useful in understanding the removal of V and the formation of VB$_2$ in molten aluminium.

4.3.1 Al-V-B system

Equilibrium calculations of liquid aluminium with 1wt% V and stoichiometry amounts of boron were conducted. During the thermodynamic assessment of the Al-V-B system, separate solid VB$_2(s)$ particles and AlB$_2$ were predicted (See Table 4.1).

In the Al-1wt% V-0.412wt% B system, vanadium diborides (VB$_2$) were predicted stable to a degree in the given temperature range but dissolve slowly at higher
temperatures (900°C). The changes in the V and VB$_2$ equilibrium concentration in Al melt, with temperature, are given in Figure 4.4. It can be seen from Figure 4.4 that in the case of the stoichiometry addition of boron, the concentration of V in the metal at 675°C was 8 to 10 ppm. The concentration of V increased with an increase in temperature, which suggested that the VB$_2$ was dissolving back into melt as the temperature increased. With excess boron, both VB$_2$ and AlB$_2$ were predicted. It appeared that the excess boron combined with Al to form AlB$_2$. By adding excess boron, the VB$_2$ also appeared to be more stable in the temperature range studied. No dissolution of VB$_2$ was predicted in the temperature range of 675°C to 900°C, as shown in Figure 4.4, i.e. no V was predicted in the Al melt as a solute.

![Figure 4.4](image)

Figure 4.4. V, VB$_2$ and AlB$_2$ equilibrium concentrations in Al melt with stoichiometry and 75wt% excess B addition i.e 1.412 to 1.720wt% Al-V-B alloy (In atomic % the alloys were 98.28%Al-0.54%V-1.08%B and 97.51%Al-0.54%V-1.88%B)

### 4.3.2 Al-V-Ti-B system

Equilibrium calculations of Al-V-Ti-B system were carried out using stoichiometry amounts and the addition of 75wt% boron excess, assuming VB$_2$ and TiB$_2$ formation. It was also assumed that both VB$_2$ and TiB$_2$ were each 50% proportion in the final diborides formed in the molten aluminium. The purpose of analysing this system is to predict the behaviour of V and VB$_2$ in the presence of Ti and TiB$_2$ in molten
aluminium in the temperature range of 675°C to 900°C. The solutes and diborides equilibrium concentrations are shown in Figure 4.5. It can be seen from Figure 4.5 that the diborides of V and Ti (VB₂ and TiB₂) are formed in the Al-V-Ti-B system, both in the case of stoichiometry amounts and with the addition of boron excess. The predicted stability of TiB₂ borides remains unaffected by the excess addition of boron, shown as a straight line in Figure 4.5(b).

The stability of VB₂ was predicted to be affected if excess boron was added in the alloy. In the case of the addition of boron to stoichiometry amounts, concentrations of VB₂ decrease gradually from the start of alloy melting and completely dissolve.

Figure 4.5. (a) V, Ti, B solutes and (b) VB₂ and TiB₂ borides equilibrium concentrations in Al melt with stoichiometric and 75% excess boron i.e 1.44 to 1.77 wt% Al-V-Ti-B alloys.
back in the melt at 875°C as shown in Figure 4.5(b). In the case of the addition of 75% boron excess, VB₂ borides remain stable until 725°C and then start dissolving relatively slowly. At 900°C, 65% of all the VB₂ borides were predicted to be dissolved in the case of the addition of excess boron, in comparison with 100% dissolution for the stoichiometry case, as shown in Figure 4.5(b).

The equilibrium concentration of solutes showed that Ti was removed from the alloy solution into stable borides, as represented by the lowest curves in the Figure 4.5(a). By adding stoichiometry boron, 90% of V was removed from the solution into VB₂ but complete removal was not possible that is predicted at 675°C. In comparison with stoichiometry boron, the addition of excess will completely remove all V out of solution into relatively stable VB₂ borides, as given in Figure 4.5(a). The excess case will leave an alloy with higher concentration of residual boron, which has much less impact on the electrical conductivity of the alloy, as compared with V and other transition metals.

4.3.3 Al-V-Zr-B system

The equilibrium calculations of Al-V-Zr-B were also carried out similarly to that previously discussed in section 4.3.2 for the Al-V-Ti-B system. The behaviour of solutes and borides in this system was predicted to be similar to the Al-V-Ti-B system and is given in Figure 4.6. The ZrB₂ borides were predicted to form in preference to VB₂ and were more stable in the given temperature conditions. The stability of ZrB₂ was not affected by the addition of excess boron and they do not dissolve once formed in the alloy in the temperature range of 675°C to 900°C. VB₂ boride stability was predicted to increase with the addition of excess boron, as shown in Figure 4.6(b). At 900°C, 93% VB₂ borides were predicted to dissolve in the case of an addition of excess boron in this system.

The predicted solute concentration is shown in Figure 4.6(a). At 675°C, it was predicted that only 80% (stoichiometry amount and additional boron) of V will be removed from solution in Al alloy containing V and Zr in equal proportion. At 875°C, 100% V was predicted to be in solution, which suggests that the VB₂ borides have dissolved and liberated V back into the melt, as shown in Figure 4.6(a). The
solute concentration of Zr showed that 100% removal was accomplished with both levels of boron addition. The addition of excess boron will leave the melt with a higher level of boron at the end, which when managed properly, will ensure the best economy for the boron treatment process.

![Figure 4.6. (a) V, Zr, B solutes and (b) VB₂ and ZrB₂ borides equilibrium concentrations in Al melt with stoichiometric and 75% excess boron i.e 1.30 to 1.53wt% Al-V-Zr-B alloys](image)

**4.3.4 Al-V-Cr-B system**

The behaviour of V and Cr in molten aluminium was also investigated adding stoichiometry amounts and excess boron. The equilibrium calculations were carried out on Al-0.50wt% V-0.50wt% Cr-0.42wt% B and Al-0.50wt% V-0.50wt% Cr-
0.73wt% B systems in the temperature range of 675°C to 900°C. The behaviour of Cr was different to Zr and Ti in Al alloys containing V. The equilibrium solutes and boride concentrations of the Al-V-Cr-B system are given in Figure 4.7. It was predicted that only VB$_2$ and AlB$_2$ borides will form in this alloy. There was no prediction of CrB$_2$ borides forming in the Al-V-Cr-B system under the given conditions. This suggested that VB$_2$ and AlB$_2$ borides are more stable in comparison with CrB$_2$ and will form in preference. In this system, the stability of VB$_2$ borides also increased, as shown by their curves in Figure 4.7(b). At 900°C, only 35% of the total VB$_2$ borides were predicted to dissolve in the excess case, in comparison with 93% dissolution in the Al-V-Zr-B system, as discussed in Section 4.3.3.

Figure 4.7. The solutes (a) V, Cr, B and (b) borides VB$_2$ and AlB$_2$ equilibrium concentrations in Al melt with stoichiometric and 75% excess boron i.e 1.42 to 1.73wt% Al-V-Cr-B alloys
The predicted solute concentration showed that Cr remained in solution with Al alloys in both cases of boron addition as shown in Figure 4.7(a). In the case of stoichiometry boron addition, most of the boron was expected to combine with V and rest to remain in solution with aluminium within the solubility limit. In the case of excess, the additional boron was predicted to combine with Al and form AlB\(_2\) in the melt. A possible reason of Cr remaining in the solution was its higher solubility in aluminium, as also given in Figure 4.2. Furthermore, it is also shown in Figure 4.1 that Gibbs free energy of AlB\(_2\) borides are less than CrB\(_2\), and hence will form in preference in molten aluminium. According to thermodynamic predictions, it could be implied that Cr cannot be removed from molten aluminium by the addition of boron in the presence of other transition metal impurities.

### 4.3.5 Al-V-Zr-Ti-B system

The behaviour of V was further analysed in the presence of Ti and Zr in molten aluminium. The diborides concentration predicted by thermodynamic modelling is given in Figure 4.8. The purpose of analysing the Al-V-Zr-Ti-B system was to understand the relative stability of VB\(_2\), ZrB\(_2\) and TiB\(_2\) borides in the given conditions. It was further aimed to predict the removal of V from molten aluminium in the presence of more reactive impurities, such as Zr and Ti. It was predicted that ZrB\(_2\) and TiB\(_2\) will form in preference to VB\(_2\) and would remain stable in the temperature range of 675°C to 900°C, as shown by their stable curves in Figure 4.8. The level of boron addition would not affect ZrB\(_2\) and TiB\(_2\) boride formation and stability, as was also predicted and in Sections 4.3.2 and 4.3.3.

VB\(_2\) borides will become more stable when excess boron is added, as shown by the stable curve under the TiB\(_2\) curves in Figure 4.8. AlB\(_2\) borides were also predicted in the case where excess boron was added, as they were unstable and dissolved 100% at 875°C. This suggests that boron will combine with Zr and Ti in preference to V and Al. Hence such impurities can easily be removed from molten aluminium via boron treatment. An equilibrium solutes concentration was also predicted for the Al-V-Zr-Ti-B system and is given in Figure 4.9. The predicted concentrations of Zr and Ti are given in the lower curves in Figure 4.9, showing their approximately 100% removal.
from the solution into their stable borides. In the case of the stoichiometry boron addition, at 675°C, 76% V was predicted to be removed in the form of their borides, but 24% was still present in the solution.

Figure 4.8. Borides (VB$_2$, TiB$_2$, ZrB$_2$ and AlB$_2$) equilibrium concentrations in Al melt with stoichiometric and 75% excess boron i.e 1.34 to 1.60 wt% Al-V-Ti-Zr-B alloys

Figure 4.9. Solutes (V, Ti, Zr and B) equilibrium concentrations in Al melt with stoichiometry additions and 75% excess boron, making 1.34 to 1.60 wt% Al-V-Zr-Ti-B alloys
A possible reason for the V remaining was the limited availability of B in the solution. When boron is added, it will fulfil the solubility requirement of the Al solution and then any excess will combine with Zr and Ti to form their borides. Finally, any remaining B will combine with V to form their borides. An additional 75wt% excess supplies sufficient boron for the 100% removal of V from the Al solution. Any excess boron added will increase its concentration in the Al solution, as shown in Figure 4.9

4.3.6 Al-V-Zr-Ti-Cr-B system

The equilibrium in this case was between Al-1wt% TM (where TM = Zr, Ti, V, Cr) with stoichiometry and 75% excess boron. In the case of only a stoichiometry addition of boron, the following diborides were predicted: (Zr,Ti)B$_2$ with very little solubility of AlB$_2$ (i.e. 0.001wt% at 750ºC), VB$_2$ and CrB$_2$. Figure 4.10 shows the equilibrium concentrations of metal diborides predicted in the system Al-1 wt% TM (TM = Zr, Ti, V, Cr each 0.25wt%)-0.357wt% B.

![Figure 4.10. Equilibrium concentration of metal diborides in the Al-V-Zr-Ti-Cr-B system with stoichiometry B addition having 1.2wt% elements in Al melts. The ZrB$_2$ and TiB$_2$ are in the form of (Zr,Ti)B$_2$](image)

Figure 4.10 shows that (Zr,Ti)B$_2$ was stable and the concentration remained unchanged in the temperature range studied. However, the diborides of Cr and V
were relatively unstable and predicted to dissolve back into the melt as the temperature increased. VB$_2$ was predicted to be stable only up to 825°C, as above this it started to dissolve. The equilibrium concentration of CrB$_2$ was predicted to be 12.5wt% at 675°C and to decrease with an increase in temperature; at 750°C CrB$_2$ was completely dissolved in the Al melt over the temperature range studied.

Figure 4.11 shows the associated equilibrium solute concentration changes in the Al melt. In the temperature range studied, no solute Zr and Ti was predicted to be in the Al melt as they were present in the stable (Zr,Ti)B$_2$ phase. V was predicted above 825°C when the VB$_2$ started to dissolve. The equilibrium concentrations of Cr and B were 0.16 wt% and 0.04wt% at 675°C, respectively. The CrB$_2$ was the least stable phase compared to the other diboride phases. It was assumed that CrB$_2$ would start dissolving first in the melt, and might result in an early increase of Cr and B concentrations as the temperature increased. Over 750°C, no further increases in Cr and B concentrations were predicted, as all the CrB$_2$ would have already dissolved. A slight increase in B solute concentration was predicted above 825°C, likely associated with the dissolution of VB$_2$ to the melt.

![Figure 4.11. Equilibrium solute concentrations in Al-V-Zr-Ti-Cr-B system with stoichiometric B addition, giving a total of 1.2wt% alloying elements](image)

Figure 4.12 shows the change of diborides concentration with changes in temperature in the case of 75% boron excess with Al-1.4wt% TM. In this case, AlB$_2$ was
predicted in addition to the (Zr,Ti)B₂, VB₂ and CrB₂ phases. Similar to the first case (Al-1wt% Ti with excess B), it was assumed that the excess boron would combine with aluminium to form AlB₂. The model predicted that there would be little solubility of Ti and Zr in the AlB₂ phase; and Al in (Zr,Ti)B₂, i.e. 0.001wt% at 750°C.

It can be seen from Figure 4.12 that (Zr,Ti)B₂ and VB₂ were more stable compared to AlB₂ and CrB₂ under the given conditions. The equilibrium concentration of CrB₂ was predicted to be 9.2wt% of the total metal borides at 675°C. As the temperature increased, CrB₂ dissolved first, hence the decrease in CrB₂ concentration up to 750°C, above which all CrB₂ was completely dissolved. After this, the AlB₂ started to dissolve. The concentration of (Zr,Ti)B₂ and VB₂ remained unchanged in the melt in the temperature range 675°C to 900°C.

Also of note is that the relative stability of phases depends upon the presence of other diboride phases. For example, in the first case (stoichiometry addition of boron), where no AlB₂ was present, the VB₂ phase remained thermodynamically stable only up to 875°C (as shown in Figure 4.10). In the presence of AlB₂ (excess boron added), VB₂ was predicted to be stable up to 900°C, as shown in Figure 4.12.

![Figure 4.12. Equilibrium concentration of metal diborides in Al-V-Zr-Ti-Cr-B system with 75% excess B added, having a total 1.4wt% of Al. The ZrB₂ and TiB₂ are in the form of (Zr,Ti)B₂](image-url)
Figure 4.13 shows the solute concentrations in the Al melt in the case of excess boron being added. The solute concentrations in the case of stoichiometric boron addition are also shown for comparison. It can be seen from Figure 4.13 that the addition of stoichiometry or excess boron may be carried out to remove Zr, Ti and V from the melt. However, the model predicts that Cr would remain in the melt, as the excess boron appeared to be reacting with Al to form AlB$_2$ rather than forming CrB$_2$.

Figure 4.13. Solutes concentration with stoichiometric and excess Boron additions in the system Al-V-Zr-Ti-Cr-B having 1.2 to 1.4wt% of solute elements

4.4 Summary of thermodynamic predictions

A thermodynamic modelling of various aluminium systems containing Ti, Zr, V, Cr and B was carried out in the temperature range of 675°C to 900°C. Two cases were analysed, one with a stoichiometry composition and other with 75wt% excess boron addition to aluminium melt. The stoichiometric case was composed of 1.20 wt% to 1.412wt% of total transition metal (Ti, Zr, V and Cr) and boron compare to 75wt% excess case that contains 1.40wt% to 1.77wt%. According to the results, the Gibbs free energy for the formation of the pure ZrB$_2$ diborides were found most stable compared to other transition metal diborides under the given conditions. The order of stability (from the most stable to the least stable) of these boride phases was predicted from ZrB$_2$, TiB$_2$, VB$_2$, AlB$_2$, CrB$_2$ within the given temperature range.
The equilibrium calculations predicted that Cr cannot be removed from aluminium above 750°C using boron treatment, as aluminium diborides (AlB₂) were more stable than chromium diborides (CrB₂). When boron was added to the aluminium melt containing Zr, Ti, V and Cr, the results suggested that boron would be tied up by Zr and Ti, then V, Al, and Cr, forming (Zr,Ti)B₂, VB₂, AlB₂ and CrB₂, respectively. In the case of excess boron, as temperature increased, the least stable CrB₂ dissociated first, followed by AlB₂ at 750°C leaving behind Al melt with stable borides (Zr,Ti)B₂, and VB₂. It could be suggested (from the thermodynamic perspective only) that boron treatment would be most effective for removing Zr, Ti and V impurities from smelter grade aluminium. Thermodynamics analyses also predicted the solutes concentration in the molten aluminium at different temperatures and boron addition that could provide further opportunity to manage impurities during boron treatment of molten aluminium.

The results from thermodynamic analysis provided the theoretical limits. However, it should be noted that the equilibrium calculations were carried out with various assumptions. These limitations aside, the results provided an insight into the relative stability and the preference of transition metal borides that might form in the aluminium melt. Experiments will be designed on the basis of previous work and thermodynamic predictions.
Chapter 5

Analysis of Vanadium Boride (VB$_2$) Formation in Molten Aluminium

5.1 Introduction

Aluminium has been considered as an alternative to copper for electrical conductor applications. However, the presence of certain impurities in aluminium, such as V, Ti, Zr, Cr and Fe, has a detrimental effect on its electrical conductivity. These impurities can be removed by boron treatment of aluminium melt using the addition of an Al-B master alloy containing AlB$_2$ or AlB$_{12}$ phases, but the thermodynamics of VB$_2$ formation in molten aluminium is not well understood. An attempt is made in this chapter to elaborate on the equilibrium phases in the Al-V-B system at industrial conditions of aluminium processing. Moreover, experimental results are compared with thermodynamic predictions for the better understanding of V removal from molten aluminium.

5.2 Previous work on VB$_2$ formation in Al melt

Gauthier (1936) experimentally studied the effect of impurities on the electrical conductivity of aluminium. He observed that transition metals, including V, have pronounced effect in reducing the electrical conductivity of high purity aluminium (Gauthier, 1936). The effect of selected impurities on the electrical resistivity (or conductivity) of smelter grade aluminium is shown in Table 5.1. It can be seen that V and Cr have the greatest effect on resistivity; and the presence of these elements in solution increases the resistivity by a factor 10 to 20. Industrially, boron treatment has been used widely for the production of 1000 series alloys (1350 EC) for electrical conductors. In the boron treatment of melt, aluminium boron master alloys containing AlB$_2$/AlB$_{12}$ phases are used. The particles of the AlB$_2$/AlB$_{12}$ in the Al-B master alloy are in the form of clusters, having varying particles size of 1µm to 100
µm. Mostly, Al-B master alloys are used in the form of rods, waffles or wire depending on the process requirement and end product.

Table 5.1. Selected transition metals solubility and their effect on the electrical resistivity of aluminium (Dean, 1967)

<table>
<thead>
<tr>
<th>Elements</th>
<th>Max. solubility in Al (wt%)</th>
<th>Avg increase in resistivity (or decrease in conductivity) per wt%</th>
<th>µΩ.cm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>In solution</td>
<td>Out of solution</td>
</tr>
<tr>
<td>Vanadium</td>
<td>0.50</td>
<td>3.58</td>
<td>0.28</td>
</tr>
<tr>
<td>Zirconium</td>
<td>0.28</td>
<td>1.74</td>
<td>0.044</td>
</tr>
<tr>
<td>Titanium</td>
<td>1.00</td>
<td>2.88</td>
<td>0.12</td>
</tr>
<tr>
<td>Chromium</td>
<td>0.77</td>
<td>4.00</td>
<td>0.18</td>
</tr>
</tbody>
</table>

It has been reported in the literature that the concentration of transition metal impurities drops quickly after the addition of an Al-B master alloy. Consequently, the resultant conductivity of aluminium increases due to the removal of transition metals from the solution state to a second solid phase (borides) (Stiller and Ingenlath, 1984, Cooper and Kearns, 1996). The borides formed during the boron treatment of melt are stable hence do not dissolve readily during the later processing of the melt. Various possible borides of vanadium (VB₂, VB, V₂B₃, V₃B₂, V₃B₄ and V₅B₆) have been reported in the literature, but VB₂ is the most stable phase in the aluminium melt, depending on the V to B ratio and the processing temperature (Okada and Lundström, 1993, Otani, 2000).

A literature review showed that the formation of transition metal borides (VB₂, ZrB₂, TiB₂ and CrB₂) and AlB₂ is not properly understood. Dube (1983), during the removal of impurities from aluminium melt, found the formation of fine complex (Ti,V)B₂ particles of size up to 10 µm. He did not provide any additional information as to whether these complex borides were in solid solution or in clusters of separate particles (Dube, 1983). Similar results were presented by Cooper and Kearns (1996). They observed during SEM/EDX analysis that borides particles were in cluster form but had a homogenous distribution of Ti, V and B with traces of Zr and Cr. Wang et al., (2002) investigated the reaction of boron with transition metals to improve the electrical conductivity and detected two kinds of boride in the sample extracts. One
of the borides was composed of 54.42mol% B, 13.70mol% Al and 23.39mol% of V, Ti and Zr metals. The other type of boride was detected as hexagonal in shape, having 78.59mol% B, 14.97mol% Al and 2.56mol% of transition metals Ti, V and Fe (Wang et al., 2002). Higashi et al., (1976) produced single crystals of VB, V₃B₄ and other transition metals in aluminium melt at 1300°C to 1550°C. They found all of the transition metal borides had limited solubility of aluminium (<0.1wt%) including V-boride crystals. This was interpreted as that AlB₂ did not form mixed crystals with the above borides (VB and V₃B₄) (Higashi et al., 1976). Otani et al., 2009 investigated the solid solution ranges of ZrB₂ with other refractory borides (TiB₂, HfB₂, TaB₂, VB₂, and CrB₂) by melting their mixed borides in an arc-melting furnace in an argon atmosphere at 1600°C. A continuous solid solution was detected in the case of ZrB₂ – TiB₂ systems having two types of solid solutions (Zr₀.₇₆Ti₀.₂₄B₂ and Zr₀.₁₁Ti₀.₈₉B₂). The ZrB₂ – VB₂ and ZrB₂ – CrB₂ systems were reported as forming a limited range of solid solution, with < 3mol% and < 1mol% respectively at 1600°C in ZrB₂ crystals (Otani et al., 2009).

Although boron treatment has been used widely for the removal of V and other transition metal impurities from aluminium melt, the formation and existence of borides is still debated in the literature. A fundamental understanding is lacking to define the behaviour of B and V in the aluminium solution. In this chapter, experimental analysis was carried out on the formation of VB₂ in molten aluminium. Based on the thermodynamic predictions described in Chapter 4, experiments were conducted using stoichiometric and 75wt% excess addition of boron in the aluminium melt. Characterization of the samples was carried out using SEM, EDX and EBSD techniques for the observation and identification of possible phases in the Al-V-B system. The concentration of V in solution with aluminium was determined by ICP-AES analysis. Finally, the experimental findings were compared with the thermodynamic predictions to evaluate the amount of V removal from the molten aluminium.
5.3 Experimental details

The materials used for the experiments of the Al-V-B systems were pure Al ingots (99.85 wt%), Al-10wt% V and Al-4wt% B master alloys. The analysis of the starting material was described in Section 3.2.2. A total mass of 1000 g Al-V-B alloy was prepared from Al-10wt% V and Al-4wt% B master alloys and balanced with pure aluminium. Based on the thermodynamic analysis of the Al-V-B system containing stoichiometric additions of boron, alloys with a targeted composition of 1wt% V, 0.412wt% B were prepared. Pure aluminium ingots were melted in a boron nitride (BN) coated clay bonded graphite crucible in an induction furnace. Master alloys (Al-10wt% V and Al-4wt% B) were added to the liquid aluminium at a temperature of 750°C. Temperature control of the melt during the isothermal hold was maintained carefully by regulating the furnace input power and measuring the temperature manually at regular intervals of 2 to 3 minutes. During the isothermal hold of the melt, a temperature of 750°C ± 10°C was maintained. A K-type thermocouple protected with an alumina sheath was employed in this experiment. The thermocouple could not be immersed continuously in the melt due to the danger of overheating in the induction field and consequently temperature control was not automatic. Sampling of the melt was carried out at intervals of 0, 15, 30, 45 and 60 minutes after the addition of the master alloys. The samples were allowed to solidify in the ambient environment.

A 1000g melt of Al-1wt% V-0.721wt% B was also prepared similarly to Al-1wt% V-0.412wt% B alloy in the induction furnace. This amount of boron was added 75wt% excess to the stoichiometry requirement for the formation of V-borides (assuming VB₂). The use of excess boron for the removal of transition metal impurities had already been suggested by previous investigators (Dube, 1983, Stiller and Ingenlath, 1984, Cooper and Kearns, 1996). Moreover, it was also predicted by thermodynamic assessment of the Al-V-B system that more boron would be required to completely remove V from the aluminium melt for the production of electrical grade conductor applications (Khaliq et al., 2011a, Khaliq et al., 2011b).

For thermodynamic experiments with an extended holding time, 25 g of each alloy ingots were melted in an alumina crucible in a vertical resistance furnace under argon
environment. The samples were held for 720 minutes at 700°C, 750°C and 850°C before quenched in a steel flange surrounded by a copper coil cooled with circulating water. Brief information relating to the alloy preparation, the processing parameters and the sampling practice is given in Table 5.2. Induction and resistant melting facilities were used for the study of VB₂ in molten aluminium. A bottom part of each sample was sectioned and prepared using standard metallographic procedures. The samples were prepared for subsequent SEM, EDX, EBSD, EPMA and ICP-AES analysis.

Wire cut samples were polished on SiC emery papers in the following sequence (320, 600, 800, 1200 grit) using water as a lubricant. Further polishing was carried out using 9, 6, 3 and 1µm diamond paste with alcohol as a lubricant for three minutes each. Polishing was finalised using OP-U (0.05 µm colloidal silica suspension) solution for 5 minutes on each sample.

Table 5.2. Melting, processing parameters and sampling details of the different Al-V-B alloy systems investigated

<table>
<thead>
<tr>
<th>Alloy systems</th>
<th>Melting practice</th>
<th>Temperature (°C)</th>
<th>Sampling time (minutes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-1wt%V-0.412wt%B (Stoichiometric B)</td>
<td>Induction</td>
<td>750</td>
<td>0, 15, 30, 45, 60</td>
</tr>
<tr>
<td>Al-1wt%V-0.412wt%B (Stoichiometric B)</td>
<td>Resistant</td>
<td>700, 750, 800</td>
<td>720</td>
</tr>
<tr>
<td>Al-1wt%V-0.721wt%B (75wt% B Excess)</td>
<td>Induction</td>
<td>750</td>
<td>0, 15, 30, 45, 60</td>
</tr>
<tr>
<td>Al-1wt%V-0.721wt%B (75wt% B Excess)</td>
<td>Resistant</td>
<td>700, 750, 800</td>
<td>720</td>
</tr>
</tbody>
</table>

For EBSD analysis, samples with dimensions 10 mm × 8 mm × 1 mm were wire cut from the lower section of each sample. After mechanical grinding to a 2400 grit SiC finish, the samples were carefully polished using 0.05 µm silica suspension for about 10 minutes and 0.05 µm alumina suspension for approximately 2 minutes. A SUPRA model 40VP-25-38 fitted with an energy dispersive x-ray spectrum (EDX) detector
was used for the observation and identification of different phases. For EBSD analysis, polished samples were examined in a JEOL JSM 7001F field emission SEM, equipped with an HKL Channel 5 EBSD system. For ICP-AES analysis, samples chips were prepared by drilling and dissolved in HCl solution. The solution was analysed for the V contents in aluminium solution. The V tied up with B in the form of VB$_2$ was not analysed by ICP-AES analysis.

5.4 Microscopy analysis (OM, SEM)

The selected samples of Al-1wt% V-0.412wt% B alloy were analysed under optical and scanning electron microscopes. The optical microscopy images of samples taken after 0 and 60 minutes are shown in Figure 5.1. It can be observed from Figures 5.1(a) and 5.1(b) that a reaction has taken place at the interface of the black phase and consequently a reaction product phase has been generated. The dark grey phase that is a reaction product has encapsulated the black phase. The black particles were added into the aluminium melt as a source of boron in the form of Al-4wt% B master alloy predominantly containing AlB$_{12}$ phase. A preliminary analysis of Al-4wt% B and Al-10wt% V master alloys is given in Sections 3.2.3.1 and 3.2.3.2. The particles of AlB$_{12}$ borides in the Al-4wt% B master alloys are present in clusters with no more than 5% AlB$_2$ in the aluminium matrix, as shown in Figure 3.4. The AlB$_2$/AlB$_{12}$ has a wide range of particle sizes (1 µm to 60 µm) and irregular polygonal morphology. The analysis of Al-10wt% V showed the elongated and polygonal (irregular) particles of Al$_7$V/Al$_{10}$V having diameter 10 µm to 80 µm in aluminium matrix, which can be seen in Figure 3.6. It also revealed that Al-10wt% V consists of two types of phases in an aluminium matrix. Those phases were suggested as Al$_7$V and Al$_{10}$V based on the Al-V binary equilibrium phase diagram (FactSage 6.2). It was concluded that the Al$_{10}$V phase shown in Figure 5.1(a) was formed during solidification.

The undissolved black particles (AlB$_{12}$) were observed in all samples, which provide boron for the completion of the reaction with V during boron treatment. Some minor secondary phases containing Al, Fe and some Si were also observed. The presence of β-Al$_3$FeSi, α-AlFeSi, Al(Fe,Mn)Si and eutectic Si compounds in pure aluminium
have been reported in literature (Zhang et al., 2011, Zhang et al., 2012). These are indicated in the optical micrograph in Figure 5.1(b), and they are mainly from Si and Fe impurities in the source materials.

![Figure 5.1. Optical microscopy image of Al-1wt% V-0.412wt% B alloys taken after (a) 0 minute (b) 60 minutes and held at 750°C.](image)

Analysis of selected polished samples from Al-1wt% V-0.412wt% B alloy was also carried out under a scanning electron microscope (SEM) fitted with an EDX detector. The SEM-SE micrographs of 0, 15, 30, 45 and 60 minutes samples are shown in Figure 5.2. A common feature related to the formation of a product ring and undissolved AlB$_{12}$ were observed in all samples, as shown in Figure 5.2. The formation of characteristic boride rings around the black particles in the 0 minute sample is shown in Figure 5.2 (a) that suggest the reaction was fast and took place in the early minutes after the addition of Al-AlB$_{12}$ master alloy in the molten aluminium. This further suggested that the chemical reaction kinetics between Al-AlB$_{12}$ and V was fast. Hence it was unlikely that the chemical reaction was the rate-controlling step in these particular conditions.

Cooper and Kearns (1996) proposed a mechanism for the removal of transition metal impurities from aluminium melt based on the boride ring formation and incomplete reaction, but no experimental evidence and kinetic analysis were presented in their work. It was further reported that transition metal impurities are removed from aluminium melt in the form of their borides in the early stage of Al-AlB$_{12}$ addition (Cooper and Kearns, 1996). Formation of V-boride rings in the early minutes
following the addition of Al-AlB\textsubscript{12} is in agreement with the Cooper and Kearns study.

Fjellstedt et.al (1999) reported the phenomenon of TiB\textsubscript{2} ring formation around AlB\textsubscript{2} particles while experimentally investigating the intermediate phases (AlB\textsubscript{2}, AlB\textsubscript{12} and TiB\textsubscript{2}) in the Al-B and Al-Ti-B systems. The reported boride (TiB\textsubscript{2}) ring thickness was reasonably less than the V-boride that has been observed in the current investigation. A possible reason for the less thickness of the boride ring could be the ratio of Ti/B (1/10), as it was less dominating phenomenon in alloy with Ti/B (1/3) (Fjellstedt et al., 1999).

It can be observed from Figures 5.2 (a), 5.2 (b), 5.2 (c), 5.2 (d) and 5.2 (e) that there is no significant difference in the thickness of characteristic V-borides rings when holding Al melt for 60 minutes at 750ºC. A similar thickness of V-borides was observed in all samples (0, 15, 30, 45 and 60 minutes). This phenomenon suggested that reaction was incomplete and further reaction was hindered by the presence of a reaction product layer. After taking the 60 minute sample, the remaining melt was cast into a graphite mould.

The SEM-SE image of Al-1wt% V-0.412wt% B, held at 750ºC for 720 minutes, is shown in Figure 5.2 (f). It can be seen that the V-boride ring thickness has increased but still there was an undissolved black phase (AlB\textsubscript{12}) present in the middle of the ring. This suggested that the diffusion of the reacting species, either V or B in the V-boride layer, is very slow, which could lead to an incomplete reaction after such a long holding time. It was clear that the characteristic boride ring thickness increased very slowly and consequently diffusion resistance of the reacting species such as V and B would increase with the passage of time.

During SEM analysis, some other phases were also detected and are reported as Al, Fe, and Si eutectic, as shown in Figure 5.2 (a) and 5.2 (d). These intermetallics were formed due to the high concentrations of Fe (0.20 wt %) and Si (0.11 wt %) impurities in the starting materials (Al, Al-10wt% V and Al-4wt% B). These intermetallics are formed during the solidification of the samples.
Figure 5.2. SEM-SE images of Al-1wt% V-0.412wt% B alloy melted and held at 750°C. The samples were taken after (a) 0 minute (b) 15 minutes (c) 30 minutes (d) 45 minutes and (e) 60 minutes and (f) 720 minutes samples.
SEM images of Al-1wt% V-0.721wt% B alloy samples taken after 0, 15, 30, 45, 60 and 720 minutes are shown in Figures 5.3 (a), 5.3 (b), 5.3 (c), 5.3 (d), 5.3 (e) and 5.3 (f). The common features of all these images include the formation of V-boride rings and undissolved Al-B (AlB$_{12}$), which are similar to the previous alloy shown in Figure 5.2. The reaction between Al-B (AlB$_{12}$) and V was fast in the early stage (0 minute) but became reasonably slow, as shown by the formation of similar thickness V-boride rings in 15, 30, 45 and 60 minutes samples. The thickness of boride ring increased comparatively more after 720 minutes in the case of the addition of 75wt% excess boron, as shown in Figure 5.3 (f). The presence of undissolved AlB$_{12}$ encapsulated by ring of V-borides suggested the system was still far from reaching the equilibrium after holding it for 12 hours. It was suggested that the diffusion of B or V through V-boride rings was the rate-controlling step for this reaction. The SEM analysis showed that the V-boride rings were growing outside, which could indicate that the outward diffusion of B through the boride layer was faster compared to V inward. The diffusion of B atoms could be faster than V due to the smaller atomic radii under similar diffusion resistance (barrier) and temperature. This particular situation could lead to the growth of a V-boride ring outside. Experimental evidences also supports this hypothesis as small V-boride particles are nucleating at the outer periphery of ring, as shown in Figure 5.3 (f).

It was suggested that the dissolution kinetics of AlB$_{12}$ was very slow and may have been obstructed by the Al, V borides ring encapsulating them. It was further proposed that the diffusion of the reacting species through the boride ring would be the reaction-rate controlling step in this case. The dissolution of AlB$_{12}$ could be controlled by the concentration of B inside the boride ring.
Figure 5.3. SEM - SE images of Al-1wt% V-0.721wt% B alloy at 750°C. The samples were taken at: (a) 0 minute (b) 15 minute (c) 30 minute (d) 45 minute and (e) 60 minute and (f) 720 minutes
5.5 EDX analysis

The EDX analysis of samples taken after 0 and 60 minutes were carried out to investigate semi-quantitative composition of phases observed under the SEM. The EDX analysis of grey shell particles is given in Figure 5.4 that detects the presence of Al, V and B.

![Figure 5.4. (a) SEM-SE image and (b) EDX analysis of boride ring in Al-1wt% V-0.412wt% B alloy](image)

It was predicted during the thermodynamic analysis that VB₂ particles will form as a separate solid phase and do not make any solid solution with Al, AlB₂ or AlB₁₂. The EDX analysis detected V, B and Al in the boride ring particles that suggested the formation of solid solution or mixed borides (AlB₂, VB₂). The EDX analysis suggested a mixed boride (Al₁₁V₃₁B₅₈) mainly composed of VB₂ with Al in solution. It could not be conclusively established from EDX analysis whether boride shells were making any solid solution or were physical clusters with Al, AlB₂ and AlB₁₂ in the aluminium matrix. Previous work relating to pure and mixed borides was presented in Section 2.7.1 and 2.7.2. There are different opinions regarding the solid solution and the stability of mixed borides. V-borides (VB, VB₂) have been reported as pure borides, which have limited solubility of other elements such as Al and Al-borides (Otani, 2000, Yeh and Wang, 2011). It has also been reported in the literature that ZrB₂ forms a solid solution with VB₂ although it has limited solubility (< 3mol %) (Otani et al., 2009). From the perspective of V-borides formation in aluminium melt, Higashi et al. (1976) reported limited solubility (< 0.1 wt%) of aluminium in
the single crystals of V-borides. Hence, they were considered to be pure compounds (Higashi et al., 1976).

Point analysis of the black phase inside the V-borides was also carried out using EDX to find its chemical composition. The EDX analysis detected that the black phase is the particles of Al-B (AlB\(_{12}\)), as shown in Figure 5.5 (b). The black phase showed partially dissolved particles of AlB\(_{12}\) inside the V-boride shell in the aluminium matrix. AlB\(_{12}\) particles were added in the molten aluminium as a source of boron to form vanadium borides.

Figure 5.5. (a) SEM- BSE image of Al-1wt% V-0.412wt% B alloy showing the location of different point analysed through EDX (b) EDX spectrum of undissolved black phase (AlB\(_{12}\)) inside VB\(_2\) ring

The chemical composition of different points on the boride ring and the internal black phase is given in Table 5.3. Points 1, 2 and 3 were taken on the grey particles (V-boride ring), as shown by the SEM-BSE image in Figure 5.5 (a) represented by a symbol of black circle. EDX analysis of points 3, 4 and 5 (represented by a symbol of white circle) reveals that the black phase is composed of boron and aluminium with approximately 10 to 1 (B: Al) ratio in atomic. This phase was proposed AlB\(_{12}\) rather than AlB\(_{10}\) because it is not a thermodynamically stable phase in the Al-B binary system, as described in Section 2.7.3.4. Later on EPMA analysis confirmed the black phase is AlB\(_{12}\) not AlB\(_{10}\) suggested by semi-quantitative EDX analysis. Moreover, the faceted particle morphology inside the V-boride rings also resembles with AlB\(_{12}\) rather than the elongated AlB\(_{3}\). It could be suggested from the particle morphology and EDX analysis that the black phase inside the ring is AlB\(_{12}\).
Table 5.3. EDX analysis of various points showing the elemental composition

<table>
<thead>
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<th>Point</th>
<th>atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Al</td>
</tr>
<tr>
<td>1</td>
<td>11.37</td>
</tr>
<tr>
<td>2</td>
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<tr>
<td>3</td>
<td>12.98</td>
</tr>
<tr>
<td>4</td>
<td>8.94</td>
</tr>
<tr>
<td>5</td>
<td>9.33</td>
</tr>
<tr>
<td>6</td>
<td>9.61</td>
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</table>

5.6 Elemental mapping

The elements mapping in the Al-1wt% V-0.412wt% B alloy (60 minutes sample) was obtained through EDX analysis. The purpose of elemental mapping was to locate and confirm the presence of V and B in aluminium matrix hence their affinity to co-exist and form V-borides in aluminium matrix.

Figure 5.6. Elements mapping in Al-1wt% V-0.412wt% B (60 minute) obtained by EDX analysis (a) SEM-SE image (b) Al mapping (c) V mapping and (d) B mapping
A SEM-SE image of 60 minute sample is given in Figure 5.6 (a) that shows a V-boride ring and an internal black phase in the aluminium matrix. Aluminium mapping is given in Figure 5.6 (b), which covers the whole matrix except the black localities in the form of V-boride rings. The ring was composed of V, as shown in Figure 5.6 (c) that is represented by a white area in black aluminium matrix. White spots in the black matrix, as shown in Figure 5.6 (d), representing boron in the centre as well as in the V-boride ring. It is worth noticing that boron was found in the same localities of V, which suggested their reaction affinity, and the formation of V-boride that was also confirmed by EDX analysis.

During the EDX analysis, grey particles were detected as Al, V borides. Despite the longer holding time (720 minutes), the particles of AlB$_{12}$ were partially dissolved and were detected in all samples.

### 5.7 EBSD analysis

Electron back-scattered diffraction (EBSD) analysis was carried out to investigate the crystallographic information of V-boride phases in the ring. This information will be useful to establish whether mixed borides of VB$_2$ and AlB$_{12}$/AlB$_2$ are formed or the presence of aluminium shown by EDX analysis is attributed from the base matrix (Al). The SEM-BSE image and an EDX spectrum of a point on a ring are shown in Figures 5.7 (a) and 5.7 (b). An EBSD raw pattern of the same point on a boride ring is shown in Figure 5.7 (c), which reveals sharp and distinguishable parallel diffracted lines from the borides crystallographic plans. This pattern further suggests that the particles have a certain crystallographic structure, which was later indexed as VB$_2$, as shown in Figure 5.4 (d). A raw EBSD pattern of V-borides was indexed with more than 95% certainty with reference to the pattern of vanadium diborides (VB$_2$). Therefore, it was confirmed by EBSD analysis that VB$_2$ are formed in the rings encapsulating the undissolved black phase of Al-B master alloys. The result indicates that VB$_2$ form as a pure compound (with a limited solubility of other elements i.e Al).

The black phase in the centre of the VB$_2$ ring was the source of boron initially added in the form of the Al-B master alloy. The Al-4wt% B master alloy analysis suggested
that the AlB$_{12}$ particles are in clusters, with varying particle sizes, and that they were the dominant phase. An effort was made to identify the crystal structure of the black phase (possible AlB$_{12}$) using EBSD analysis but the diffracted lines of the raw pattern were not sharp enough to be indexed by the used facility.

It was realised that it is difficult to obtain a flat surface due to the greater hardness of the AlB$_{12}$/AlB$_2$ particles as compared with the soft aluminium matrix. For better polishing, ion milling was used and the corresponding SEM-BSE image is shown in Figure 5.5 (a). It was not possible to obtain a distinguishable diffraction pattern from the internal black phase even after polishing by ion milling. It was concluded from EDX analysis given in Section 5.5 and the morphology of particles that internal black phase was AlB$_{12}$ rather than AlB$_2$.

![Figure 5.7](image)

**Figure 5.7.** SEM-BSE image of Al-1wt% V-0.412wt% B held at 750°C (a) SEM-BSE image showing ring of reaction product (b) EDX spectrum of VB$_2$ ring (c) EBSD raw pattern of VB$_2$ ring particle and (d) EBSD pattern indexed as VB$_2$.
5.8 EPMA analysis

Electron probe micro analysis (EPMA) was carried out on 0 and 60 minutes samples to determine the B, V and Al profiles in the undissolved black phase (AlB\textsubscript{12}), VB\textsubscript{2} ring, Al-V phase and Al inside and outside VB\textsubscript{2} ring. The selected areas and phases analysed are marked on the SEM images of Al-1wt\% V-0.412wt\% B alloy and are shown in Figures 5.8 (a) and 5.10 (a). Each phase was analysed at a distance of 0.5 µm between each point and the concentration profiles of B, V and Al are shown in Figures 5.8 (b), 5.8 (c), 5.8 (d) and 5.8 (e) and Figures 5.10 (b), 5.10 (c), 5.10 (d), 5.10 (e) and 5.10 (f).

The concentration of boron inside and outside of VB\textsubscript{2} ring was analysed. The analysed area inside and outside VB\textsubscript{2} ring is shown in Figure 5.8 (a). The profile of boron concentration for sample taken after 0 minute is shown in Figure 5.8 (b). It was found that boron concentration is more than 20 wt\% inside and approximately 0 wt\% outside VB\textsubscript{2} ring except two points showing 1.32 wt\% and 0.24wt\% B. It has been reported earlier that Al-B (AlB\textsubscript{12}) master alloy was added as a source of boron in aluminium alloys under investigation.

In the early stage (0 minute), reaction between V and B was immediate that nucleate the particles of VB\textsubscript{2} outside AlB\textsubscript{12} phase forming a ring. The dissolution rate of AlB\textsubscript{12} particle that provides B for reaction to forms VB\textsubscript{2} depends on the concentration gradient and mass transfer of B, and interfacial area of AlB\textsubscript{12} in contact with molten alloy. In the early stage, dissolution of AlB\textsubscript{12} will be fast due to larger concentration gradient of B and interfacial area in contact with aluminium melt. At the same time, mass transfer of V will take place towards the interface of AlB\textsubscript{12}. Faster dissolution of AlB\textsubscript{12} in the early stage resulted in the higher concentration of B inside as compared with outside of ring. The formation of VB\textsubscript{2} rings covering AlB\textsubscript{12} particles did not provide opportunity to the mass transfer of boron to the bulk liquid that could increase its level outside which is shown in Figure 5.8 (b).

The concentration profile of V inside and outside VB\textsubscript{2} ring was also measured by EPMA. The analysed area for V inside and outside VB\textsubscript{2} ring is similar to B that is shown in Figure 5.8 (a). The aluminium alloys under investigation contains 1wt\% V
that is much higher than its solubility (0.46 wt%) in aluminium at 750°C. The excess amount of V than the solubility limit will be in the form of Al-V intermetallics (Al$_3$V/Al$_{10}$V) in the molten alloy. In the early stage, higher concentration of V inside VB$_2$ ring will be most likely due the entrapment of Al-V intermetallic or the formation of small VB$_2$ particles inside main VB$_2$ ring.

Other possibility could be the mass transfer of V from liquid phase to the boundary of AlB$_{12}$ particle. The mass transfer of V will increase further by the induction stirring during the holding of melt at 750°C. Due to the concentration gradient of V between liquid aluminium and at AlB$_{12}$ interface, mass transfer will be increased. In the early stage, larger mass transfer of V will increased its concentration inside VB$_2$ ring and small particles of VB$_2$ will be formed. The concentration of V outside VB$_2$ ring is within the solubility limit. The concentration of V in aluminium decreased when going away from VB$_2$ ring that suggested the mass transfer from bulk melt to the vicinity of AlB$_{12}$ particles. The higher concentration of V inside VB$_2$ ring could be due to the presence of smaller VB$_2$ particles that are shown in Figure 5.9.

The EPMA analysis of VB$_2$ ring was also carried out for 0 minute sample and is given in Figure 5.8 (d). Aluminium was also detected in VB$_2$ ring with V and B. It has already been discussed in Sections 5.5 and 5.6 that the presence of Al could be from aluminium matrix. It was confirmed by EBSD analysis that the particles in ring are composed of VB$_2$ with limited solubility of Al and V. It was concluded from EPMA analysis that V and B reacted to form VB$_2$ ring encapsulating black phase that is a source of boron. The EPMA analysis of black phase covered by VB$_2$ ring was also carried out and is given in Figure 5.8 (e). The analysed area is also marked on SEM image as shown in Figure 5.8 (a). The black phase contains approximately 16wt% Al and 84wt% B. There was no evidence of V in the black phase. The composition of black phase suggested AlB$_{12}$ that has been discussed in Section 5.5.
Figure 5.8. Concentration profile of B, V and Al measured in different areas of Al-1wt% V-0.412wt% B alloy (0 minute) obtained by EPMA analysis. (a) SEM image, (b) Boron profile inside and outside VB$_2$ ring, (c) V profile inside and outside VB$_2$ ring, (d) V, B, Al profiles in VB$_2$ ring and (e) B and Al profiles in AlB$_{12}$ phase

EPMA analysis of Al-1wt% V-0.412wt% B alloy sample taken after 60 minutes was also carried out and is given in Figure 5.10. The analysed areas inside and outside boride ring, VB$_2$ ring, internal black phase and Al-V intermetallic are marked on
Figure 5.10 (a). The concentration profile of B inside and outside VB₂ ring is shown in Figure 5.10 (b). It was detected that the concentration of B in aluminium inside the ring is higher as compared with outside. This is due to the dissolution of AlB₁₂ particle that caused the saturation of B inside VB₂ ring. The diffusion of B was restricted due to product layer shown in Figure 5.10 (a). The possible reason of lesser B concentration in 60 minutes samples may be due to its consumption with the passage of time to form VB₂. It is suggested that the thickness of VB₂ ring increased with extended reaction time that has been shown in Figures 5.2 (f) and 5.3 (f). It is observed that in the early stage, VB₂ ring is not a uniform solid layer and there are a number of least resistant paths for the diffusion of either V or B as shown in Figure 5.9 (a).

Figure 5.9. SEM-SE images of Al-1wt% V-0.412wt% B alloy samples taken after (a) 0 minute showing pores in VB₂ ring and (b) 60 minute

There is a possibility of V and B mass transfer in the early stage through some least resistant paths in VB₂ ring hence it may grow inside and outside until it become a complete solid layer. It can be seen from Figure 5.9 (b) that the VB₂ layer is thicker and uniform. Once it becomes a solid layer, further reaction will be obstructed due to barrier of B and V diffusion through VB₂ layer.

As the dissolution of AlB₁₂ depends on the concentration gradient and mass transfer coefficient in liquid aluminium, further dissolution will obstruct due to B saturation inside VB₂ ring. It should be noted that the concentration of boron was higher inside VB₂ ring in the both 0 and 60 minute samples supporting the argument of AlB₁₂ dissolution and boron saturation in aluminium. The concentration profile of V inside
and outside VB₂ ring in the case of 60 minutes sample is given in Figure 5.10 (c). The higher concentration inside ring may be due to entrapment of Al-V intermetallic and formation of VB₂ inside main ring that has already been explained in this section. Vanadium concentration outside ring is within the solubility limit and less than inside as shown in Figure 5.10 (c).

The concentration profiles of V, Al and B in the VB₂ ring for 60 minute sample are shown in Figure 5.10 (d). The curves showed similar concentrations of V, B and Al as was discussed in Figure 5.8(d). The concentration of B and Al in black phase is shown in Figure 5.10 (e) that is also similar to previously discussed for 0 minute sample. This black phase was detected as AlB₁₂ that was added as a source of B in molten aluminium alloy.

The analysis of polygonal grey particle shown in Figure 5.10 (a) was also carried out by EPMA. The concentration profile of elements is shown in Figure 5.10 (f). It was detected that this phase was an intermetallic of Al-V binary system that remains undissolved from the source alloy or formed during solidification of sample due to limited solubility of V in solid aluminium. This particle consists of 82wt% Al and 18wt% V suggesting Al₁₀V binary phase of Al and V as shown in Figure 5.10 (f). An intermetallic phase such as Al-V (Al₁₀V) has also been shown in Figures 5.2 and 5.3.

It could be suggested from EPMA analysis that V in the vicinity of AlB₁₂ reacted and formed a VB₂ layer. At the start of the reaction, the thickness of the boride ring increased inside and consumes V to form further VB₂ that caused the thickening of the ring. Over time, the least resistant paths in the ring were also blocked with the freshly formed VB₂ by consuming V and B from the inside. The diffusion barrier for V and B increased with the thickening of the VB₂ layer. Consequently, further reaction was obstructed, leaving behind undissolved AlB₁₂ and V in solution with aluminium. Vanadium diborides shells were observed in all the samples taken after 0, 15, 30, 45 and 60 minutes following the addition of the Al-AlB₁₂ master alloy into the melt at 750°C. It was suggested from above discussion, that the mechanism of VB₂ formation in an Al-V-B system is complex that involves chemical reaction, mass transfer in bulk liquid and inside VB₂ ring, and diffusion of B and V through VB₂ layer.
Figure 5.10. Concentration profile of B, V and Al measured in different areas of Al-1wt% V-0.412wt% B alloy (60 minute) obtained by EPMA analysis. (a) SEM image (b) Boron profile inside and outside VB$_2$ ring (c) V profile inside and outside VB$_2$ ring (d) V, B, Al profiles in VB$_2$ ring (e) B and Al profiles in AlB$_{12}$ phase and (f) V and Al in Al-V binary phase

The SEM, EDX and EBSD analyses of Al-V-B samples have confirmed the formation of VB$_2$ in the shells around the initially added AlB$_{12}$ particles. The
presence of AlB\textsubscript{12} in VB\textsubscript{2} shells after a longer melt holding (720 minutes) suggested that the dissolution of AlB\textsubscript{12} was sluggish. This was due to the formation of a VB\textsubscript{2} shell, which promotes boron saturation in aluminium inside the shell, obstructing further dissolution of AlB\textsubscript{12} particles.

5.9 ICP-AES analysis

Inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis of Al-1wt\% V-0.412wt\% B and Al-1wt\% V-0.721wt\% B alloys was carried out on samples taken after 0, 1, 3, 5, 7, 15, 30, 45, 60 and 720 minutes. The purpose of the ICP analysis was to quantify the extent of the reaction between Al-B (AlB\textsubscript{12}) and V in both alloys. Moreover, the addition of excess boron was investigated by measuring the remaining V in solution with aluminium alloys. For ICP-AES analysis, a 50% HCl acid solution was used to dissolve aluminium alloys leaving VB\textsubscript{2} in the filtrate. The use of HNO\textsubscript{3} or HF acid with HCl will dissolve a small amount of VB\textsubscript{2}, as was reported by previous investigators (Simensen and Strand, 1981) thus was not used in the current study. A decrease of V content in solution with aluminium melt by the addition of Al-B (AlB\textsubscript{12}) master alloy is shown in Figure 5.11. It can be observed from the curves of the stoichiometry and 75 wt\% boron excess additions in the Al-1wt\% V alloys that the concentration of V was decreased with the passage of time. It can also be seen from the steep slope of the curves that approximately 50\% of V was removed in the early stage (~ 15 minutes) of the reaction following the addition of Al-B (AlB\textsubscript{12}) into aluminium melt. The curves become shallow with extended holding time, with very little decrease in V concentration. The presence of V and undissolved black phase in the sample taken after 720 minute suggested that the system was far from reaching equilibrium. Comparatively, less V in solution was observed in alloys containing 75wt\% boron excess as compared with others having stoichiometric addition of boron. The trends of V removal in both cases suggested that the action mechanism of Al-B (AlB\textsubscript{12}) with V was similar. A sharp decrease in V was noted in the early stage of reaction that gradually becomes slower with the passage of time.
It could be argued from ICP-AES analysis that the reaction between Al-B (AlB$_{12}$) was fast in the early stage of process that became slower with the passage of time due to the thickening of VB$_2$ ring (> 20 μm).

![ICP-AES analysis of Al-1wt% V-0.420wt% B and Al-1wt% V-0.721wt% B alloys (0, 1, 3, 5, 7, 15, 30, 45, 60, 720 minutes)](image)

Figure 5.11. ICP-AES analysis of Al-1wt% V-0.420wt% B and Al-1wt% V-0.721wt% B alloys (0, 1, 3, 5, 7, 15, 30, 45, 60, 720 minutes)

The presence of high amount of V, even after holding the melt for a longer time (720 minutes), suggested that the system was far from equilibrium and obviously prolonging melt holding would not provide much more decrease in V. From an industrial perspective, boron treatment of molten aluminium with long holding time is not economical. Additional work is required to improve the process by reducing the holding time and lowering the consumption of Al-B master alloys for a given reduction in V, Ti, Zr and Cr impurities.

5.10 Comparison of thermodynamic predictions and experimental results

Experimental results of change in V concentration in molten aluminium were compared with thermodynamic predictions and are presented in Figure 5.12. The ICP-AES analysis of quenched samples revealed that the alloys contained much higher V than the thermodynamic predictions. At 700°C, equilibrium calculations predicted 348 ppm V in solution with Al-1wt% B-0.412wt% V alloy. However,
experiments revealed that the alloy contains 0.38wt% V (3800 ppm) that is much higher than the thermodynamic predictions. Similar variations in experimental and thermodynamic results were found at 750°C and 800°C, as shown in Figure 5.12. The SEM image of Al-1wt% V-0.412wt% B alloy, melted and held at 750°C, is shown in Figure 5.2(f). The presence of undissolved AlB₁₂ inside the ring of VB₂ suggested that the system was far from reaching equilibrium. Boron added was not completely consumed due to the sluggish dissolution of AlB₁₂ and the formation of VB₂ ring. Consequently, there was a deficiency of B in the bulk melt that causes V to remain in solution as shown in Figure 5.12.

The thermodynamic and experimental results in the case of 75wt% boron excess was also analysed and are given in Figure 5.12. At 700°C, equilibrium calculations predicted approximately 1 ppm V in solution with Al-1wt% V-0.721wt% B alloy. However, ICP-AES analysis revealed that 200 ppm V was still present in the solution, which is also much higher than thermodynamic predictions. At 750°C and 800°C, the concentration of V was 200 ppm and 100 ppm respectively. The larger decrease in the concentration of V was due to the addition of excess boron than the stoichiometric requirement for the formation of VB₂. Undissolved AlB₁₂ would be present but their number was high enough to provide a sufficient amount of B to reduce the contents of V from 1wt% to 0.02wt% (200 ppm), as shown in Figure 5.12. The SEM image of Al-1wt% V-0.721wt% B alloy, melted and held at 750°C, is shown in Figure 5.3(f). The presence of undissolved AlB₁₂ inside the VB₂ ring and the remaining V in the alloy suggested that the system is far from reaching equilibrium.

It could be concluded from the experimental and thermodynamic predictions that the kinetics of AlB₁₂ dissolution was slow that may be due to the formation of VB₂ rings. Both alloys investigated were far from equilibrium, and consequently the remaining amount of V in solution was much higher than the predicted values. Equilibrium calculations were carried out using pure Al, V and B that will show a different solute behaviour to the experimentally investigated systems.
5.11 Summary

Thermodynamically, it is possible to remove V in the form of borides in the temperature range of 650°C to 900°C because VB₂ have lower Gibbs free energy of formation as compared with AlB₁₂/AlB₂. Investigation of Al-1wt% V-0.412wt% B and Al-1wt% V-0.721wt% B alloys revealed that the reaction between AlB₁₂/B and V aluminium solution was quick in the early minutes. Consequently, reaction product layer of VB₂ was formed in the start of reaction. The layer of VB₂ contains least resistant paths in the early minutes of reaction. Moreover, AlB₁₂ particles initially added as a source of boron was encapsulated by VB₂ layer which halted further reaction. Although the reaction between AlB₁₂/B was fast in the early minutes of reaction but was incomplete due to kinetic limitations. The presence of a black phase inside the ring suggested the slow dissolution of AlB₁₂ in the given working conditions. The EPMA analyses revealed higher concentration of boron inside ring compared to outside suggest the diffusion barrier that may obstruct further reaction. The comparison of thermodynamic predictions and experimental results also revealed that the alloys were for from equilibrium.

The mechanism of VB₂ formation is complex due to the involvement of a series of steps during the reaction of AlB₁₂/B with V in molten aluminium. The SEM, EDX
and EBSD analysis confirmed the formation of VB₂ in the grey shell encapsulating the initially added AlB₁₂ particles from the Al-B master alloy. There were strong evidences from EBSD analysis that the reaction product ring was composed of VB₂ and not making solid solution with AlB₁₂/Al.

The presence of undissolved AlB₁₂ particles in the samples held at 750°C for 720 minutes suggested that the dissolution of AlB₁₂ was controlled by the formation of VB₂ boride layer. The mass transport resistance increased with the passage of time due to the thickening of the VB₂ layer that ultimately slow down the reaction between B and V. It could be concluded from the formation and thickening of VB₂ layer and the evidence of undissolved AlB₁₂ particles that the reaction was controlled by the mass transport of species through the boride rings.
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Chapter 6

Kinetic Analysis of V Removal from Molten Aluminium

6.1 Introduction

The removal of transition metals (V, Ti, Zr, Cr and Fe) from molten aluminium has been a focus of various researchers. The removal of vanadium and other transition metals were usually treated together in the published literature. The increase in electrical conductivity of aluminium was correlated with the removal of V and other transition metals from solution into their borides. Previous investigators mostly measured the increase in electrical conductivity or the % borides settled versus time. Cooper and co-workers have conducted pilot plant trials and recorded the decrease in transition metals with time by the addition of Al-B master alloys in molten aluminium. They proposed a reaction mechanism between AlB$_{12}$/AlB$_2$ and transition metals in solution with aluminium but no experimental evidences were reported in their work (Cooper and Kearns, 1996, Cook et al., 1997).

Various investigators had worked on solid-fluid (gas or liquid) reactions and have developed different models. Mainly they are divided into progressive conversion and shrinking core models. In the case of shrinking core particle, models are developed for liquid/gas film, ash (product) layer and chemical reactions controls depending on different systems (Wen and Huebler, 1965a, Wen and Huebler, 1965b, Ishida and Wen, 1968, Ishida and Wen, 1971, Levenspiel, 1972, Yagi and Kunii, 1955, Dickinson and Heal, 1999, Órfão and Martins, 2002, Markus et al., 2004, Grénman et al., 2007).

The information related to the kinetics of transition metals removal especially V is lacking in the published literature. Moreover, reaction mechanism of B or AlB$_{12}$/AlB$_2$ with V impurities in molten aluminium has not been identified and reported in literature. The understanding of reaction mechanism will be important to
optimise and improve the current boron treatment process. If the exact mechanism of VB₂ formation in aluminium melt is identified, measures could be taken to improve the economy of process by decreasing the consumption of Al-B master alloys and processing time in the current industrial practices. In the current chapter, kinetics analyses of V removal from molten aluminium are carried out to identify the reaction mechanism of VB₂ formation.

Table 6.1. Experimental plan for the kinetic analysis of V removal from molten aluminium

<table>
<thead>
<tr>
<th>Exp. batch</th>
<th>Level of B addition</th>
<th>Temp(°C)</th>
<th>Stirring and type</th>
<th>Sampling (minutes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Stoi (AlB₁₂)</td>
<td>700, 750, 800</td>
<td>Nil</td>
<td>0, 2, 4, 6, 8, 10, 15, 30, 45, 60</td>
</tr>
<tr>
<td>2</td>
<td>75wt% excess (AlB₁₂)</td>
<td>700, 750, 800</td>
<td>Nil</td>
<td>0, 2, 4, 6, 8, 10, 15, 30, 45, 60</td>
</tr>
<tr>
<td>3</td>
<td>150wt% excess (AlB₁₂)</td>
<td>750</td>
<td>Nil</td>
<td>0, 2, 4, 6, 8, 10, 15, 30, 45, 60</td>
</tr>
<tr>
<td>4</td>
<td>75wt% excess (AlB₂)</td>
<td>750</td>
<td>Nil</td>
<td>0, 2, 4, 6, 8, 10, 15, 30, 45, 60</td>
</tr>
<tr>
<td>5</td>
<td>75wt% excess (AlB₁₂)</td>
<td>750</td>
<td>Mech. stirring (100, 350, 550 rpm)</td>
<td>0, 2, 4, 6, 8, 10, 15, 30, 45, 60</td>
</tr>
<tr>
<td>6</td>
<td>75wt% excess (two instalments) (AlB₁₂)</td>
<td>750</td>
<td>100 rpm</td>
<td>0, 2, 4, 6, 8, 10, 15, 30, 45, 60</td>
</tr>
<tr>
<td>7</td>
<td>75wt% excess (AlB₁₂)</td>
<td>750</td>
<td>Gas stirring (N₂)</td>
<td>0, 4, 6, 10, 15, 30, 45, 60</td>
</tr>
</tbody>
</table>

- Stoi – 0.412wt% B
- 75wt% excess – 0.721wt% B
- 150wt% - 1.03wt% B

6.2 Kinetics of V removal by the addition of AlB₁₂ in molten aluminium

In the case of reaction between V and B/AlB₁₂(α) in the molten aluminium, it has been shown that VB₂(α) are formed (Dean, 1967, Dube, 1983, Stiller and Ingenlath, 1984, Cooper and Kearns, 1996, Wang et al., 2002, Karabay and Uzman, 2005a, Karabay and Uzman, 2005b, Khaliq et al., 2011b). It was predicted during thermodynamic
analysis that diborides of transition metals are more stable than their other possible borides in the temperature range of 675°C to 900°C. Moreover, it was also predicted that transition metal diborides, once formed are stable and do not dissolve back into in molten aluminium under aluminium processing conditions (Khaliq et al., 2011a). The possible overall reaction in the case of Al-1wt% V alloy having stoichiometric addition of boron can be written as Equations (6.1) and (6.2). The values of Gibbs free energies given in Equations (6.1) and (6.2) were calculated from FactSage 6.2.

\[
6[V] + Al_{1(2)} \rightarrow 6VB_{2(2)} + [Al] \quad \Delta G^o = -10977372 + 1367777T, J
\]  

\[
[V] + 2[B] \rightarrow VB_{2(2)} \quad \Delta G^o = -3180809 + 65.923T, J
\]

Where “[ ]” indicates that elements are dissolved and form solution with molten aluminium and “(s)” represents that compounds are in solid state. From thermodynamic perspective, reactions given in Equations (6.1) and (6.2) are feasible hence the kinetics of VB₂ formation can be investigated.

Figure 6.1. The change in the vanadium concentration in Al-1wt% V-0.412wt% B (In atomic % 98.28%Al-0.54%V-1.08%B) alloy at 700°C, 750°C and 800°C without external melt stirring

Figure 6.1 shows the change in V concentration containing stoichiometric addition of boron at 700°C, 750°C and 800°C. General observation of the experimental results showed that the rate of V removal was fast in the first 10 minutes of reaction and was
halted after 15 to 60 minutes depending on the experimental conditions. It could also be observed from the curves in Figure 6.1 that the system is far from equilibrium.

It is worth to mention that the alloys under investigations have 1wt% V in molten aluminium. Due to the limited solubility of V in aluminium (0.28wt% at 700°C, 0.46wt% at 750°C and 0.73wt% at 800°C) (Dybkov and Dybkov, 1998), a significant proportion will exist as Al-V intermetallics. Equilibrium calculations using FactSage 6.2 predicted higher solubility of V in molten aluminium compared to that reported by Dybkov (1998). A comparison of vanadium solubility in liquid aluminium at different temperature is given in Table 6.2.

The analysis of Al-V binary system showed that at room temperature Al_{10}V will be present in Al-1wt% V master alloy. At 750°C, Al_{3}V will be stable which is formed by the peritectic reaction of Al_{23}V_{4} (Al_{6}V) and Al. The EDX analysis of Al-10wt% V master alloy as shown in Section 3.2.3.2 detected Al_{3}V binary phase in aluminium matrix. Equilibrium calculations of Al-1wt% V alloy using FactSage 6.2 also predicted Al_{10}V, Al_{6}V (Al_{23}V_{4}) and Al_{3}V at temperature of 650°C, 700°C and 750°C respectively.

Table 6.2. The solubility of vanadium in liquid aluminium

<table>
<thead>
<tr>
<th>Temperature(°C)</th>
<th>Weight %</th>
<th>Dybkov (1998)</th>
<th>FactSage 6.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>700</td>
<td>0.28</td>
<td>0.311</td>
<td></td>
</tr>
<tr>
<td>750</td>
<td>0.46</td>
<td>0.61</td>
<td></td>
</tr>
<tr>
<td>800</td>
<td>0.73</td>
<td>0.99</td>
<td></td>
</tr>
</tbody>
</table>

Dissolution kinetics of Al-V intermetallic particles will be important in molten aluminium. It will release V back into molten aluminium to balance its removal from solution form into stable diborides. The starting concentration shown in Figure 6.1 represents V in solution with aluminium.

The excess amount of V than its solubility will be present in the form of Al_{3}V/Al_{10}V intermetallics that is shown in Figure 6.2. Al-V intermetallics are settled at the bottom of crucible during the holding of alloys at 750°C in the absence of external stirring. It could also be observed from Figure 6.2 that Al-V particles are dissolving
that compensate the deficiency of V in solution with molten alloy. There will be a
erchemical reaction according to Equations (6.1) and (6.2) to form \( \text{VB}_2 \) and also the
dissolution of Al-V (Al\(_3\)V) particles in the molten alloy.

![Al-1wt% V-0.412wt% B alloy residue at 750°C]

Figure 6.2. The SEM-SE image of Al-1wt% V-0.412wt% B alloy residue collected
from the bottom of crucible after casting at the end of experiment

It could be observed from Figure 6.1 that the rate of V removal is a weak function of
temperature. The increase in temperature is not making significant effect on the
overall rate of V removal from molten aluminium particularly between 750°C and
800°C. Equation 6.3 describes the conversion of V into \( \text{VB}_2 \). The calculated
conversion of V into \( \text{VB}_2 \) by the addition of Al-B master alloy versus reaction time is
given in Figure 6.3. Similar rates for the first 10 minutes of reaction at temperature of
750°C and 800°C are shown in Figure 6.3.

\[
Conversion(\alpha) = \frac{(wt\%V)_i - (wt\%V)}{(wt\%V)_o}
\]  

(6.3)

Where \( (wt\%V)_i \) = initial concentration of V and \( (wt\%V) \) = concentration of V at
time, \( t \). The final conversion at 800°C was higher as compared with 700°C and 750°C
and a significant rate difference was observed in the beginning of the reaction. It is
shown in Figure 6.3 that maximum 67% of V was converted into \( \text{VB}_2 \) at 800°C
suggesting the system was far from equilibrium in the given conditions.

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The stoichiometric addition of boron as shown in Figure 6.1 revealed that the remaining amount of V in alloy was high, e.g. 31% at 800°C and about 46% at 700°C and 750°C. Keeping in view the higher contents of V in molten alloy after 60 minutes, 75wt% excess boron was added. It has been reported in literature to use excess boron than the stoichiometric requirement of transition metals to form their borides (Cooper and Kearns, 1996, Stiller and Ingenlath, 1984, Setzer and Boone, 1991).

The change in V concentration by the addition of 75wt% excess boron is shown in Figure 6.4. Trends similar to stoichiometric case were observed for 75wt% boron excess addition (Al-1wt% V-0.720wt% B alloy). The conversion of V reached 90% using 75wt% boron excess. The conversion of V with reaction time for 75wt% excess is given in Figure D.1 (Appendix). The removal of V was increased by the addition of excess boron in the Al-1wt% V alloy.

The kinetic plots shown in Figure 6.1 and 6.4 revealed that the rate of V removal has two stages. The early stage of reaction is rapid and the later stage is much slower (after 10 minutes of reaction). For kinetics analyses and to find the mechanism of VB$_2$ formation in molten aluminium, the plots of V were divided into two sections. First section represents the early stage of reaction (up to 10 minutes) that has higher
rate of V removal and the formation of VB₂. It was assumed that the kinetics was controlled by either chemical reaction at AlB₁₂ interface or liquid phase mass transfer in this early stage of reaction. Contrary to first, second stage observes slower rate of V removal as shown by the flat curves in Figure 6.1 and 6.4 (after 10 minutes).

Figure 6.4. Kinetic plots of change in V concentration at 700°C, 750°C and 800°C in the case of 75wt% boron excess (in atomic % 97.51%Al-0.54%V-1.88%B) addition in Al-1wt% V alloy

The general observations of slower rate of V removal and also microstructural analysis suggested that the kinetics in the later stage of reaction may be controlled by diffusion through product layer. In the following section, kinetics of reaction for each stage was analysed individually.

6.3 Reaction order and interfacial area

Let us assume that kinetics is controlled by the chemical reaction at interface between AlB₁₂ particles and liquid metal phase in the first stage of reaction. It was also assumed that the interfacial area will remain constant in the first 10 minutes of reaction. It is reasonable to assume constant interfacial area in the beginning of reaction because the increase in the thickness of product layer and the dissolution of AlB₁₂ particles were not significant. Consequently, the interfacial area of AlB₁₂ particles remains constant during the first stage of reaction. The SEM images shown in Figures 5.2 and 5.3 of Al-1wt% V-0.412wt% B and Al-1wt% V-0.721wt% B
alloys also revealed that there was no significant reduction in area of AlB$_{12}$ (black phase inside VB$_2$ shell) in the early stage of reaction. Under such situation, a general kinetics equation for an $n^{th}$ order rate with respect to $V$ can be written as:

$$
\frac{1}{1-n} \left[ \omega t\% V^{(1-n)} - \omega t_{0}\% V^{(1-n)} \right] - \frac{kA}{V}t
$$

(6.4)

Where $\omega t\% V$ and $\omega t_{0}\% V$ are the concentrations of $V$ in molten aluminium at time $t$ and at time zero, $n$ is the reaction order, $A$ is the interfacial area of AlB$_{12}$ particles, $V$ is the volume of alloy, and $k$ is the reaction rate constant. In this case the volume of molten aluminium alloy was also assumed constant.

The kinetics analysis was carried out for $n = 1$ and $n \neq 1$ by testing the experimental results for $n^{th}$ order reaction kinetics. The purpose of this exercise was to observe deviation of experimental results as the values of $n$ goes away from 1. The value of reaction order was assumed $n < 1$ and $n > 1$ to find the best fit to the experimental data. The left hand side of Equation (6.4) was plotted against the reaction time for different values of reaction order ($n$).

![Kinetics plot of Al-1wt% V-0.412wt% B alloy at 750°C assuming nth order reaction with n = 0.1](image)

Figure 6.5. Kinetics plot of Al-1wt% V-0.412wt% B alloy at 750°C assuming nth order reaction with $n = 0.1$

Figures 6.5, 6.6 and 6.7 showed the kinetic plots of Al-1wt% V-0.412wt% B alloy at 750°C for $n = 0.1$, 1 and 2.0. More plots for different values of reaction orders at
700°C, 750°C and 800°C are given in Appendix D1. It could be observed from Figure 6.5 that the experimental data deviate from linearity because the linear curve fitting gave 92% $R^2$ value. The experimental data for reaction order $n = 1$ gave a better linear fit with 96% $R^2$ as shown in Figure 6.6.

![Figure 6.6. Kinetics plot of Al-1wt% V-0.412wt% B alloy at 750°C assuming nth order reaction with $n = 1$](image1)

$n = 1.0$

$R^2 = 0.96$

![Figure 6.7. Kinetics plot of Al-1wt% V-0.412wt% B alloy at 750°C assuming nth order reaction with $n = 2.0$](image2)

$n = 2.0$

$R^2 = 0.97$
The experimental data was also plotted using $n = 2$ and is given in Figure 6.7. The linear curve fitting gave 97% value of $R^2$ that is better than $n = 1$ and $n < 1$. The value of $R^2$ did not change significantly from $n = 1$ and $n = 2$. Considering that most metallurgical reactions are first order. It is most likely that the order of reaction in the case of present study is also first order (e.g. diffusion or mass transfer control).

The kinetic plots of V in the case of stoichiometric, 75wt% and 150wt% boron excess addition of at 750°C are shown in Figure 6.8. The plots of V removal are similar to that shown in Figure 6.1 and 6.4.

![Figure 6.8. Kinetic plots of V removal in the case of stoichiometric, 75wt% and 150wt% excess boron addition in Al-1wt% V alloy at 750°C](image)

The total conversion of V into VB$_2$ was higher in the case of 150wt% boron excess addition but still the final concentration of V was higher than the predicted equilibrium. It could be argued that only the excess addition of boron will not serve the purpose of removing V from molten aluminium. Other factors need to be considered for determining the optimum amount of boron that can improve the economy of boron treatment process.
6.4 Liquid metal phase control kinetics

It has been shown that the reaction is first order with respect to V in molten Al-1wt% V-0.412wt% B alloy. It is likely that the kinetics of reaction in the first stage will be controlled either by chemical reaction at the interface of AlB₁₂ solid particles or mass transfer through liquid aluminium alloy. The mass transfer of V/B will take place in the melt to the reaction interface for the formation of VB₂. Further kinetics analysis was carried out by considering mass transfer control scenario. The kinetic equation for liquid phase mass transfer can be written as given in Eq. (6.5) (Pomfret and Grievson, 1983). Derivation of the liquid phase mass transfer model is described in Appendix D2.

\[-\frac{d(\text{wt\%V})}{dt} = \frac{kA}{V} \left(\frac{\text{wt\%V}_t}{\text{wt\%V}_e} - \frac{\text{wt\%V}_e}{\text{wt\%V}_o}\right)\]  \hspace{1cm} (6.5)

Where \(k\), \(A\) and \(V\) are the mass transfer coefficient in liquid phase, interfacial area of AlB₁₂ particles and volume of molten alloy respectively. Moreover \(\text{wt\%V}_t\), \(\text{wt\%V}_o\) and \(\text{wt\%V}_e\) are the concentrations of V in molten aluminium at time \(t\), zero and at equilibrium (predicted by FactSage 6.2). The integration of Eq. (6.5) and by re-arranging the variables, the kinetic equation for liquid phase control can be written as:

\[\frac{V}{A} \left(\frac{\text{wt\%V}_t - \text{wt\%V}_e}{\text{wt\%V}_o - \text{wt\%V}_o}\right) \ln \left[\frac{\text{wt\%V}_t - \text{wt\%V}_e}{\text{wt\%V}_o - \text{wt\%V}_o}\right] = -kt\]  \hspace{1cm} (6.6)

Equation (6.6) can be written as:

\[Y\ln Z = -kt\]  \hspace{1cm} (6.7)

Where \(Y = \frac{V}{A} \left(\frac{\text{wt\%V}_t - \text{wt\%V}_e}{\text{wt\%V}_o - \text{wt\%V}_o}\right)\) and \(Z = \left[\frac{\text{wt\%V}_t - \text{wt\%V}_e}{\text{wt\%V}_o - \text{wt\%V}_o}\right]\)

Equation (6.7) can also be used for chemical reaction control at the interface of AlB₁₂ particles that are added as a source of boron in the molten aluminium alloy. The left hand side of Eq. (6.6) was plotted against the experimental data of V removal from Al-1wt% V-0.412wt% B alloy at 700°C, 750°C and 800°C. One of the important
steps to analyse the solid-liquid reaction kinetics is the determination of representable interfacial area. In this case, interfacial area of AlB$_{12}$ particles was calculated by SEM image analysis of pieces of Al-10wt% B (AlB$_{12}$) master alloy added to the system. The procedure of estimating interfacial area using image processing software (ImageJ, version 1.47 h) is described in Appendix D3. Initial interfacial area was estimated that will change due to reaction and agglomeration over the period of experiment.

The results at different temperature for stoichiometric addition of boron are shown in Figures 6.9, 6.10 and 6.11. It could be observed that each set of experimental data fit well and gave $R^2$ values more than 95%. This suggested that the kinetics in the first stage of reaction could be controlled by mass transfer of V through the liquid metal phase. The overall mass transfer coefficient of V was also calculated.

![Integrated rate plot of Al-1wt% V-0.412wt% B alloy at 700°C](image)

Figure 6.9. Integrated rate plot of Al-1wt% V-0.412wt% B alloy at 700°C

Figures 6.9, 6.10 and 6.11 showed the rate of reaction increased with increase in temperature, although the increase was not pronounced. The calculated values of mass transfer coefficient were $1.49 \times 10^{-3}$ m/sec, $2.15 \times 10^{-3}$ m/sec and $2.59 \times 10^{-3}$ m/sec at 700°C, 750°C and 800°C respectively for Al-1wt% V-0.412wt% B alloy.
It has already been explained in literature that the excess addition of boron is required to remove the transition metals into their stable borides during the boron treatment of molten aluminium. The experimental data for three levels of boron addition was presented in Figure 6.8 that is used to plot integrated rate given in Eq. (6.6) versus time. The results are shown in Figure 6.12. It could be observed from the plots in Figure 6.12 that the global rate of reaction increased by the addition of
excess boron. Although, reaction rate was not similar in the first couple of minutes but the overall rate of reaction was enhanced by increasing the amount of boron. The average overall mass transfer coefficient calculated at 750°C for Al-1wt% V alloy having stoichiometric, 75wt% excess and 150wt% excess addition of boron was 1.76 x 10^{-3} m/sec.

The calculated mass transfer coefficient shown in Figures 6.9, 6.10, 6.11 and 6.12 also represents the rate constant if chemical reaction control kinetics was assumed. The activation energy can be determined by plotting the ln $k$ versus reaction temperatures ($1000/T, K^{-1}$). The plot from the experimental data is shown in Figure 6.13. The data can be fitted into a straight line with $R^2$ value equal to 98% which has a slope of -3.12. The activation energy was calculated to be 25.94 kJ/mol. The calculated activation energy was close to the 34.6 kJ/mol, reported by (Sarma and Ravi Chandran, 2011).

![Figure 6.12. Integrated rate plots of Al-1wt% V-XB alloy (where X = stoichiometric, 75wt% B excess and 150wt% B excess), assuming V mass transport in liquid, showing the effect of different level of boron on the reaction rates](image)
They assessed the activation energy of impurities diffusion in liquid aluminium including V. It has been reported that most of chemical reactions at high temperatures are much faster than the liquid phase mass transport of reactants hence chemical reaction is unlikely to be the rate controlling step (Brimacombe, 1974). Guthrie (1992) reported that the typical values of mass transfer coefficient in a liquid – solid reaction around an alloying addition is in the range of $10^{-4} – 10^{-3}$ m/sec (Guthrie, 1992). The calculated mass transfer coefficients from experimental data at three different temperatures were within the range reported by Guthrie.

Considering that:

1. Quick formation of VB$_2$ in the early minutes of reaction suggested the kinetics is not controlled by chemical reaction (Figure 5.2(a) and 5.3(a))
2. Temperature has a weak effect on rate of reaction
3. Addition of boron excess has a weak effect on mass transfer ($k_m$)
4. The rate of activation energy and mass transfer coefficient are within the range of reported values for mass transfer controlled kinetics

It was concluded that the global rate of reaction in the early stage is controlled by the mass transfer of V in metal phase and not by the chemical reaction at the interface of AlB$_{12}$ particles.
6.5 Diffusion through product layer controlled kinetics

The kinetics plots of experimental data shown in Figure 6.1 and 6.4 revealed that the reaction of V with AlB$_{12}$ was obstructed after 10 minutes. This was assigned as a second stage of reaction that is affected by the formation of dense product (VB$_2$) layer encapsulating the primary source of boron (AlB$_{12}$). The formation of product layer has also been shown in Figures 5.2 and 5.3. It was observed from SEM images of samples taken after 0 and 720 minutes that the thickness of product (VB$_2$) layer increased from less than 1 μm to more than 20 μm during the isothermal hold of alloy at 750°C. During the course of time, AlB$_{12}$ was mostly consumed that promotes reaction for the formation of VB$_2$ in the molten alloy. It was suggested from microstructural and kinetic plots analyses that the later stage of reaction was most likely controlled by the diffusion of either V/B through the product (VB$_2$) layer. Diffusion control models have been developed for chemical processes that involve the interaction of liquid and solid and the formation of reaction product layer. The lists of solid-liquid kinetics models and the possible mechanisms involved are discussed in Section 2.6.3.

The second stage of reaction for the formation of VB$_2$ was analysed using Jander and Ginstling – Brounshtein diffusion through product layer models. The integral forms of these diffusion models are given in Equations (6.8) and (6.9) (Jander, 1927, Ginstling and Brounshtein, 1950).

\[
\begin{align*}
\left(1 - \alpha^{7/3}\right) &= k't \quad \text{(Jander model)} \quad \text{(6.8)} \\
1 - \left(\frac{2}{3}\right)\alpha^{2/3} &= k't \quad \text{(Ginstling-Brounshtein model)} \quad \text{(6.9)}
\end{align*}
\]

Where $\alpha$ is conversion of V in solution into solid VB$_2$ particles at time $t$ during the solid-liquid reaction that was obtained using Eq. 6.3. The rate constant $k'$ depends on the diffusion coefficient of the reacting species, concentration gradient and molar density of product layer (VB$_2$). The rate constant in Jander model is given in Eq. (6.10). The value of $k$ is given in Eq. 6.11 and $R^2$ is the initial radius of spherical particle inside the reaction product (Schmidt et al., 2007, Jander, 1927).
\[ k' = \frac{k}{R^2} \]  

(6.10)

\[ k = \frac{2D M_{VB} C_2 - C_1}{\rho_{VB2} M_B} \]  

(6.11)

Where \( D \) is the diffusivities of reacting species in the product layer and \( C_2, C_1 \) are the concentration of V and B in inner and outer boundaries of VB\(_2\) product layer and \( \rho_{VB2} \) is the molar density of product layer (VB\(_2\)), \( M_{VB2} \) is the molecular weight of VB\(_2\) and \( M_B \) is the molecular weight of diffusing species (boron). The rate constant in the case of Ginstling-Brounshtein model is given in Eq. (6.12).

\[ k = \frac{DC_2}{\varepsilon} \]  

(6.12)

Where \( D \) is the diffusion coefficient, \( \varepsilon \) is the proportionality constant that is equal to \( \frac{\rho n}{\mu} \) (\( \rho \) and \( \mu \) are the specific gravity and molecular weight of the product (VB\(_2\)) and \( n \) is the stoichiometric coefficient of reaction (0.5 for V for VB\(_2\) formation with one mole of B) (Ginstling and Brounshtein, 1950).

The experimental data shown in Figure 6.1 was plotted against the left hand side of Equations (6.8) and (6.9) and are shown in Figure 6.14. The curve fitting to experimental data for the second stage (15 to 60 minutes) of reaction showed a linear relationship with \( R^2 \) values > 99% at 700\(^\circ\)C and > 97% at 750\(^\circ\)C and 91% at 800\(^\circ\)C as shown in Figure 6.14.

According to Jander’s diffusion model, the rate of increase in thickness of the reaction product is inversely proportional to its thickness for spherical particles. The plots of experimental data using Jander diffusion model are shown in Figure 6.14(a), 6.14(b) and 6.14(c). Analysis of experimental data using Jander model showed an increase in reaction rate with reaction time. The positive slopes for the rate constant \( k' \) are \( 8.1 \times 10^{-6} \text{s}^{-1} \), \( 6.62 \times 10^{-6} \text{s}^{-1} \) and \( 1.58 \times 10^{-5} \text{s}^{-1} \) at 700\(^\circ\)C, 750\(^\circ\)C and 800\(^\circ\)C respectively. It showed the reaction is proceeding to reach equilibrium but with slower rate.
Figure 6.14. The plots of the analysis of experimental data using Jander (a, b and c) and Ginstling – Brounshtein (d, e and f) diffusion models through product layer
Ginstling – Brounshtein model is based on the steady-state diffusion of species around a spherical particle. The integral form of this model is shown in Eq. (6.8). Experimental data at 700°C, 750°C and 800°C was also plotted using Ginstling-Brounshtein diffusion model. The plots are given in Figure 6.14(d), 6.14(e) and 6.14(f) that also show a positive slope with reaction time. The calculated values of rate constants are $6.35 \times 10^{-6} \text{s}^{-1}$, $4.93 \times 10^{-6} \text{s}^{-1}$, and $1.14 \times 10^{-5} \text{s}^{-1}$ at 700°C, 750°C and 800°C respectively. A similar range of rate constant i.e $3.42 \times 10^{-6} \text{s}^{-1}$ has been reported in literature for the formation of spinel ferrite at 800°C using Jander and Ginstling-Brounshtein diffusion models (Paik et al., 2005).

Considering that:

1. Experimental data can be fitted using diffusion models
2. There is evidence of thickening of dense solid product (VB$_2$) as shown in Figures 5.2 (f) and 5.3(f).
3. The direction of growth of the VB$_2$ product is outwards as shown in Figure 5.3(f). Small particles nucleate at outer boundary of VB$_2$ ring.

It was concluded that the second stage of the reaction is controlled by the diffusion of B through the VB$_2$ layer. The calculated values of the rate constant are 1000 time slower compared to first stage of reaction.

### 6.6 Effect of stirring on Kinetics of V removal

The kinetic analysis of V removal and the formation of VB$_2$ for liquid phase mass transfer (first stage) and diffusion through product layer (second stage) was exercised for a molten alloy without external stirring. There was no other stirring of melt except that caused by sampling. The effect of stirring rate on the removal of V was investigated using 75% excess addition of boron in Al-1wt% V alloy held at 750°C. The stirring of melt was performed using mechanical rotator at a frequency of 100 rpm, 350 rpm, and 550 rpm. Additional stirring by N$_2$ gas purging at a flow rate of 1.764 l/min was also tested.

The plots of change in V concentration for the cases of mechanical stirring are shown in Figure 6.15. It could be observed from the concentration of V at 0 minutes that the
alloy initially has about 48% V out of solution that is in the form of Al-V intermetallics. The remaining 52% V is in solution which was reported as a starting composition in all the plots in Figure 6.15. It was reported and shown in Figure 6.2 that V out of solution with aluminium settled at the bottom of graphite crucible in the form of Al$_3$V/Al$_{10}$V particles. The mechanical stirring energy input (watt/tonne) into the molten alloy is summarised in Table 6.3. The calculations of mechanical stirring energy are described in Appendix D4.2.

Table 6.3. Stirring energy input in molten aluminium using mechanical stirrer

<table>
<thead>
<tr>
<th>Rotation (rpm)</th>
<th>Rotation (rps)</th>
<th>Torque (N.m)</th>
<th>Power (W)</th>
<th>Stirring energy (W/ton)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>1.67</td>
<td>0.0535</td>
<td>0.5623</td>
<td>5.62 x 10$^{-4}$</td>
</tr>
<tr>
<td>350</td>
<td>5.83</td>
<td>0.0635</td>
<td>2.33</td>
<td>2.33 x 10$^{-3}$</td>
</tr>
<tr>
<td>550</td>
<td>9.17</td>
<td>0.065</td>
<td>3.75</td>
<td>3.75 x 10$^{-3}$</td>
</tr>
</tbody>
</table>

A sharp increase in V was observed during melt stirring at 100 rpm, which is possibly due to the re-suspension of Al-V intermetallics back into melt and trapped during sampling. This phenomenon was not observed in the cases of 350 rpm and 550 rpm, because rotator insertion in the melt and then sampling was performed with precautions. It was calculated that apparently 23.1%, 67.92% and 39.22% of V was removed during stirring of melt at rotator frequency of 100 rpm, 350 rpm and 550 rpm.

The process of Al-V intermetallics dissolution was taking place simultaneously with other kinetics mechanism (liquid phase and diffusion through product layer). The dissolution of Al-V intermetallics was compensating the decrease in V concentration in the molten alloy. The settled sludge at the bottom of crucible was 4 to 5 times lighter in weight than the sludge of alloy without external stirring. From the evidence of sludge weight, it could be suggested that the actual removal of V was 60%, 83% and 69% for 150 rpm, 350 rpm and 550 rpm melt stirring.

It could be suggested that the overall removal of V was higher in mechanical stirred alloy compared to others without external stirring. The mechanical stirring of melt possibly increased the global rate of mass transport of V in the molten alloy that
increased the kinetics of reaction. However, this was not reflected in the current study due the reasons mentioned above caused by higher initial V concentration than the solubility limit.

![Figure 6.15. The removal of V in the case of mechanical (100 rpm, 350 rpm and 550 rpm) and gas stirring having 75wt% boron excess in Al-1wt% alloy at 750°C](image)

It was shown in Figures 5.2 and 5.3 that a reaction product of VB₂ formed in the early stage of reaction that grew in thickness with the passage of reaction time. Moreover, the kinetic analysis of second stage of reaction shown in Section 6.5 also revealed that the diffusion through product layer is the controlling mechanism. The diffusion of reacting species V/B across the VB₂ shell controls further reaction and the thickening of VB₂ layer. It was hypothesized that the rate of reaction could be enhanced by breaking/removing the VB₂ ring encapsulating the AlB₁₂ particles as a source of boron.

The melt was purged with nitrogen (N₂) gas for 1 minute before each sampling during experiments. Stirring time was 10 minutes because 10 samples were taken during the 60 minute experiment. Induction, mechanical and gas stirring energies input to the molten alloy are summarised in Table 6.4. This table will help to analyse the effect of different stirring on the removal of V from molten aluminium. It could be seen from Table 6.4 that the energy input by induction stirring is higher than mechanical and gas purging.
Table 6.4. Calculation of stirring energy for induction, mechanical rotator and gas stirring

<table>
<thead>
<tr>
<th>Stirring of molten alloy</th>
<th>Stirring energy (W/tonne)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Induction</td>
<td>$9.32 \times 10^{-2}$</td>
</tr>
<tr>
<td>Mechanical rotator (350 rpm)</td>
<td>$2.33 \times 10^{-3}$</td>
</tr>
<tr>
<td>Gas purging (1.764 LPM)</td>
<td>$3.06 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

A plot of V concentration with time in the case of $N_2$ purging is shown in Figure 6.16. It was observed that the rate of V removal was significantly increased and a minimum concentration i.e 0.02wt% of V was achieved in the first 10 minutes of reaction. This showed a V removal of 98% in 10 minutes compared to 83% after 60 minutes during mechanical stirring of molten alloy.

![Figure 6.16. Effect of gas stirring on the removal of V from Al-1wt% V-0.72wt% B at 750°C](image)

Gas purging was effective for V removal, although the energy input was less than induction and mechanical stirring. Moreover, gas stirring was carried out for 10 minutes compared to 60 minutes of induction and mechanical stirring.
The SEM-SE images of alloys boride sludge collected from the bottom of crucible after performing experiments without external, mechanical and gas stirring are shown in Figure 6.17. It was observed from Figure 6.17(a) that VB₂ rings are coherent and are encapsulating the undissolved AlB₁₂. The undissolved particles of Al-V are also present as shown in Figure 6.17(a). In the absence of external stirring, the dissolution of Al-V particles was slow leaving approximately 48% of V in the settled sludge at the bottom of crucible. Figure 6.17(b) showed the presence of VB₂ rings similar to given in Figure 6.17(a). The only difference is the absence of Al-V particles that are most likely dissolved during the mechanical stirring of melt. The SEM image of boride sludge after gas purging is shown in Figure 6.17(c). It could be observed that the undissolved AlB₁₂ particles have no rings of VB₂ as were shown in without external and mechanical stirred alloys. During gas purging of molten alloy, VB₂ borides rings was effectively broken that provided further effective interfacial area for the completion of reaction.

VB₂ inclusions are non-wetted by the molten aluminium and preferred to form as clusters. There could be a possibility of VB₂ particles floatation if VB₂ are wetted by gas bubbles. Gas bubbles took small inclusions from bottom to the surface of molten alloy during the purging cycle. It could be concluded from the faster kinetics of V removal using gas purging that bubbles moved away smaller VB₂ particles from the interface of AlB₁₂ and did not provide opportunity for the formation of consistent and dense layer. As soon as product layer is formed, gas stirring of melt takes away the particles of VB₂ and leaving behind AlB₁₂ with maximum reactive interfacial area. Moreover, AlB₁₂ particles will be re-suspended during each stirring cycle which will also increase the availability of reactive interfacial area.
Figure 6.17. SEM – SE images of borides sludge collected from the bottom of crucible after the completion of experiment at 750°C (a) natural stirring, (b) mechanical stirring and (c) gas stirring
In the current situation, a consistent solid layer will not form immediately with the nucleation of VB$_2$ around AlB$_{12}$ particles. The thickness of layer will increase with extended holding time. The analysis of SEM images also suggested that VB$_2$ layer was not consistent in the early stage of reaction and VB$_2$ clusters were present around AlB$_{12}$. Although, few AlB$_{12}$ particles have VB$_2$ rings after gas purging that most likely formed during solidification of alloy. Borides have a tendency to cluster that leads to the formation of broken ring during the solidification of boride sludge.

It was concluded from the results of gas purging that the rate of V removal enhanced. The possible reasons include the increase in mass transfer of species, floatation of VB$_2$ and the breaking of product layer. The requirement of external force to break borides agglomerates was also reported by (Vainik et al., 2006) This also suggested that the flow patterns in the molten alloy are important to enhance the kinetics of process. The induction and mechanical stirring generates smooth flow patterns in the melt that cannot break the VB$_2$ rings generated during the process. Gas purging generates uneven flow patterns and facilitate the floatation of VB$_2$, hence do not provide opportunity for the formation of a consistent solid layer around AlB$_{12}$ particles.

This raised an important implication in industrial practice. It may be useful to combine the boron treatment with other refining processes that involve gas purging. For example, it may be beneficial to combine the boron treatment with sodium removal through gas/salt injection.

### 6.7 Effect of AlB$_{12}$ and AlB$_2$ for V removal

It has been shown in literature that Al-B master alloys have AlB$_{12}$ and AlB$_2$ intermetallics present based on the processing parameters. The kinetics of V removal was investigated using Al-B (AlB$_{12}$) because mostly industry is using this master alloy. It was reported that Al-B (AlB$_2$) master alloy should be used for shorter reaction time (Karabay and Uzman, 2005a) (Setzer and Boone, 1991). Experiments were conducted using Al-10wt% B (AlB$_{12}$) and Al-5wt% B (AlB$_2$) to investigate their relative effect on the removal of V from Al-1wt% V-0.72wt% B alloy at 750°C. The plots of V removal with reaction time for both master alloys are shown in Figure.
It could be observed that the rate of reaction is faster in the case of AlB$_2$ phase compared to AlB$_{12}$. The possible reason is the availability of higher surface area for reaction with AlB$_2$ particles in Al-B master alloys.

The morphology of AlB$_{12}$ and AlB$_2$ particles in Al-10wt% B and Al-5wt% B master alloy are shown in Figures 6.19(a) and 6.19(b). Both phases are present in clusters but having different morphology. The AlB$_{12}$ particles have larger particle size compared to AlB$_{12}$ and are also irregular in shape. On the other hand, AlB$_2$ particles are elongated with higher aspect ratio as shown in Figure 6.19(b).

![Figure 6.18. Kinetics plots of V removal in the case of AlB$_{12}$ and AlB$_2$ addition in Al-1wt% V alloy at 750°C (with 5.01% error bar shown in Appendix F)](image)

The large surface area associated with AlB$_2$ particles enhances the reaction kinetics that was found experimentally. This will allow larger proportion of boron in contact with V to form VB$_2$ hence the kinetic of process will be enhanced. However, the settling velocity of smaller and elongated AlB$_2$ particles will be slower compared with larger and irregular AlB$_{12}$ particles during the boron treatment of molten alloy.

It was suggested from the comparison of AlB$_{12}$ and AlB$_2$ that the kinetics of process was faster when Al-B (AlB$_2$) based master alloys are used. The rate of reaction will be faster but the settling of borides will take longer time due to slower settling...
velocity. Therefore, AlB$_2$ based master alloys may be used for faster reaction (reaction in launders) and AlB$_{12}$ for longer processing time (e.g. holding furnaces).

Figure 6.19. SEM –SE images of Al-B master alloys (a) Al-10wt% B (AlB$_{12}$) and (b) Al-5wt% B (AlB$_2$)

6.8 Mechanism of VB$_2$ formation in molten aluminium

The mechanism of VB$_2$ formation is complex due to a series of events taking place in molten aluminium. Figure 6.20 show schematically the mechanisms of VB$_2$ formation and V removal from molten aluminium. The followings explain in more details of each step;
Formation of solid layer of aluminium

When Al-B (AlB$_{12}$/AlB$_2$) master alloys are introduced into molten aluminium, a frozen shell of aluminium (originated from the melt) is formed due to quenching effect (steps a and b in Figure 6.20).

Figure 6.20. Schematic representation of action mechanism of B with V and the formation of VB$_2$ in molten aluminium
The melting of the shell depends on the thermal conduction of solid layer and the heat transfer within the Al-B master alloy. The shell formation period depends on the radius ($R$) of Al-B alloy pieces (proportional to $R^3$) and is inversely proportional to thermal diffusivity ($\alpha$) of solid aluminium (Engh, 1992). It has been estimated that it takes approximately 20 seconds for the formation and melting of solid aluminium layer.

**Melting of boron saturated Al and dissolution of AlB$_{12}$**

After the melting of solid shell aluminium constituent of Al-B alloys pieces and, AlB$_{12}$ particles are released into the melt. The dissolution reaction can be written as in Eq. (6.13).

$$AI - B(AlB_{12}) \rightarrow AlB_{12(s)} + Al_{(l)}$$  \hspace{1cm} (6.13)

It should be noted that the Al constituents from Al-B alloy pieces will be saturated with boron. Once the B-saturated aluminium melts, the dissolution of AlB$_{12}$/AlB$_2$ will then follow immediately and this will depend on the concentration gradient, diffusion coefficient ($D_B$) and solubility of B (0.022 wt%) in the molten aluminium. The dissolution of AlB$_{12}$ and the releasing of boron into molten aluminium can be written as Eq. (6.14).

$$AlB_{12(s)} \rightarrow Al_{(l)} + 12[B]$$  \hspace{1cm} (6.14)

**Mass transfer of V and its reaction with boron**

The boron in aluminium or in the vicinity of AlB$_{12}$ particle reacted to form VB$_2$ according to Equations (6.1) and (6.2). The mass transfer of V will take place to the interface of AlB$_{12}$ within 10 minutes of reaction as shown in Figure 2.20(c). The chemical reaction at the interface of AlB$_{12}$ take place and nuclei of VB$_2$ are formed. In the early stage of reaction, mass transfer of both V and B will take place in and outside of VB$_2$ layer due to the existence of some least resistant paths.

**Thickening of VB$_2$ layer**

The second stage of reaction is represented by Figures 6.20(e) and 6.20(f). During the second stage of reaction, the VB$_2$ layer will grow inside or outside depending on the direction of diffusing species. The VB$_2$ layer will grow outside if B will diffuse
out to complete chemical reaction at the outer boundary of the ring. If V diffuses inside the VB$_2$ layer, the ring will grow inside. According to the Fick’s law, the flux depends on diffusion coefficient, concentration gradient and diffusion barrier (thickness of VB$_2$ layer). It is most likely that the diffusion of B will take place across the VB$_2$ layer due to smaller atomic radii and higher concentration gradient (~ 22.0 wt %) across ring. With the extended holding of melt, least resistant paths will be closed by newly formed VB$_2$ nuclei. Gradually, the thickness of VB$_2$ layer will increase that represents the second stage of reaction.

For the explanation of possible mechanism of VB$_2$ formation, a plot of V removal from Al-1wt% V-0.412wt% B alloy at 750°C is shown in Figure 6.21. From the proceeding section, following controlling mechanisms were identified for the formation of VB$_2$ and the of V removal from molten Al-1wt% V-0.412wt% B alloy:

Figure 6.21. A kinetic plot of V removal from Al-1wt% V-0.412wt% B alloy at 750°C, explaining the mechanism of VB$_2$ formation

**Stage 1:** This early stage of reaction is controlled by the mass transport of V in molten aluminium
Stage 2: The second stage of reaction is controlled by the diffusion of B and V through VB$_2$ layer formed during the early stage of reaction.

During the first stage of reaction, the mass transport of V took place in the molten aluminium alloy to the reaction sites. The region in the vicinity of AlB$_{12}$ will be saturated with B, thus the V will react with B to form VB$_2$ in an area further away from AlB$_{12}$ surface. The SEM image within the first stage of boron treatment process is shown in Figure 6.21. It can be observed that VB$_2$ layer is formed that cover the undissolved AlB$_{12}$ black particles. The higher resolution SEM image revealed that VB$_2$ ring has least resistant paths in the early stage of reaction. First stage of reaction is shown as steps 3 and 4 in Figure 6.20. The SEM images shown in Figures 6.21 (720 minutes) and 5.3(f) also suggested that the VB$_2$ ring grew at the outer periphery during the second stage of reaction. The rate of reaction will gradually decrease due to the increase in the diffusion barrier according to Fick’s first law of diffusion. The growth of the VB$_2$ shell will be halted once AlB$_{12}$ is consumed at the end of reaction.

Second stage is the slowest step during the formation of VB$_2$ in molten aluminium. The diffusion of B through VB$_2$ layer will control the kinetics of reaction. During this stage, the liquid inside VB$_2$ ring will also saturate with B and the dissolution of AlB$_{12}$ will be obstructed. Therefore, the slowest step in the boron treatment is the diffusion of B through VB$_2$ ring that controlled the kinetics of boron treatment.

6.9 Summary

The kinetics analysis of V removal and the formation of VB$_2$ were carried out in this chapter using Al-1wt% V alloy and the addition of Al-10wt% B (AlB$_{12}$) master alloy. From the kinetic plots of V, it was found that the reaction was first order with respect to V in molten aluminium. It was observed that the reaction was fast in the beginning of reaction and obstructed after 10 minutes. The SEM images analyses suggested the formation of VB$_2$ shell in the early stage of reaction. The VB$_2$ layer thickness increased with the passage of time, depleting AlB$_{12}$ and B from the molten alloy. The process of V removal and the formation of VB$_2$ were divided into two stages. It was found that the kinetics of reaction was controlled by the mass transfer of V in the liquid phase during the first stage. The calculated mass transfer
coefficients and activation energy were $2.15 \times 10^{-3}$ m/s and 25.94 kJ/mol respectively at 750°C. The second stage of reaction was analysed using diffusion through product layers models and it was found that the experimental data fit well with the Jander and Ginstling-Brounshtein models.

The effect of stirring on the removal of V suggested that gas stirring was most effective due to the generation of uneven flow patterns in the molten pool of metal. A mechanism of floatation may play an active role in moving VB$_2$ particles away from AlB$_{12}$ thus providing fresh effective interfacial area for chemical reaction. A comparative analysis of AlB$_2$ and AlB$_{12}$ showed that the rate of reaction was faster when AlB$_2$ based Al-B master alloys were used. The possible reason for the faster reaction was the availability of larger interfacial area due to smaller particle size and elongated morphology.
Chapter 7

Analysis of Al-Zr-B and Al-V-Zr-B Alloys

7.1 Introduction

The presence of zirconium (Zr) in solution form reduces the electrical conductivity of aluminium similar to V that has been discussed in Chapter 2. In the solution form, Zr decreases the electrical conductivity of smelter grade aluminium by 35 to 40 times more as compared with borides (ZrB$_2$) (Dean, 1967). Zirconium is also removed from smelter grade aluminium through boron treatment similar to V.

The objective of this chapter is to experimentally analyse the Al-Zr-B and Al-Zr-V-B systems i.e. to evaluate the formation of ZrB$_2$ and VB$_2$, and their relative stability. It was predicted from the thermodynamic analysis of transition metal borides formation in aluminium melt that ZrB$_2$ is more stable than VB$_2$ in the temperature range of 675°C to 900°C. Thus ZrB$_2$ was predicted to form in preference to VB$_2$ at this temperature range (Khaliq et al., 2011a). Experiments were designed based on the thermodynamic predictions explained in Chapter 4. The systems of Al-1wt% Zr-0.23wt% B and Al-0.50wt% Zr-0.50wt% V-0.115wt% B alloys were chosen and analysed. The experimental results were compared with the thermodynamic predictions to establish the preference of ZrB$_2$ formation hence the Zr removal from molten aluminium.

7.2 A brief review of master alloys characteristics

Aluminium master alloys ingots Al-10wt% V, Al-15wt% Zr and Al-4wt% B (AlB$_{12}$) were used to produce the target Al-1wt% Zr-0.23wt% B and Al-0.50wt% Zr-0.50wt% V-0.115wt% B alloys as discussed in Section 3.2.4.1. The analysis of aluminium master alloys chemistry and morphology was important in order to understand the mechanism of the formation of boride phases. It was further emphasized that the dissolution kinetics of the initial Al-borides phases are important from the perspective of boron treatment, and hence the removal of transition metals
such as V, Zr and Ti from molten aluminium. In casthouse, alloying additions are carried out in the form of master alloys rather than their elemental forms. The most important parameters when considering Al master alloys for alloying include the solubility of the alloying element in aluminium, the chemistry and morphology of intermetallics, the size distribution of intermetallics in aluminium matrix, and surface properties. Aluminium master alloys are available in the form of rods, ingots, pigments, waffles and compact briquettes (Totten and MacKenzie, 2003).

The analysis of Al-B master alloys revealed AlB$_{12}$ and AlB$_2$ phases in the aluminium matrix, as described in Section 3.2.3.1. AlB$_{12}$ particles (1 μm to 100 μm) have polygonal morphology and are found in clusters in aluminium matrix. In comparison, AlB$_2$ possess an elongated needle like morphology and high aspect ratio. These particles are also found in clusters in aluminium matrix. The AlB$_2$ particles have approximately 5 μm in diameter and 10 μm to 200 μm in lengths. It has been reported in the literature that AlB$_2$ is more reactive than AlB$_{12}$ in forming transition metal borides but borides formed by reaction with AlB$_2$ take longer time to settle due to their fineness (Setzer and Boone, 1991). The analysis of Al-V master alloy showed two phases in aluminium matrix, as described in Section 3.2.3.2. The EDX analysis of both phases in the Al-V alloy suggested that they are Al$_{10}$V and Al$_3$V, which form at different temperatures during solidification. The analysis of Al-15wt% Zr master alloy revealed Al$_3$Zr phase in the aluminium matrix. The analysis of Al-15wt% Zr master alloy is given in Section 3.2.3.3.

### 7.3 Experimental details

The right compositions of Al-10wt% V, Al-15wt% Zr and pure Al ingots were melted in a boron-nitride-coated graphite-crucible in an induction furnace and held at 750°C for one hour. The target amount of Al-V-Zr-B and Al-Zr-B alloys was 1000 g. Once the mixture was melted, Al-4wt% B (AlB$_{12}$) ingots were added. Samples were then taken at different time intervals and cooled in air within the sampling scope. Scanning electron microscopy (SEM) analysis was carried out on 0, 15, 30, 45 and 60 minute samples for further investigation. The details of the experiments are given in Table 7.1. The Al-Zr-B system was composed of 1wt% Zr and a stoichiometry
addition of boron i.e 0.023 wt%, assuming ZrB₂ formation in the alloy. The targeted system contains 1.23 wt% alloying additions in the molten aluminium.

The second batch of experiments was composed of Al-V-Zr-B system, which contains 0.50wt% Zr and 0.50wt% V in the molten aluminium. The boron was added stoichiometric to Zr only i.e 0.115wt% B, assuming the formation of ZrB₂ borides.

Table 7.1. Experimental plan for Al-Zr-B and Al-V-Zr-B systems

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Level of B addition</th>
<th>Melting practice</th>
<th>Temperature</th>
<th>Sampling (minutes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-Zr-B</td>
<td>0.23wt% B*</td>
<td>Induction</td>
<td>750±10°C</td>
<td>0, 15, 30, 45, 60</td>
</tr>
<tr>
<td>Al-V-Zr-B</td>
<td>0.115wt% B*</td>
<td>Induction</td>
<td>750±10°C</td>
<td>0, 15, 30, 45, 60</td>
</tr>
</tbody>
</table>

*Boron was added stoichiometry to Zr amount (assuming ZrB₂ formation)

It was hypothesised that Zr will react with boron in preference to V and will form ZrB₂ in the molten alloy. The V would remain in solution or intermetallic form in molten aluminium and would not form VB₂ borides because boron will be tied up with Zr in Al-0.50wt% Zr-0.50wt% V-0.115wt% B alloy.

7.4 Analysis of Al-Zr-B system

Al-Zr-B system was analysed as a part of understanding the removal of transition metal impurities from aluminium melt in the form of their borides. From the thermodynamic analysis of Al-Zr-B system, it was predicted that ZrB₂ are more stable compared to AlB₁₂/AlB₂ in the temperature range of 675°C to 900°C. It was further suggested that ZrB₂ will form in preference to any other borides and hence can be removed from aluminium melt by the addition of boron-bearing substance (Khaliq et al., 2011a, Khaliq et al., 2011b). Samples taken at different time intervals were prepared for optical and scanning electron microscopy (SEM) analysis. Qualitative compositional analysis of Al-1wt% Zr-0.23wt% B samples were carried using SEM equipped with EDX detector. The optical microscopy image of 0 minute sample is shown in Figure 7.1.

It can be seen in Figure 7.1 that a reaction has taken place at early minutes at the interface of solid Al-boride, which produced a reaction product. Black particles are
encapsulated by the reaction product layer, as shown in the 0 minute sample. It further reveals that the reaction was fast, because the ring was formed immediately after the addition of the Al-B master alloy to the molten aluminium. The needle-like features in the aluminium matrix are most likely a eutectic of Al, Fe and Si alloy shown in Figure 7.1. The possible reactions of the formation of ZrB$_2$ are given in Eq. (7.1) to (7.3).

$$\text{AlB}_{12(s)} + [\text{Zr}]_{(l)} \rightarrow \text{Al}_{(l)} + \text{ZrB}_{2(s)} \quad (7.1)$$

$$2[B]_{(l)} + [\text{Zr}]_{(l)} \rightarrow \text{ZrB}_{2(s)} \quad (7.2)$$

$$2[B]_{(s)} + \text{Al}_z\text{Zr}_{(s)} \rightarrow \text{ZrB}_{2(s)} + 3\text{Al}_{(l)} \quad (7.3)$$

![Figure 7.1](image)

**Figure 7.1.** An optical microscopy image of polished Al-1wt% Zr-0.23wt% B alloy taken at 0 minute showing Al-borides and (Al,Zr) borides.

The reaction given in Equation (7.3) is unlikely to take place, as Al$_3$Zr is mostly formed during solidification of the Al-Zr alloy. The reactions given in Eq. (7.1) and (7.2) are more likely to occur. The boron will prefer to combine with Zr rather than Al$_3$Zr intermetallic to form ZrB$_2$ in the molten alloy. Boron in solution with Al melt or solid AlB$_{12}$ will react with Zr in solution in the locality of Al-AlB$_{12}$ and form a boride ring. The SEM images of Al-1wt% Zr-0.23wt% B at longer time intervals are shown in Figure 7.2. It can be seen from Figure 7.2 that similar characteristic boride rings are formed in all samples. The presence of a reaction product in the 0 minute sample (sample taken just after the addition of Al-B master alloy into Al melt), as
shown in Figure 7.2 (a) indicates that the initial reaction between the solid Al-boride particles with solute Zr was immediate and readily generated a solid layer of reaction product. This gives an indication of fast reaction kinetics between these reacting species (B and Zr).

Figure 7.2. SEM-SE images of Al-1wt% Zr-0.23wt% B alloy taken at (a) 0 minute (b) 15 minutes (c) 30 minutes (d) 45 minutes and (e) 60 minutes after the addition of Al-4wt% B (AlB₁₂) master alloy and held at 750°C

Moreover, it can be observed from the SEM images of other samples (15, 30, 45 and 60 minutes) as shown in Figures 7.2 (b), 7.2 (c), 7.2 (d) and 7.2 (e) that the thickness of the reaction product was not affected much during the holding melt time up to 60
minutes in the induction stirring. Another common characteristic of all the samples is the presence of undissolved black particles covered by the solid product layer. The phenomenon of ring formation and undissolved black phase is similar to that observed in the Al-V-B system discussed in Chapter 5 and 6. It was observed that ZrB$_2$ ring contains platelike and less dense as compared to equiaxed and uniform particles in the rings of Al-V-B system. An Al$_3$Zr intermetallic phase was also observed in the sample. Since the boron reacted incompletely, there would also have been Zr remaining in the liquid that will precipitates as Al$_3$Zr (shown as a fine needle like particles in Figure 7.1).

The EDX analysis and elemental mapping of the characteristic boride ring is given in Figure 7.3. The EDX analysis showed that Zr and B are present in the aluminium alloy. Light elements (low atomic number) such as boron are difficult to detect accurately due to the detector limitations. The x-ray peaks of boron were observed at 0.188 keV accelerating voltage, which pulls up electrons from the K-shell. The quantitative detection of light elements is beyond the detector limits, and do not show the presence of boron in the quantitative analysis mode. In this particular case, the existence of boron was endorsed by the presence of a small peak at the start of the EDX spectrum, as shown in Figure 7.3 (b). The quantitative analysis of boron was carried out by comparing the number of counts of different elements in the EDX spectrum. Elements with higher atomic numbers such as Zr, Al can be easily detected and quantified by the EDX detector used in the current investigation.

The energy dispersive x-ray spectrum (EDX) shows the peaks of Zr at 2.04 keV accelerating voltages, which represents the jumping of electrons from energy levels of Lα shell. As the alloy is mainly aluminium (< 98.5 wt%), the dominating peaks in the EDX spectrum belong to aluminium. Aluminium is a light metal and far away from heavy metals such as Zr, Ti and V, which require an accelerating voltage of 1.56 keV to release electrons from the K-shell (Kα and Kβ at 1.49 and 1.55 keV respectively), as shown in Figure 7.3 (b). Peaks of O at 0.54 keV is due to the presence of oxygen in Al-1wt% Zr-0.23wt% B samples. Oxygen was from starting materials (pure aluminium and Al-master alloys) or pick up from the melting environment.
Figure 7.3. EDX analysis and element mapping of Al-1wt% Zr-0.23wt% B alloy taken at 0 minute and held at 750°C; (a) SEM image (b) EDX spectrum (c) Zr map (d) B map and (e) Al map

Elements mapping obtained through EDX analysis is shown in Figures 7.3 (c), 7.3 (d) and 7.3 (e). It can be observed from Figure 7.2 (c) that Zr is mostly present in the ring encapsulating the AlB₁₂ phase in the aluminium matrix. It can be proposed that Zr from the bulk metal has been transported to the surface of Al-boride particles during the melt holding and reacted with B from the Al-boride particles. This was also supported by the presence of B in the ring area as shown in Figure 7.3 (d). The
centre of the characteristic boride rings contains un-dissolved Al-boride particles as shown in Figure 7.2 and also Figure 7.3 (d). Aluminium is present in the matrix except for the boride rings and interior black phase (AlB₂), as shown in Figure 7.3(e).

The EDX point analysis of the 60 minute sample (Al-1wt% Zr-0.23wt% B alloy) was also obtained. The locations of the EDX point analyses, on the boride ring and internal black phase of Al-boride are shown in Figure 7.4. Quantitative composition of point 1 (boride ring) and point 2 (Al-boride) are given in the Table 7.2. According to boride ring analysis, Al and Zr are the main elements having an atomic ratio of 1.49 (Al to Zr). Boron was detected in the elements spectrum but was quantified separately due to detector limitation, as described earlier in this section. It was calculated from the counts of boron peak that ZrB₂ ring contains 5.08 at% boron that is given in Table 7.2. The black phase was composed of Al and B, as shown in the EDX spectrum 7.4 (c). The composition of black phase showed that it contains 89.31 at% Al and 10.69 at% B suggesting undissolved original AlB₁₂. It has been confirmed from SEM, EDX and point analysis of different phases that a reaction took place between the Zr and B in molten aluminium. Boron is present in the solution as well as in the solid phases (AlB₁₂/AlB₂).

The Al-B master alloy phases could not be confirmed by EDX analysis, because it only gives the qualitative analysis of possible elements. Crystal structure information should be required to confirm the presence of ZrB₂, AlB₁₂ or AlB₂ in Al-1wt% Zr-0.23wt% B alloys. According to thermodynamic investigation given in Chapter 4, ZrB₂ will be the stable phase in the given working conditions (750°C). It could be suggested that the ring of product layer around Al-boride particles is composed of ZrB₂ borides. The detection of aluminium in the ring could be due to the possibility of the formation of (Al, Zr) boride solid solution. Detailed discussion of transition borides solid solutions was given in Section 2.7.1.
Refractory borides have been reported as pure compounds as well as a solid solution by different investigators. Higashi et al. (1976) reported the solubility of aluminium in various borides while growing their single crystals from aluminium melt at 1300°C to 1500°C. They reported maximum solubility of 0.1 wt% aluminium in refractory borides (TiB₂, ZrB₂, HfB₂, VB, V₃B₄, NbB₂, TaB and W₂B₅) (Higashi et al., 1976). The presence of aluminium in the ZrB₂ ring is in agreement with the findings of Higashi et al. however the measured concentration of aluminium in the product layer was found to be higher i.e 38.06 at% as given Table 7.2.

Table 7.2. EDX analysis of boride ring and internal black phase at locations shown in Figure 7.4 (a)
From the perspective of Zr impurities removal from Al melt, the Al-B master alloy could be used. Experimental findings are in agreement with thermodynamic predictions that ZrB$_2$ borides are more stable as compared with Al-borides at the working temperature of 750°C. Zirconium impurity will combine with boron present in the solution or Al-borides (AlB$_2$/AlB$_{12}$) to form their stable borides (ZrB$_2$), which are heavy and will settle at the bottom of furnace. It is worth noting that the undissolved AlB$_{12}$/AlB$_2$ particles in the ZrB$_2$ ring suggested that the reaction was incomplete and far away from equilibrium. From the perspective of overall kinetics of Zr removal, the dissolution of AlB$_{12}$/AlB$_2$ within the ring will be crucial. When the Al within the ring is saturated with B, no further AlB$_{12}$/AlB$_2$ dissolution can occur. Therefore, product layer suppresses the dissolution of AlB$_{12}$/AlB$_2$. A boride ring can also obstruct further reaction by limiting the access of solute Zr to the reaction surface of AlB$_{12}$/AlB$_2$. It can be concluded that ZrB$_2$ borides are more stable compared to AlB$_{12}$/AlB$_2$ because it dissociates Al-borides and also combine with boron to form ZrB$_2$. It can be summarized from the analysis of Al-1wt% Zr-0.23wt% B alloy that Zr forms stable ZrB$_2$ and can be removed from aluminium melt during boron treatment.

### 7.5 Analysis of Al-V-Zr-B system

The experimental investigation on the Al-V-Zr-B system was also carried out and the results analyses are given in this section. It was predicted from the thermodynamic investigation of transition metals (V, Zr, Ti and Cr) in aluminium melt that ZrB$_2$ will be more stable and form in preference to V, Ti and Cr borides in aluminium melt in the temperature range of 675°C to 900°C (Khaliq et al., 2011a). This may imply that during boron treatment of aluminium melt containing Zr, V, Ti and Cr impurities, the Zr will be removed in the form of their borides before the removal of any other impurities such as V, Ti and Cr. The detailed discussion of transition metal impurity analysis in aluminium melt is given in Chapter 4.

By considering the thermodynamic predictions, an alloy of Al-V-Zr-B was prepared, which was composed of 0.50wt% of both V and Zr. The boron was added to the
stoichiometry requirement of Zr only, assuming ZrB$_2$ formation in the given conditions (750 ± 10°C). The rationales behind selecting the composition were to observe reactions and to evaluate whether ZrB$_2$ forms in preference of VB$_2$ in molten aluminium. Air-cooled samples from the experiments were sectioned and the lower part of each (0, 15, 30, 45 and 60 minutes) sample was prepared for subsequent optical, SEM and EDX analysis.

A typical optical micrograph of Al-0.50wt% V-0.50wt% Zr-0.115wt% B alloy held at 750°C and taken after 30 minutes is shown in Figure 7.5. The black phase was observed in a wide range of particle size, which was detected as individual as well as in clusters with other needle-like phases. Other phases are elongated polygonal, having particles size from 1 μm to 100 μm and are also needle-like, as shown in Figure 7.5.

![Figure 7.5. An optical microscopy image of Al-0.5wt% Zr-0.50wt% V-0.115wt% B alloy held at 750°C and taken at 30 minutes](image)

The reactions were similar to that given in Equations (7.1), (7.2) and (7.3) and can take place at the possible interface of solid AlB$_{12}$ and Zr/Al$_3$Zr in the molten alloy. The alloy under investigation also contains V, which may react with B or AlB$_{12}$ to form their borides. Assuming VB$_2$ formation, the following reactions could take
place depending upon the kinetics of VB$_2$ formation and AlB$_{12}$ dissolution in the molten alloy.

$$AlB_{2(s)} + [V]_{(t)} \rightarrow Al_{(t)} + VB_{2(s)} \quad (7.4)$$

$$2[B]_{(t)} + [V']_{(t)} \rightarrow VB_{2(s)} \quad (7.5)$$

$$2[B]_{(s)} + Al_{10}V_{(s)} \rightarrow VB_{2(s)} + 3Al_{(s)} \quad (7.6)$$

Reactions given in Eq. (7.5) would be favourable but others would depend upon the dissolution of AlB$_{12}$ and Al$_{10}$V in the melt. It was further suggested that a boride ring may slow down further reactions.

Thermodynamic investigations predicted the formation of ZrB$_2$ in the Al-0.50wt% V-0.50wt% Zr-0.115wt% B alloy and no VB$_2$ was predicted to form (Khaliq et al., 2011b). Scanning electron microscopy (SEM) analysis was carried out to detect the possible phases formed and the reaction behaviour of the ZrB$_2$ formation in the Al-0.50wt% V-0.50wt% Zr-0.115wt% B alloy. The SEM-SE images of 0, 15, 30, 45 and 60 minutes samples and the EDX analysis are shown in Figure 7.6. It can be observed from Figure 7.6 (a) that a reaction has taken place at the interface of the black Al-B (AlB$_{12}$) phase at the early minutes of reaction. At extended reaction times (beyond 15 minutes), the boride ring encapsulating the original AlB$_{12}$ was still observed, as shown in Figure 7.6 (b) to 7.6 (e). This phenomenon is similar to that observed in the Al-Zr-B and Al-V-B systems as described in previous sections.

During melting and holding of an alloy at 750°C in the induction currents, Al$_3$Zr particles from the Al-15wt% Zr master alloy will dissolve leaving Zr in solution with aluminium, which will be available to react with boron and form ZrB$_2$. The solubility of Zr decreases with temperature and it appears that in the vicinity of the ZrB$_2$ ring, Al$_3$Zr in the form of needle was precipitated as shown in Figures 7.6 (b) to 7.6 (e). One would expect that the area in the vicinity of the ring will be rich in Zr which facilitates the Al$_3$Zr precipitation upon solidification. The morphology of this Al$_3$Zr is quite different compared to Al$_3$Zr observed in the original master alloy that is shown in Figure 3.6(a). Polygonal particles were also observed, which are different from those phases observed in either of Al-10wt% V or Al-15wt% Zr master alloys given in sections 3.2.3.2 and 3.2.3.3. This could be an intermetallic product of Al, Zr
and V which are elongated but thicker in diameter than Al$_3$Zr particles. These intermetallics varied from 10 µm to 30 µm in diameter and have faceted equiaxed morphology. A eutectic of Al, Si and Fe in the form of a needle-like (thinner than Al$_3$Zr) and also rounded shapes phase were observed, as shown in Figure 7.6 (c) and 7.6 (e). Such phases were generated as a consequence of Fe and Si impurities in the starting materials used for the making of alloys.

Figure 7.6. SEM-SE images of Al-0.50wt% V-0.50wt% V-0.115wt% B alloy held at 750°C and taken at (a) 0 minute (b) 15 minutes (c) 30 minutes (d) 45 minutes, (e) 60 minutes and (f) EDX analysis
The energy dispersive x-ray spectrum (EDX) analyses confirmed the presence of Zr, V and B in the aluminium matrix, as shown in Figure 7.6 (f). Due to the boron deficit in the Al-Zr-V-B system, ZrB\(_2\) will form in preference to VB\(_2\) due to the much lower Gibbs free energy of formation (Khaliq et al., 2011b).

Figure 7.7. (a) SEM-SE image, EDX analysis of (b) undissolved AlB\(_{12}\) and (c) ZrB\(_2\) ring in Al-0.50wt% Zr-0.50wt% V-0.115wt% B alloy
The chemical composition obtained through EDX analysis of different points is given in Table 7.3. Due to the limits of the EDX detector used in this current study, boron was not quantified, although its strong peaks were observed in spectrums of black phase marked as point 1 in Figure 7.7 (a). The quantification of boron was carried out separately based on the number of counts in its peak as described in Section 7.4. The number of counts of the boron peak, as compared with aluminium, suggested that the black phase was AlB$_{12}$ rather than AlB$_2$. Moreover, quantitative composition showed that 84.05 at% Al and 15.95 at% B was present in the black phase. The spectra from point 2 detected Al, Zr and V in the aluminium matrix that may be their intermetallic.

Table 7.3. Point analysis of Al-Zr-V-B alloy obtained by EDX

<table>
<thead>
<tr>
<th>Points</th>
<th>Elements (at %)</th>
<th>Al</th>
<th>Zr</th>
<th>V</th>
<th>B</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td>84.05</td>
<td>Nil</td>
<td>Nil</td>
<td>15.95</td>
<td>Nil</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>78.7</td>
<td>6</td>
<td>4.6</td>
<td>Nil</td>
<td>10</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>88.63</td>
<td>6.78</td>
<td>2.77</td>
<td>Nil</td>
<td>1.82</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>39.3</td>
<td>49.30</td>
<td>2.21</td>
<td>7.21</td>
<td>1.97</td>
</tr>
</tbody>
</table>

The large polygonal particles observed were predominantly composed of Al, Zr and V, showing a limited presence of O (point 3). Strong peaks of Zr were observed with aluminium but B and V peaks were weak, suggesting their limited presence at the reaction interface as marked point 4 in Figure 7.7 (a). Oxygen was also detected during point analysis, which may suggest the presence of solute oxygen in the aluminium matrix.

Elemental mapping of the reaction interface and the aluminium matrix was obtained through the EDX analysis of Al-0.50wt% V-0.50wt% Zr-0.115wt% B alloy, given in Figures 7.8 (a), 7.8 (b), 7.8 (c), 7.8 (d), 7.8 (e) and 7.8 (f). It can be observed from Figure 7.8(c) that O is uniformly distributed throughout in the aluminium matrix, except in the locality of black phase. The black area belongs to boron as shown in Figure 7.8 (b) Silicon was also present in the small particles in the aluminium matrix, as shown in Figure 7.8 (d). Silicon impurities most likely came from the starting
materials. The maps of V showed their uniform distribution throughout the aluminium matrix, except for the slightly higher concentration in the product ring encapsulating AlB_{12} black phase, as shown in Figure 7.8 (e). Similarly, Zr was also uniformly distributed in the aluminium matrix but a reasonably higher concentration was found in the boride rings, as shown in Figure 7.8 (f). This higher concentration of Zr in the product ring is consistent with the thermodynamic analysis where it was predicted that Zr would react with B in preference to V to form ZrB_{2} borides.

Figure 7.8. Elemental mapping of Al-0.50wt% V-0.50wt% Zr-0.23wt% B alloy sample taken at 15 minutes and held at 750°C (a) SEM –SE image (b) Al maps (c) O maps (d) Si maps (e) V maps and (f) Zr maps

The alloy under investigation has similar contents of both Zr and V (0.50 wt% each) but the chemistry of the product ring suggested a higher concentration of Zr as compared with V. Moreover, the product ring also contained B in the same vicinity
of Zr, suggesting the formation of a main phase of Zr-boride (ZrB$_2$). The presence of Al and V in the product ring proposed the formation of solid solution with ZrB$_2$, which could be verified by the crystallographic investigation of phases in the ring. The electron back-scattered diffraction (EBSD), together with EDX, was used to exclusively identify the phases in the Al-Zr-V-B system. A boride ring and the faceted intermetallic of an Al-V-Zr phase were identified and are given in Figure 7.9.

![Figure 7.9](image)

Figure 7.9. (a) SEM-BS image of Al-0.50 wt% V-0.50wt% Zr-0.115wt% B alloy taken after 60 minutes, (b) EDX analysis of faceted Al,V,Zr phase, (c) EBSD pattern indexed according to ZrB$_2$ and (d) Raw EBSD pattern of Al-Zr-V intermetallic phases.

The EDX analysis of the boride ring showed a near composition ratio of 39.3: 49.3:2.21: 7.21 (at%) between Al, Zr, V and B which suggested a solid solution of borides (Al$_{39}$Zr$_{49}$V$_3$B$_8$). The diffracted parallel lines pattern of the boride ring obtained from EBSD analysis was indexed according to the ZrB$_2$ crystal structure.
(AlB$_2$ type, $a = 0.31694$ nm, $c = 0.35307$ nm and hP3 Pearson’s symbol), as shown in Figure 7.9 (c) (Villars, 1997). It could be suggested from EBSD analysis that boride rings are mainly composed of ZrB$_2$ and do not make a solid solution with other borides (AlB$_2$ or VB$_2$). The presence of Al and V detected by EDX could be attributed from the base metal, not from ZrB$_2$. A well-defined pattern of lines was also obtained for the Al-Zr-V phase, which suggests a certain crystal structure. This intermetallic could not be indexed due to the lack of information available for the Al-Zr and V phases in the used database. The EDX analysis showed a near composition ratio of 90.50: 8.57: 0.92 (at %) between Al, V and Zr, as shown in Figure 7.9 (b), suggesting an intermetallic with the following possible formula Al$_{90}$V$_9$Zr$_1$. From EBSD and EDX analyses, it could be concluded that boride ring is mainly composed of ZrB$_2$ and may contain small proportion of Al making solid (Al, Zr)B$_2$ solid solution. However, from this analysis it could not be established whether ZrB$_2$ and AlB$_2$ are making solid solution in the ring.

7.6 Summary

The results from the present investigation indicated that the formation of initial borides ZrB$_2$ were very fast. The reaction occurred within the early minutes after the addition of the Al-B master alloy in the molten alloy. The transition metal boride phases were formed in the vicinity of Al-AlB$_{12}$ interface, which is the region where the initial solute flux of dissolving boron in the melt reacts with V and/or Zr. If a continuous ring formed then this would obstruct the easy diffusion within the liquid and would require diffusion of reacting species through the diborides (VB$_2$ or ZrB$_2$), leading to slow thickening of the di-boride ring. There is a little evidence of thickening of the ring with holding time up to 60 minutes, and so it may be that the dominant path for reacting elements is through gaps in the shell. Such gaps would not necessarily be observed in the polished sections. In any case, the reactions appear to be incomplete. This was possibly exacerbated by the relatively high concentrations chosen for the elements under study, as these were in some cases above the binary solubility limits.
Thermodynamic modelling predicted that boron can effectively remove Zr and V from aluminium melt in the form of solid borides. It is worth emphasising that this analysis was based purely on the thermodynamic considerations and did not incorporate the kinetic factors. Experimental results showed that, in all the systems under study, the transition metal borides formed rapidly as a ring around the AlB$_{12}$ particles that were the principal source of boron in the alloy. Substantial AlB$_{12}$ remained in the microstructure, even after one hour at 750°C, indicating that the systems were far from reaching the predicted equilibrium. It was likely that the boride largely or completely enclosed the remaining AlB$_{12}$ heavily suppressing reaction to completion.

It could be concluded from this analysis that,

- The systems Al-Zr-B and Al-Zr-V-B behave similarly to Al-V-B. The formation of boride ring and undissolved AlB$_{12}$ were the main features of these systems.
- The boride ring in these systems was less dense and composed of platelike particles as compared to equiaxed and uniform layer in Al-V-B system. Moreover, gap between particles in the ring was more in these alloys as compared with Al-V-B system.
- Experimental results suggested that ZrB$_2$ forms in preference to VB$_2$ in Al-Zr-V-B system. Although, ZrB$_2$ was the main phase in the ring, EDX results suggest the presence of small amount of Al and V. This suggested the formation of ZrB$_2$ with limited solubility of Al and V.
- The excess amount of Zr precipitates as Al$_3$Zr in the vicinity of AlB$_{12}$ upon solidification and has platelike morphology that is different from source Al-Zr master alloy.
- The excess amount of V in Al-Zr-V-B system appears to precipitates as Al-V and Al-V-Zr intermetallics, presumably Al$_3$V/Al$_{10}$V and Al$_{90}$V$_6$Zr$_1$. 
Chapter 8
Analysis of Industrial Boron Treatment Practice

8.1 Introduction
There is no standard procedure in industry for the removal of vanadium and other transition metal impurities from smelter grade aluminium. Electrical grade aluminium manufacturers develop their own in-house processes for the boron treatment of smelter grade aluminium depending on their working capabilities and available facilities. This chapter describes the boron treatment trials carried out at one of the main electrical grade aluminium manufacturers in Australasia. In these smelters, primary aluminium is produced using reduction cell technology and treated in-house for the removal of V and other transition metal impurities. The purpose of the industrial trials was to obtain a better understanding of current boron treatment practice. Furthermore, the proposed recommendations for smelters operators are outlined for the improvement of boron treatment practice. The proposed recommendations should be helpful in improving the quality of the end product and also the economy of the process.

8.2 Current practice of boron treatment
A literature review showed that Al-B master alloys have AlB$_2$ or AlB$_{12}$ phases that are employed in different forms such as rods, waffles, ingots and wires during the boron treatment of molten aluminium. Al-B master alloys are usually produced having 3, 4, 5, 6, 8 and 10wt% boron, depending upon the targeted intermediate phase in the aluminium matrix and process requirements. The analysis of different Al-B master alloys is presented in Section 3.2.3. In the current trials, an Al-8wt%B master alloy, containing AlB$_{12}$ phase, was used during the boron treatment practice. The SEM image of the Al-B master alloy is shown in Figure 8.1. It is shown in Figure 8.1 that AlB$_{12}$ particles are present in the form of clusters having polygonal...
shape. The particle sizes varied from 1 μm to 50 μm and are shown as a black phase in a white aluminium matrix. The Al-B master alloy was used in the form of cast cut ingots having a 40 mm x 30 mm cross section. The cast cut ingots were 1.1 meter long and each weighed 3 kg. The Al-B master alloys were obtained from London and Scandinavian Metallurgical (LSM) Co Limited, UK. In the current practice, boron is added as per the stoichiometric requirement of transition metals (assuming their diborides formation) in the first stage of process. Further additions are made in the middle of the process, based on the level of transition metal impurities and the quality requirement of end product.

Figure 8.1. SEM-SE image of Al-8wt% B (AlB₁₂) master alloy used for the boron treatment of smelter grade aluminium

Boron treatment of smelter grade aluminium is carried out in a 50 tonne furnace whose schematic is shown in Figure 8.2. It is a gas fired furnace with three equally spaced burners fitted on one wall, which supply continuous heat to maintain a temperature of 750±15°C throughout the process. The furnace bath depth is about 2 meters when filled with molten metal. The empty furnace is charged with primary aluminium tapped from reduction cells using 5.0 tonnes crucibles. At the start of the heating process (filling empty furnace), in-house scrap is also charged in the furnace. Currently at these smelters, Al-B master alloys ingots are introduced at the entrance spout of the furnace. Primary molten aluminium is introduced through the spout, which flushes the Al-B master alloy in the furnace during the pouring process, as
shown in Figure 8.2. Most likely, Al-B master alloys will be in the solution with aluminium during the feeding of the second crucible in the furnace. The furnace fills in approximately 120 minutes and, on average, consumes 10-12 crucibles. Once the furnace is filled, stirring of the melt is carried out for 120 seconds with a long paddle using a fork lifter from the back door, as shown in Figure 8.2. The melt is stirred using a paddle attached to a forklift. The paddle was immersed at one side and the stirring was done by moving the paddle back and forth. The melt is then allowed to settle once the dross has been skimmed from the top.

![Figure 8.2. A schematic diagram of gas fired furnace](image)

The experimental detail of both trials is given in Tables 8.1 and 8.2. After stirring and skimming, the melt is held for different periods, depending on the final level of purity required. To achieve a higher level of purity, the melt is held for longer, depending on customer requirements. Prior to casting, the melt composition was analysed again, and more Al-B master alloy was added if required. The Al-B treated melt was held for 613 minutes (10.22 hours), followed by casting, which was completed in 115 minutes (1.92 hours).
8.2.1 Sampling practice

Melt sampling was carried out using a 2.5 m long steel scoop. The molten aluminium samples were cast into standard spectrometer discs and allowed to solidify in air.

Table 8.1. The details of events and sampling during first trial

<table>
<thead>
<tr>
<th>Addition of molten Al</th>
<th>Marking of samples</th>
<th>Time</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crucible 1</td>
<td></td>
<td></td>
<td>30 kg Al-8% B added</td>
</tr>
<tr>
<td>Crucible 2</td>
<td>TS1A17</td>
<td>17</td>
<td>top</td>
</tr>
<tr>
<td></td>
<td>TS1A18</td>
<td>17.5</td>
<td>top</td>
</tr>
<tr>
<td>Crucible 3</td>
<td>TS1A27</td>
<td>27.5</td>
<td>top</td>
</tr>
<tr>
<td></td>
<td>TS1A28</td>
<td>28</td>
<td>bottom</td>
</tr>
<tr>
<td>Crucible 4</td>
<td>TS1A36</td>
<td>36</td>
<td>top</td>
</tr>
<tr>
<td></td>
<td>TS1A37</td>
<td>37</td>
<td>bottom</td>
</tr>
<tr>
<td>Crucible 5</td>
<td>TS1A43</td>
<td>43</td>
<td>top</td>
</tr>
<tr>
<td></td>
<td>TS1A44</td>
<td>44</td>
<td>bottom</td>
</tr>
<tr>
<td></td>
<td>TS1A54</td>
<td>54</td>
<td>top</td>
</tr>
<tr>
<td></td>
<td>TS1A55</td>
<td>55</td>
<td>bottom</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Stirring start</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Stirring end</td>
</tr>
<tr>
<td>Crucible 6</td>
<td>TS1A64</td>
<td>64</td>
<td>top</td>
</tr>
<tr>
<td></td>
<td>TS1A65</td>
<td>65</td>
<td>bottom</td>
</tr>
<tr>
<td>Crucible 7</td>
<td>TS1A72</td>
<td>72</td>
<td>top</td>
</tr>
<tr>
<td></td>
<td>TS1A73</td>
<td>73</td>
<td>bottom</td>
</tr>
<tr>
<td>Crucible 8</td>
<td>TS1A88</td>
<td>88</td>
<td>top</td>
</tr>
<tr>
<td></td>
<td>TS1A89</td>
<td>89</td>
<td>bottom</td>
</tr>
<tr>
<td>Crucible 9</td>
<td>TS1A97</td>
<td>97</td>
<td>top</td>
</tr>
<tr>
<td></td>
<td>TS1A98</td>
<td>98</td>
<td>bottom</td>
</tr>
<tr>
<td>Crucible 10</td>
<td>TS1A120</td>
<td>120</td>
<td>Skimming start</td>
</tr>
<tr>
<td></td>
<td>TS1A121</td>
<td>121</td>
<td>Skimming end</td>
</tr>
<tr>
<td></td>
<td></td>
<td>188</td>
<td>9 kg Al-8% B</td>
</tr>
<tr>
<td></td>
<td></td>
<td>248</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>308</td>
<td>3 kg Al-8% B</td>
</tr>
<tr>
<td></td>
<td></td>
<td>613</td>
<td>Pouring started</td>
</tr>
<tr>
<td></td>
<td></td>
<td>658</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>693</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>728</td>
<td>Cast finished</td>
</tr>
</tbody>
</table>

*TS1A17 – represents testing samples of aluminium from first trial and last digits represents sample timings*
The furnace location from where the samples were taken is shown in Figure 8.2.

Table 8.2. Details of events and sampling during second trial of boron treatment

<table>
<thead>
<tr>
<th>Crucible 1</th>
<th>Cruci...</th>
<th>TS2A9</th>
<th>9.5</th>
<th>Addition of 24 kg Al-8wt% B (AlB$_{12}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>TS2A10</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Crucible 2</td>
<td>TS2A25</td>
<td>17</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>TS2A26</td>
<td>17.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Crucible 3</td>
<td>TS2A38</td>
<td>38</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>TS2A39</td>
<td>39</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Crucible 4</td>
<td>TS2A57</td>
<td>57</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>TS2A58</td>
<td>58</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Crucible 5</td>
<td>TS2A70</td>
<td>70</td>
<td>top</td>
<td>755°C</td>
</tr>
<tr>
<td></td>
<td>TS2A71</td>
<td>71</td>
<td>bottom</td>
<td></td>
</tr>
<tr>
<td>Crucible 6</td>
<td>TS2A74</td>
<td>74</td>
<td>top</td>
<td>759°C</td>
</tr>
<tr>
<td></td>
<td>TS2A75</td>
<td>75</td>
<td>bottom</td>
<td></td>
</tr>
<tr>
<td>Crucible 7</td>
<td>TS2A81</td>
<td>81</td>
<td>top</td>
<td>764°C</td>
</tr>
<tr>
<td></td>
<td>TS2A82</td>
<td>82</td>
<td>bottom</td>
<td></td>
</tr>
<tr>
<td>Crucible 8</td>
<td>TS2A101</td>
<td>101</td>
<td>top</td>
<td></td>
</tr>
<tr>
<td></td>
<td>TS2A102</td>
<td>102</td>
<td>bottom</td>
<td></td>
</tr>
<tr>
<td>Crucible 9</td>
<td>TS2A107</td>
<td>107</td>
<td>top</td>
<td></td>
</tr>
<tr>
<td></td>
<td>TS2A108</td>
<td>108</td>
<td>bottom</td>
<td></td>
</tr>
<tr>
<td>Crucible 10</td>
<td>TS2A115</td>
<td>115</td>
<td>top</td>
<td></td>
</tr>
<tr>
<td></td>
<td>TS2A116</td>
<td>116</td>
<td>bottom</td>
<td></td>
</tr>
<tr>
<td>Crucible 11</td>
<td>TS2A122</td>
<td>122</td>
<td>top</td>
<td>739°C</td>
</tr>
<tr>
<td></td>
<td>TS2A123</td>
<td>123</td>
<td>bottom</td>
<td></td>
</tr>
<tr>
<td>Crucible 12</td>
<td>TS2A203</td>
<td>203</td>
<td>top</td>
<td></td>
</tr>
<tr>
<td></td>
<td>TS2A204</td>
<td>204</td>
<td>bottom</td>
<td></td>
</tr>
<tr>
<td></td>
<td>TS2A245</td>
<td>245</td>
<td>top</td>
<td>Skimming start</td>
</tr>
<tr>
<td></td>
<td>TS2A246</td>
<td>246</td>
<td>bottom</td>
<td>Skimming end</td>
</tr>
<tr>
<td></td>
<td>TS2A300</td>
<td>300</td>
<td>top</td>
<td></td>
</tr>
<tr>
<td></td>
<td>TS2A301</td>
<td>301</td>
<td>bottom</td>
<td></td>
</tr>
<tr>
<td></td>
<td>TS2A394</td>
<td>394</td>
<td>top</td>
<td>3 kg (1 stick added)</td>
</tr>
<tr>
<td></td>
<td>TS2A395</td>
<td>395</td>
<td>bottom</td>
<td></td>
</tr>
</tbody>
</table>
Two samples were taken each time, after the addition of each crucible into furnace. One sample was taken from the top and other from the bottom of furnace. The first sample was taken just after the addition of the first crucible (5 tonne). Tables 8.1 and 8.2 show the timings of furnace charging with fresh molten crucibles, sampling practice, stirring and skimming of molten aluminium during boron treatment trials.

8.3 Results

The samples, taken at regular intervals of time during both trials were analysed for the composition and morphology of borides. The chemical composition of the aluminium disc samples were analysed under a high purity module, using the in-house spark emission spectroscopy facility. Selected disc samples from both trials were sectioned and prepared for microscopy (i.e OM, SEM and EDX) analysis. The sample preparation procedure was explained in Section 3.2.4.1. Microscopy analysis was carried out at Swinburne University of Technology, Melbourne. The kinetic results of the transition metal impurities and microscopy analysis are discussed in the following sections.

8.3.1 Kinetics of V removal from smelter grade aluminium

The kinetics of V removal from smelter grade aluminium is shown in Figures 8.3 and 8.4. In this particular case, smelter grade (primary) aluminium contains 80 ppm V, 45 ppm Ti and 4.5 ppm of both Zr and Cr. It was observed that V constitutes 60% of all other transition impurities such as Ti, Zr, V and Cr. The investigation of V removal from molten aluminium was therefore crucial if the quality of electrical grade aluminium is to improve, which is the major focus of this thesis. It has already been discussed in Chapter 2 that the level of V is increasing in the smelter grade aluminium. Various researchers have reported the increase of V in the petroleum coke and its impact on the final properties of aluminium (Vogt et al., 2004, Grandfield and Taylor, 2009, Rhamdhani et al., 2013, Sweet et al., 2013). Many aluminium smelters are facing challenges due to rise of impurities especially V in the petroleum coke (Coney et al., 2013, Lindsay, 2013, Metson et al., 2013).
Keeping in view the increase of V and its high proportion in the smelter grade aluminium, the impurities analysis and the optimisation of boron treatment is important to maintain the quality of electrical grade aluminium alloys.

It can be seen from Figure 8.3 that the concentration of V decreased from 67 ppm to 11 ppm during boron treatment cycle of 740 minutes (12.33 hours). The observed trend of V concentration versus time, as shown in Figure 8.3 and Figure 8.4, is similar to the laboratory results that were discussed in Chapter 6. It is worth noticing that approximately 65% of V reacted during the first 100 minutes, i.e. the early stage of boron treatment process. The concentration of V dropped to 22 ppm at the start of the process when the furnace was filled with primary metal. It was observed during the trials that the stirring of molten metal reduced with the passage of time. The surface turbulence generated due to the addition of fresh molten aluminium decreased as the volume of melt increased in the furnace. The stirring of melt will help homogenise the distribution the solid $\text{AlB}_{12}$ particles and other transition impurities to form their borides. Stirring also increases the mass transfer coefficients of impurities that enhanced the reaction kinetics as was discussed in Chapter 6.

The larger drop in the concentration of V during the furnace filling stage was also due to the fast reaction kinetics between $\text{AlB}_{12}$ and V as explained in Chapters 5 and 6. The chemical reaction kinetics of V and boron was very fast, and produced $\text{VB}_2$ within the first couple of minutes after the addition of Al-B master alloys into the aluminium melt. The kinetics of the V removal from the smelter grade aluminium and the concentration of born in the second trial are shown in Figure 8.4. Similar trends compared to Figure 8.3(first trial) were observed. The second trial was completed in 395 minutes (6.6 hours). It is worth noted that the required purity was achieved with less holding time. The V concentration dropped from 80 ppm to 11 ppm during the course of the melt treatment. Similar to the first trial, approximately 70% of the V was removed in the form of their borides within the first hour of treatment when the furnace was being filled.

It can be seen from Figures 8.3 and 8.4 that the boron concentration was high at the start of process. The sample taken just after the addition of the first crucible into the furnace showed the concentration of 168 ppm boron in the first trial, which is nearly
4 times in excess of the stoichiometric requirements for the formation of transition metal diborides. Initially, the melt was concentrated with boron, due to the addition of the Al-8wt% B (AlB$_{12}$) master alloy at the filling stage of furnace. In the second trial, even more boron was added, compared to the first trial, due to the greater concentration of transition metal impurities initially (134 ppm).

Figure 8.3. The concentration (ppm) of V and B in molten aluminium in first trial

Figure 8.4. The concentration (ppm) of V and B in molten aluminium in second trial
The second trial had 4.65 times excess of boron at the early stage of the process, which was diluted as more and more primary metal was introduced into the furnace. Bearing in mind the initial concentration of transition metal impurities and the total furnace capacity (50 to 55 tonnes), the addition of boron was in the stoichiometric requirement of transition metal impurities to form their stable diborides such as VB$_2$, TiB$_2$, ZrB$_2$ and CrB$_2$.

8.3.2 Kinetics of Ti, Zr and Cr impurities removal from aluminium

Other transition metal impurities such as Ti, Zr and Cr were 33%, 3.5% and 3.5% of the total impurities in the smelter grade aluminium. The removals of Ti, Zr and Cr by the addition of Al-B (AlB$_{12}$) in both trials are shown in Figures 8.5 and 8.6.

![Figure 8.5](image_url)

Figure 8.5. The concentration (ppm) of Ti, Zr and Cr impurities in molten aluminium in the first trial

The changes in the concentration of Zr, Ti and Cr during the first and second trials are shown in Figures 8.5 and 8.6. The drop in the concentration of Ti was similar to V as shown in Figures 8.3 and 8.4. The concentration of Ti decreased from 31 ppm to 2 ppm during the boron treatment process. The decrease in Ti concentration was not as fast as V. Moreover, the concentration of Zr and Cr only experienced a little change during the boron treatment. Further analyses were carried out by comparing the correlations between the transition metals concentration. It was predicted
thermodynamically, that the removal of impurities would be in the order of Zr, Ti, V and Cr in the form of their stable diborides. However, in the industrial trials, it was found that V was removed faster than Ti and the concentration of Zr and Cr not changes much. This behaviour can be understood as the following: (1) – The driving force for the reaction of VB$_2$ formation is much bigger as the concentration of V in Al melt is much higher compared to Ti, and (2) – It is possible the overall kinetics of TiB$_2$ formation slower (i.e kinetically limited) than VB$_2$ in molten aluminium.

Figure 8.6. The concentration (ppm) of Ti, Zr and Cr in molten aluminium in the second trial

The correlations between concentrations of Ti and V after different time intervals during the boron treatment in the first trial were plotted and are given in Figure 8.7. It can be seen from Figure 8.7 that a linear relationship exists between the concentration of Ti and V in the molten aluminium. A linear curve fitting with actual experimental data gives $R^2 = 0.971$, which shows the best-fit scenario. It can be assumed from the experimental results shown in Figure 8.7 that the removal of Ti and V in the form of their borides has a linear relationship during the boron treatment of smelter grade aluminium. The slope of the line in Figure 8.7 is 0.57 which corresponds to a slope of 0.6 in mol% (i.e slope in mol% = slope in ppm x Molecular weight of V divided by Molecular weight of Ti). However, since the slope is lower than 1, it means that the rate of removal of V is higher than that of Ti. It was
predicted using the thermodynamic analysis of Ti, Zr, V and Cr impurities in molten aluminium that TiB$_2$ is more stable than VB$_2$ hence will form preferentially. It was concluded from the thermodynamic predictions that Ti will be removed in preference to V in the form of their stable borides at 750°C (Khaliq et al., 2011a). The experimental results shown in Figure 8.7 contradict these thermodynamic predictions.

Figure 8.7. The relationship between the concentrations Ti and V during first trial

![Graph showing the relationship between Ti and V during first trial](image)

\[ y = -3.289 + 0.5676x \]
\[ R^2 = 0.97059 \]

Figure 8.8. The relationship between the concentration of Ti and V in second trial

![Graph showing the relationship between Ti and V in second trial](image)

\[ y = 0.331 + 0.591x \]
\[ R^2 = 0.97305 \]
The concentrations of Ti and V impurities after different intervals of time during the boron treatment of smelter grade aluminium in the second trial are also shown in Figure 8.8. The results obtained from the second trial are similar to first and also show a linear relationship between the removal of Ti and V from molten aluminium. The slope of the curve is 0.591 which correspond to a slope of 0.63 in mol%. This also suggest that both Ti and V reacted simultaneously to form their borides but with faster removal for V.

The concentrations of V and Ti were also plotted versus B, and are shown in Figures 8.9 and 8.10. A linear relationship between transition metal impurities V, Ti and boron were observed. The scatter in the data at the beginning of the process represents the different results from samples obtained from the top and bottom of the furnace. An intercept of 15.96 suggested that the remaining amount (ppm) of V was in solution with the aluminium, although the residual level of boron was zero at this stage. This suggests that a high level of boron will be required for a 100% removal of V from molten aluminium. Similar trends were observed for Ti and are shown in Figure 8.10. Such a linear relationship gives $R^2 = 0.725$ that is much less than V and B values given in Figure 8.9.

![Figure 8.9. The relationship between V and B in molten aluminium in second trial](image)

$$R^2 = 0.833$$

Second trial

$$y = 15.96 + 0.23x$$
The concentrations of Zr and Cr were also analysed and are presented in Figure 8.11. The residual concentrations of Zr and Cr were much lower but within the limits of electrical grade conductor aluminium. A linear relationship was observed between both impurities, as shown by the straight line in Figure 8.11. These impurities are
also within the solubility limits of aluminium and were unaffected by the boron treatment.

The concentrations of Fe, V and B in the first trial were also plotted and are given Figure 8.12. It can be observed from Figure 8.12 that the concentration of V and B has decreased during the boron treatment of molten aluminium as discussed earlier in Section 8.3.1. The concentration of Fe decreased initially and then increased and remained unchanged when the melt was held for longer time. Non-reactive impurities in aluminium such as Fe and Ni are a great challenge to researchers (Poirier, 1994, Grandfield and Taylor, 2009, Dewan et al., 2011, Rhamdhani et al., 2013). Removal of Fe from molten aluminium was investigated recently by Gao et al. (2009). It was reported that the minimum level of Fe that could be achieved using boron additives in molten aluminium was 11.9 wt%. This Fe content is much higher than the particular situation (ppm level) under investigation. Moreover, it was found that Fe could not be removed by the addition of boron like other transition metals such V, Zr, Ti and Cr (Gao et al., 2009b, Gao et al., 2009a).

![Figure 8.12. The change in the concentration of V, Fe and B during first trial](image)

Experimental results obtained from trials also showed that Fe cannot be removed by the addition of Al-B master alloys, as shown in Figure 8.12. The initial decrease in concentration of Fe could be due to the formation of FeB or FeB caused by the
higher concentration of boron at the start of process that settles at the bottom of the furnace. The increase in the level of Fe after 100 minutes may have been due to the stirring of melt, which may re-suspend Fe-borides back into the melt. Other possible reason may be the higher concentration of Fe in each crucible tapped from electrolytic cells. At this stage, the Ti and V reduced the Fe-boride back into Fe to form their stable borides (TiB$_2$ and VB$_2$) because of their lower Gibbs free energy of formation in the processing conditions.

The change in the concentration of Fe during the boron treatment of molten aluminium in the second trial was also plotted and is given in Appendix E. The observed behaviour of Fe was similar to that discussed in this section and given in Figure 8.12.

8.4 Mass balance analysis

The mass balance analysis of V, Ti, Zr, Cr and B was carried out for both for trials and given in Table 8.3 and Table 8.4. It is given in Tables 8.3 and 8.4 that V and Ti are major impurities in smelter grade aluminium. The mass balance analysis showed that 83.89% V and 93.49% Ti was removed from molten aluminium during first trial of boron treatment. The starting concentration of Zr and Cr was much less than V and Ti and their removal was 43.59% and 30.61% as shown in Table 8.3.

Table 8.3. The change in concentration and % removal of V, Ti, Zr and V during first trial

<table>
<thead>
<tr>
<th>Elements</th>
<th>Concentration (ppm)</th>
<th>Impurities proportion (wt %)</th>
<th>% Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Starting</td>
<td>End</td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>62.7</td>
<td>10.1</td>
<td>61.35</td>
</tr>
<tr>
<td>Ti</td>
<td>30.7</td>
<td>2</td>
<td>30.04</td>
</tr>
<tr>
<td>Zr</td>
<td>3.9</td>
<td>2.2</td>
<td>3.82</td>
</tr>
<tr>
<td>Cr</td>
<td>4.9</td>
<td>3.4</td>
<td>4.79</td>
</tr>
<tr>
<td>B</td>
<td>168</td>
<td>23</td>
<td>---</td>
</tr>
</tbody>
</table>

The results of V, Ti, Zr, Cr and B obtained during second trial were similar first that are given in Table 8.4.
Table 8.4. The change in concentration and % removal of V, Ti, Zr and V during second trial

<table>
<thead>
<tr>
<th>Elements</th>
<th>Concentration (ppm)</th>
<th>Impurities proportion (wt %)</th>
<th>% Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Starting</td>
<td>End</td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>80</td>
<td>11.5</td>
<td>60.15</td>
</tr>
<tr>
<td>Ti</td>
<td>44.3</td>
<td>5.3</td>
<td>33.31</td>
</tr>
<tr>
<td>Zr</td>
<td>4.5</td>
<td>2.6</td>
<td>3.38</td>
</tr>
<tr>
<td>Cr</td>
<td>4.2</td>
<td>2.2</td>
<td>3.16</td>
</tr>
<tr>
<td>B</td>
<td>267</td>
<td>16.6</td>
<td>---</td>
</tr>
</tbody>
</table>

The mass balance analysis of boron is shown in Table 8.5. The stoichiometric requirement of boron was calculated assuming VB₂, TiB₂, ZrB₂ and CrB₂ formation during boron treatment of smelter grade aluminium. Initial concentration of V, Ti, Zr and Cr are also shown in Table 8.5. It was observed that the initial addition of boron was less than the stoichiometric requirement based on the total initial concentration of impurities. The results given in Table 8.3 and Table 8.4 revealed the presence of residual impurities after boron treatment. Based on the proportion of impurities removed, it was calculated that the initial addition of boron was 5.5 wt% less than their diborides formation in first trial. In the second trial, initial concentration of impurities was higher as given in Table 8.5.

Table 8.5. Analysis of boron in first and second trials

<table>
<thead>
<tr>
<th>Trials</th>
<th>Total TM impurities (ppm)</th>
<th>Req. of B (assuming diborides), kg</th>
<th>Actual addition of B, kg</th>
<th>B excess or deficit (wt %)</th>
<th>B remained in Al, kg</th>
<th>Total TM impurities remained (ppm)</th>
<th>Holding time (minutes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>First</td>
<td>102.2</td>
<td>12.19</td>
<td>9.36</td>
<td>-5.5</td>
<td>1.151</td>
<td>17.6</td>
<td>740</td>
</tr>
<tr>
<td>Second</td>
<td>133.0</td>
<td>15.77</td>
<td>13.35</td>
<td>+4.39</td>
<td>0.830</td>
<td>21.6</td>
<td>395</td>
</tr>
</tbody>
</table>

The signs (-) and (+) represent boron deficit and excess respectively in Table 8.5
TM – Transition metal impurities such V, Ti, Zr and Cr

The addition of boron was 4.39 wt% excess than stoichiometric requirement for the formation of diborides. It is observed from these trials that long holding of melt will be required for high purity electrical grade aluminium. The addition of boron just to stoichiometry of diborides formation will be sufficient to meet the electrical grade
conductor specifications. Shorter melt holding could be practiced with higher addition of Al-B master alloys and better stirring practice.

8.5 Microscopy analysis

Selected samples from both trials were prepared for microscopy analysis. Microscopy analysis provided important information regarding the morphology of inclusions and undissolved AlB$_{12}$ particles. Samples taken at 17 and 728 minutes were chosen from first trial and 9 and 82 minutes from the second trial. Optical and scanning electron microscopic results are shown in the following sections.

8.5.1 Optical microscopy

The optical microscopy images of samples taken after 17 minutes during first trial and 82 minutes from second trial are shown in Figure 8.13 that revealed inclusions in aluminium matrix. Inclusions have a wide range of particle sizes, ranging from 1 $\mu$m to 25 $\mu$m. These inclusions could have been undissolved borides which came from the Al-8wt% B added initially as a source of boron. There are also possibilities for the formation of oxides such as Al$_2$O$_3$ or exogenous inclusions (SiO$_2$, FeO) during the filling of an empty furnace that will float on the top of the molten metal.

![Figure 8.13. The optical microscopy image of samples taken after 17 minutes in the first trial and 82 minutes in the second trial](image)

It can be seen from samples taken after 82 minutes in second trial that the concentration of inclusions was much less than the 17 minute sample taken from first
trial. This was due to the settling of borides and oxides inclusions that occur with a longer holding time of aluminium melt.

8.5.2 Scanning electron microscopy (SEM) analysis

The samples taken from both trials were also investigated using SEM to further investigate the morphology of the inclusions in the aluminium matrix, as shown in Figure 8.14. The composition of the inclusions was determined using an EDX detector equipped with a SEM unit. SEM-SE images of samples taken at 17 and 728 minutes during first trial and 9 and 82 minutes from second trial are shown in Figure 8.14 and Figure 8.15.

The inclusions shown in Figure 8.14 (17 minutes from first trial) have irregular morphology. The particles are polygonal in shape and mostly found in clusters. The concentration of such clusters was higher in 17 minute sample compared to 728 minutes. The inclusions found in the 728 minute samples have a particle size less than 5 μm, and are uniformly distributed in the aluminium matrix. This suggested that the settling of large and heavy particles during the holding of melt for the longer (728 minutes) time left behind a melt with lighter and smaller inclusions. The other inclusions found are most likely oxides, which trapped in dross that formed on the surface of molten aluminium during stirring and holding. There is a possibility of (Al, Si) oxides formation or pick up during the boron treatment cycle and such oxides also come from furnace refractories and tools used during stirring of melt.

![Figure 8.14. SEM-SE image of sample taken at 17 and 728 minutes from first trial](image.png)
The SEM-SE images of samples taken after 9 and 82 minutes during second trial are shown in Figure 8.15. Found inclusions were similar to those in the 17 minute sample that are given in Figure 8.14, with the additional feature of a black particle. These black particles have morphology similar to those particles shown in Figure 8.1. Such black particles are possibly undissolved AlB$_{12}$, initially added as a source of boron in the form of an Al-B master alloy. It was suggested that the black phase is borides from Al-B master alloy, which were added during the charging of the furnace. Transition metals from smelter grade aluminium will react with solid AlB$_{12}$/B to produce heavy borides that settle at the bottom of furnace. Solid AlB$_{12}$ will also dissolve during the course of time to release boron, which will react with transition metal impurities in molten aluminium. Moreover, it can be seen from the SEM image of 82 minute sample in Figure 8.15 (b) that the inclusions have a wide range of particle sizes, varying from 1 $\mu$m to 10 $\mu$m.

8.5.3 EDX analysis

The EDX analysis of the black phase and inclusions is shown in Figures 8.16 (a) and 8.16 (b). The EDX analysis shows that the black phase is composed of Al and B. It was suggested that these borides are probably a residue from the Al-B master alloy. The quantitative compositional analysis suggested that they were the AlB$_{12}$ rather than AlB$_{2}$ phase of Al-B master alloys. Moreover, the morphology of the black particles also suggested the AlB$_{12}$ phase because the AlB$_{2}$ phase exists in elongated and needle-like particles in the aluminium matrix. The EDX spectrum of inclusions is shown in Figure 8.16 (b). The compositional analysis obtained by EDX shows that Al, Si and O are present in inclusions in the aluminium matrix. The inclusions contain 25.55% Al, 53% O and 16% Si (all in atomic %), which suggests that the inclusions are mainly oxides (Al$_2$O$_3$ and SiO$_2$).

It was difficult to find the borides of transition metal impurities due to low (ppm) concentration in the aluminium melt especially from samples taken from the top area of the furnace. Moreover, it could be assumed that transition metal borides formed during the course of boron treatment were fine ($<1$ $\mu$m) and might have stuck to the walls of the furnace or agglomerates with dross.
Figure 8.15. SEM-SE image of the samples taken after (a) 9 and (b) 82 minutes after the addition of Al-8wt% B master alloy during second trial.

The point analyses of different inclusions through EDX are given in Appendix E4. The spectrum of elements for different inclusions gave similar results, as shown in Figure 8.16 (b). There was no evidence of transition metals of Ti, V, Zr, Cr or boron in the spectrum obtained from inclusions from both trials.

Figure 8.16. EDX analysis of sample taken after 17 and 728 minutes during first trial.
8.6 Recommendations for Industry

Based on the study carried out and compared with the current practice at aluminium smelters, the following recommendations have been proposed for the optimisation of current boron treatment process,

1- By changing the source of boron, the melt treatment time can be improved. Al-B master alloys having an AlB$_2$ phase that is more reactive due to the availability of a large surface area for reaction with transition metal impurities. Al-B master alloys should be used in consultation with suppliers to meet the required level of recovery, and hence the purity of the aluminium.

2- The addition of boron should be carried out in multiple stages. The practicing of adding full quantity of the Al-B master alloy at the beginning of process will increase boron concentration. Consequently, concentration gradient will be minimised for impurities. Moreover, there will be a possibility that the larger particles of Al-B (AlB$_{12}$) will settle at the bottom of the furnace. The addition of Al-B master alloy in two or three stages during the charging of the furnace will be helpful in maximising the boron content from the Al-B master alloy.

3- Better stirring of the melt will help to redistribute the impurities. This will also increase the concentration gradient and the mass transfer of transition metal impurities and boron. Stirring with smooth flow patterns will have less effect compared to intermittent gas injection as described in Chapter 6. Injection of neutral/ inert gas (at least once during the treatment) will help to redistribute and break the solid shells of the transition metal borides around AlB$_{12}$/AlB$_2$, as described in Chapter 5. The gas bubbling will also enhance the mechanism of inclusions removal through flotation.

4- The holding of the melt should be optimised to improve the economics of the process. A shorter melt holding can be managed by using an Al-B master alloy with the comparatively larger AlB$_{12}$ particles. There is then a trade-off between melt holding and the consumption of Al-B master alloy. Based on the priorities of the cast house and its economics, an optimised boron treatment process can be developed.
5- Smaller borides could be removed by the application of appropriate filters available in industry.

8.7 Summary

It was realised that each casthouse has procedure for the removal of transition metal impurities from smelter grade aluminium but there is no agreed strategy across industry. Electrical grade aluminium producers have developed their own practices, depending on the quality of the final product and cast house capabilities. Similarly, at aluminium smelters in Australasia, different melt holding practices are carried out depending on the final concentration of inclusions and impurities based on the customer requirements. A longer holding time is required to produce a high quality product that has a minimum level of impurities as well as inclusions.

The kinetics analyses of both trials suggested a linear relation between the removal of V and Ti from smelter grade aluminium. It was observed that 70wt% V and Ti was removed in the first hours of boron treatment. The remaining 15wt% - 20wt% was removed in approximately 12 hours. It was calculated that 10% boron was left un-reacted in the end molten alloy that could be minimised by optimising the current treatment process. The results showed that Fe and Ni were not removed during both trials that are also a challenge for high purity aluminium producers.

The SEM analysis of early stage showed undissolved AlB₁₂ particles, however, no ring of VB₂/TiB₂ was observed. Transition metal borides were not observed during microscopy analyses that may due to low concentrations of borides in the molten aluminium. SEM/EDX analyses detect oxides of Al, Si in the polished aluminium samples.

The boron treatment processes can be more economical if the consumption of Al-B master alloys is reduced, that can be achieved by adding Al-B master alloy in multiple stages. Moreover, a better stirring of the melt with intermittent gas injection will further improve the reaction time by breaking boride rings, and also by improving the mass transfer of impurities. It can be concluded that the boron treatment of smelter grade aluminium should to have a standard procedure, providing guidelines for electrical grade manufacturers.
Chapter 9

Summary and Conclusions

Thermodynamic modelling of various aluminium systems with V, Ti, Zr, Cr and B was carried out in the temperature range of 675°C to 900°C and is given in Chapter 4. Thermodynamic packages as FactSage 6.2 and HSC Chemistry 7.0 were used for the assessment of stable borides and predicting the solutes concentration in various Al alloy systems. Stoichiometric and 75 wt% boron excess addition was modelled assuming transition metal diborides formation based on the recommendations of previous investigators. It was predicted from thermodynamic modelling that transition metal impurities such as V, Ti and Zr can be removed in the form of their stable diborides from molten aluminium by the addition of boron bearing substances at 750°C.

In this study, experiments were designed based on the thermodynamic predictions. For the analysis of VB$_2$ formation in molten aluminium, alloys were prepared containing stoichiometric and 75 wt% boron excess addition that are given in Chapter 5. The formation of VB$_2$ in the target alloys of Al-1wt% V-0.412wt% B and Al-1wt% V- 0.720wt% B were investigated using optical and SEM microscopes, EDX, EBSD, EPMA and ICP-AES characterisation techniques. The formation of VB$_2$ product layer in the early minutes of reaction confirmed the reaction between AlB$_{12}$/B and V was immediate as observed in the SEM images. A comparative analysis of experimental and thermodynamic results showed that the system was far from equilibrium.

In Chapter 6, kinetics models for the formation of VB$_2$ (removal of V) in molten aluminium was developed. The approach adopted satisfactorily describes the reaction mechanisms for the formation of VB$_2$ in molten Al-V-B system. Gas purging with inert/neutral gas enhanced the reaction kinetics, and this could be implemented for better boron treatment of molten alloy in industry. The mechanism of VB$_2$ formation in molten aluminium was also explained in this chapter.
In Chapter 7, the Al-Zr-B and Al-Zr-V-B alloys were investigated for the formation of borides. It was predicted during thermodynamic modelling in Chapter 4 that ZrB$_2$ is more stable than VB$_2$ in the temperature range of 675°C to 900°C, hence will form in preference during the boron treatment of molten aluminium. The SEM, EDX and ICP-AES analysis confirmed that ZrB$_2$ formed in preference to VB$_2$.

Industrial trials for the boron treatment of smelter grade aluminium were carried out at one of electrical grade aluminium producers in Australasia. Boron treatment practice was critically analysed and is given in Chapter 8. Finally, recommendations were suggested to electrical grade aluminium producers to increase the economy and quality of alloys. It is also emphasised to develop a standard procedure for boron treatment of smelter grade aluminium that can be used as guideline in cast-houses.

The following detailed conclusions were drawn from the current study:

1. It was predicted from thermodynamic modelling using FactSage 6.2 and HSC Chemistry 7.0 that diborides (ZrB$_2$, TiB$_2$, VB$_2$, CrB$_2$, AlB$_2$) of Zr, Ti, V, Cr and Al are more stable compared to other possible borides (TiB, VB, V$_3$B$_4$, V$_3$B$_6$, CrB, Cr$_3$B$_4$, Cr$_3$B$_3$, AlB$_{12}$) in the temperature range of 650°C to 900°C.

2. The Gibbs free energy formation of ZrB$_2$ is less than other diborides (TiB$_2$, VB$_2$, CrB$_2$ and AlB$_2$), therefore the order of stability (from the most stable to the least stable) of these boride phases was predicted as ZrB$_2$, TiB$_2$, VB$_2$, AlB$_2$ to CrB$_2$.

3. The equilibrium calculations predicted that Cr could not be removed from aluminium above 750°C using boron treatment, as AlB$_2$ was more stable than CrB$_2$. When boron was added to the aluminium melt containing Zr, Ti, V and Cr, the results predicted that boron would be tied up by Zr and Ti, then V, Al, and Cr, forming (Zr,Ti)B$_2$, VB$_2$, AlB$_2$ and CrB$_2$, respectively.

4. Therefore, it could be suggested (from the thermodynamic perspective only) that boron treatment would be most effective for removing Zr, Ti and V impurities from smelter grade aluminium.

5. It has been shown from thermodynamic analysis that the addition of excess boron would be beneficial in reducing the transition metal impurities concentration within the requirement of electrical grade aluminium.
6. The SEM observation of Al-1wt% V-0.412wt% B and Al-1wt% V-0.720wt% B alloys sample showed the reaction between AlB$_{12}$ and V has taken place in the early minutes. Consequently, a reaction product was formed encapsulating the AlB$_{12}$ particles initially added as a source of boron.

7. The formation of reaction product in the early minutes of reactions suggested the reaction between AlB$_{12}$ with V was immediate. There was a little evidence of VB$_2$ ring thickening with extended holding time (up to 60 minutes). The thickness of the VB$_2$ ring was increased from approximately 1µm to 20 µm for longer holding (720 minutes) of alloys.

8. The EDX analysis suggested the formation of VB$_2$ as the reaction product ring. Aluminium was also detected in the boride ring suggested the formation of mixed borides (Al,V)B$_2$. EBSD analysis also confirmed the reaction product ring was mainly composed of VB$_2$. It was concluded from the characterisation analyses that the ring was mainly composed of pure VB$_2$ with little solubilaty of other elements such as Al and V.

9. The reaction between AlB$_{12}$ and V was hindered after the formation of VB$_2$ ring. It was suggested that the dissolution of AlB$_{12}$ (source of B) was obstructed by the saturation of B inside the VB$_2$ ring shown by EPMA analysis. Undissolved AlB$_{12}$ was observed inside VB$_2$ ring that suggested that the reaction between B and V was incomplete.

10. Comparison of thermodynamic modelling and experimental results showed that the system was far from equilibrium. The V concentration in the alloy was much higher (100 ppm) than the equilibrium predictions (1 ppm) at 800°C even in the case of 75 wt% boron excess addition.

11. The kinetic curves of V removal from molten aluminium can be divided into two stages. The rate of V removal was very rapid in the first stage (up to 10 minutes) of reaction. In the second stage (after 15 minutes), the rate was slower and remained unchanged up to 60 minutes.

12. It was shown that the kinetic was first order with respect to V in the alloy. The kinetic curves of V removal at 700°C, 750°C and 800°C showed a little effect of temperature, hence it was concluded that the kinetics of reaction was not controlled by chemical reaction at the interface of AlB$_{12}$ and liquid phase.
13. Kinetic analysis of the first stage showed the reaction of VB$_2$ formation was controlled by the mass transfer of V in liquid phase. The calculated mass transfer of V in molten aluminium alloy was $2.15 \times 10^{-3}$ m/sec at 750°C that is within range of mass transfer ($10^{-3}$ to $10^{-4}$ m/sec) for elements around alloying additions reported by Guthrie (1992). The calculated activation energy 25.94 kJ/mol was also comparable with 34.6 kJ/mol reported by Du et al. (2003) for the diffusion of V impurities in molten aluminium.

14. The experimental data from the second stage of reaction fit well with Jander and Ginstling-Brounshtein diffusion models. This suggested that the second stage of VB$_2$ formation was controlled by the diffusion of B/V through VB$_2$ ring. The thickening of VB$_2$ (by growing outwards) ring during longer holding of melt confirm the boron diffusion control kinetics in the second stage of reaction. Thickening of VB$_2$ layer in the outward direction also supported the notion that the diffusion of B from inner side to outer side of layer was occurring.

15. The kinetic of reaction was enhanced by injecting inert/neutral gas in the molten alloy. The gas bubbles broke the reaction product and further formation of the ring was hindered by the movement of broken VB$_2$ particles away from the interface of AlB$_{12}$ and liquid metal. The breaking of weaker VB$_2$ rings and the mechanism of floatation plays an important role in enhancing the kinetics of the reaction.

16. Stirring of molten alloy by induction and mechanical rotator did not enhance the kinetics of reaction. It was concluded that the boride rings were not broken by these stirring effects which cannot enhance the kinetics of reaction.

17. The mechanism of VB$_2$ formation in molten aluminium alloy was complex that was composed of series of events. The reaction between AlB$_{12}$/B and V was immediate. The VB$_2$ particles nucleate around AlB$_{12}$ in the molten alloy and form a ring that hindered further reaction. Initially, reaction was controlled by the mass transfer of V in liquid phase. Later stage of reaction was controlled by the diffusion of B/V through VB$_2$ ring formed in the first stage of reaction. The reaction in the second stage proceeds very slow that consume AlB$_{12}$/V causing the thickening of VB$_2$ with the passage of time.
18. The reaction between AlB\(_{12}\)/B and Zr was similar to that observed in Al-V-B systems but ZrB\(_2\) ring was less dense as compared with VB\(_2\). The ZrB\(_2\) particles possess needle-like compared to VB\(_2\) irregular polymorphic morphology.

19. The analysis of Al-0.50wt\% Zr-0.50wt\% V-0.115wt\% B alloy showed that ZrB\(_2\) were forming in preference to VB\(_2\) at 750\(^\circ\)C. It was not established conclusively from EDX and EBSD analysis of ZrB\(_2\) ring whether it was in solid solution with Al/AlB\(_{12}\) or pure ZrB\(_2\). The presence of Al in ZrB\(_2\) ring detected by EDX analysis suggested a solid solution with a limited solubility of Al.

20. From the experience of industrial trials, it was concluded that there is no standard procedure for the boron treatment of smelter grade aluminium.

21. It was shown that the removal of V and Ti have linear relation during boron treatment trials. It was also observed that 70wt\% of V and Ti was removed from molten aluminium in the first hours of boron treatment practice.

22. Mass balance of boron showed 90% consumption and 10% was left unreacted in the molten melt.

23. Transition metal borides were not observed under SEM that was due to their low concentration in molten aluminium and also the resolution limitations of SEM used in the current investigation.

24. For the economy and quality of industrial boron treatment following recommendations were proposed:
   - By optimising the source of boron, particles shape and size of AlB\(_{12}\)/AlB\(_2\) in Al-B master alloy
   - Addition of Al-B (AlB\(_{12}\)/AlB\(_2\)) in multiple stages
   - Better stirring (injecting inert/neutral gas) of molten alloy
   - Optimisation of melt holding for better economy of process
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Appendices

Appendix A: Temperature profile in vertical tube furnace

Figure A-1. Temperature profile in vertical tube furnace at 700°C

Figure A-2. Temperature profile in vertical tube furnace at 750°C
Figure A-3. Temperature profile in vertical tube furnace at 800°C

**Appendix B: Melting facilities**

Figure B-1. Induction melting facility (a) melting unit (b) control panel
Figure B-2. Resistant pot furnace (a) molten Al in graphite crucible (b) control panel

Figure B-3. Mechanical stirring of molten alloy (a) melt containing rotator (b) mechanical rotator

Figure B-4. Multiple sampling practices (a) multiple scopes assembly (b) working floor
Figure B-5. Gas stirring practice showing top lance inserted inside molten metal

Figure B-6. Vertical tube resistant furnace used for extended time experiments
Appendix C: Others results of thermodynamic modelling

Figure C-1. Gibbs free energy of AlB$_2$ and AlB$_{12}$

Figure C-2. Gibbs free energy of possible vanadium borides
Figure C-3. Gibbs free energy of TiB and TiB₂

Figure C-4. Gibbs free energy of chromium borides
Appendix D: Kinetics of V removal from molten Al

Figure D-1. Conversion of [V] in Al-1wt%V-0.720wt%B with reaction time at 700°C, 750°C and 800°C

D1: Reaction order analysis

Figure D-2. Kinetics plot of Al-1wt%V-0.412wt%B alloy at 700°C assuming n\textsuperscript{th} order reaction with n = 1.2
Figure D-3. Kinetics plot of Al-1wt%V-0.412wt%B alloy at 750°C assuming $n^{th}$
order reaction with $n = 0.5$

Figure D-4. Kinetics plot of Al-1wt%V-0.412wt%B alloy at 800°C assuming $n^{th}$
order reaction with $n = 0.5$

**D2: Liquid phase control kinetic model**

The rate of mass transfer for liquid phase mass transfer model can be described as following:

$$R = k_m (C_m^b - C_m^i)$$
Assume equilibrium is achieved at the interface of liquid phase (Al) and the very first 
VB$_2$ covering the initial AlB$_{12}$. Under such situation, the equilibrium constant, $K$, can 
be written as:

$$K = \frac{C_{VB2}^b}{C_{m}^i} = \frac{C_{VB2}^e}{C_{m}^i} \frac{n_{m}^e}{n_{m}^f} \frac{V_e}{V_{VB2}}$$

Where, $R =$ mass transfer rate, $k_m =$ mass transfer coefficient, $n_m =$ number of mol V 
in liquid phase, $n_{VB2}^o =$ number of mol V in VB$_2$ boride layer, $n_{VB2}^e =$ mol V in VB$_2$ at 
equilibrium, $n_{m}^e =$ mol V in liquid phase at equilibrium, $V_m =$ volume of metal phase 
and $V_{VB2} =$ volume of VB$_2$ phase. Thus,

$$R = k_m (C_{m}^b - C_{m}^i)$$

$$R = k_m \left( \frac{n_m}{V_m} - \frac{1}{K} \frac{n_{VB2}^e}{V_{VB2}} \right), \text{ where } C_{m}^b = \frac{n_m}{V_m}, C_{m}^i = \frac{C_{VB2}^i}{K} = \frac{1}{K} \frac{n_{VB2}^e}{V_{VB2}}$$

$$R = \frac{k_m}{V_m} \left( n_m - \frac{n_{VB2}^e}{V_{VB2}} \frac{n_{m}^e}{n_{m}^f} \frac{V_{m}}{V_{VB2}} \right) = \frac{k_m}{V_m} \left( n_m - n_{VB2}^e \frac{n_{m}^e}{n_{m}^f} \right)$$

$$R = \frac{k_m}{V_m} \left( \frac{n_{m}^o n_{m}^e - n_{m}^o n_{m}^f}{n_{m}^e - n_{m}^f} \right)$$

From mass balance, we will get:

$$n_{m}^o - n_m = n_{VB2}^o - n_{m}^o$$

$$n_{m}^o - n_{m}^e = n_{m}^e - n_{VB2}^o$$

Where, $n_{m}^o =$ initial mol of V in liquid metal phase, $n_{m}^o =$ initial mol of V in VB$_2$ 
ingo. Let us assume, initially there was no concentration of V in VB$_2$ ($n_{m}^e = 0$). It is 
reasonable to consider as there will be no VB$_2$ layer in the early stage of reaction. 
Now the rate of mass transfer will be:

$$R = \frac{k_m}{V_m} \left( \frac{n_m (n_{m}^o - n_{m}^e - n_{m}^o n_{m}^e / n_{m}^e - n_m)}{n_{m}^o - n_{m}^e} \right) = \frac{k_m}{V_m} \left( \frac{n_m n_{m}^o - n_{m}^e n_{m}^o + n_m n_{m}^e}{n_{m}^o - n_{m}^e} \right)$$

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The rate of reaction at the interface of AlB₁₂ and liquid phase will be:

$$R = \frac{k_m}{V_m} \left( \frac{n_m n^o_m - n^e_m n^o_m}{n^o_m - n^e_m} \right) = \frac{k_m}{V_m} \left( \epsilon_m - n^e_m \left[ \frac{n^o_m}{n^o_m - n^e_m} \right] \right)$$

In terms of weight % V in the molten aluminium alloy, it can be written as:

$$- \frac{d[\%V]}{[\%V]_0 - [\%V]_e} = - \frac{k_m A}{V_m} \left( \frac{[\%V]_0}{[\%V]_0 - [\%V]_e} \right) d$$

D3: Estimation of AlB₁₂ interfacial area

The calculation of representable interfacial area is important for liquid-solid reactions. From the perspective of kinetic analysis of V removal and the formation of VB₂ in molten aluminium, the initial surface area of AlB₁₂ particles was calculated. The image processing software (ImageJ) was used. Area calculation was carried out for Al-1wt% V-0.412wt% B alloy. Following procedure was used for interfacial area calculation:

For 1000 gram of Al-1wt% V-0.412wt% B master alloy, 100±2 g Al-1wt% V and 41.24±1.5 g Al-10wt% B (AlB₁₂) master alloys were used. The balance of the alloy was composed of 99.85wt% Al. Assuming the 2.95g/cm³ density, the volume of 42.44 g of ingot of Al-10wt% B master alloy will be:

$$Volume = \frac{mass}{density} = \frac{42.44g}{2.95g/cm^3} = 14.39 \text{ cm}^3 = 1.4 \times 10^{-5} \text{ m}^3 \text{ (Al-10wt\% B containing AlB₁₂). Assuming Al-B master alloys were in cube, the dimensions of the cube will be:}$$

Al-B ingot (cube) dimensions = 2.45 cm x 2.45 cm x 2.45 cm
The SEM-SE image of Al-10wt% B (AlB\textsubscript{12}) used for analysis is shown in Figure C3.1. The same image processed for the number and size of particles is shown in Figure C3.2.

Figure D-5. SEM-SE image of Al-10wt% B master alloy analysed for AlB\textsubscript{12} particles

Figure D-6. Processed image of Al-10wt% B as shown in Figure D-7
The calculated number of particles in the image shown in Figure C3.2 has following size distribution:

Table D-1. AlB\textsubscript{12} particles size distribution in Al-10wt\% B image shown in Figure D-5

<table>
<thead>
<tr>
<th>Particle size distribution</th>
<th>&gt; 30 um</th>
<th>10 – 30 um</th>
<th>&lt; 10 um</th>
</tr>
</thead>
<tbody>
<tr>
<td>No of particles</td>
<td>7</td>
<td>22</td>
<td>142</td>
</tr>
<tr>
<td>% of total</td>
<td>4.1%</td>
<td>12.87%</td>
<td>83.04%</td>
</tr>
</tbody>
</table>

The area of Al-B ingot observed under microscope = 0.380 cm \times 0.260 cm = 0.099 cm\textsuperscript{2}, however, the total surface area of one face of Al-B ingot will be = 2.45 cm \times 2.45 cm = 6.0025 cm\textsuperscript{2}. The calculated ratio of SEM observed and un-observed area will be 1 to 60. Now total number of AlB\textsubscript{12} particles observed under SEM was 171, however, full ingot of Al-B will have 60 \times 171 = 10,260 AlB\textsubscript{12} particles.

Figure D-7. Schematic representation of SEM observed and un-observed area

Now let us assume that AlB\textsubscript{12} particles are in spherical and are also uniformly distributed in Al-B master alloy, The surface area of 171 AlB\textsubscript{12} particles will = 357459.9 \mu m\textsuperscript{2}. One face of Al-B cube will have 60 times more surface area of AlB\textsubscript{12} as compared with SEM observed area. Now, the total surface area of AlB\textsubscript{12} in one face of cube will:
The cube is divided into equal 50 slices and it is assumed that each slice have 50 μm diameter particles on average. Each side (2.45 cm) of cube will have 49 slices based on 50 μm diameter particles.

Figure D-8. Schematic representation of possible slices in a 2.45 cm x 2.45 cm plane

So total surface area of AlB₁₂ in (2.45 cm x 2.45 cm x 2.45 cm) cube of Al-10wt% B master alloy will be:

$$49 \times 21447596 \text{μm}^2 = 1050932219 \text{μm}^2 = 1.05 \times 10^{-3} \text{m}^2$$

**Total surface area of AlB₁₂ particles = 1.05 \times 10^{-3} \text{m}^2**

Table D-2. AlB₁₂ surface area calculation from three different Al-10wt% B SEM images

<table>
<thead>
<tr>
<th></th>
<th>Case 1</th>
<th>Case 2</th>
<th>Case 3</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-B(AlB₁₂)</td>
<td>0.00105</td>
<td>0.00000105</td>
<td>0.0000015</td>
<td>0.000351</td>
</tr>
</tbody>
</table>

Volume of the Melt will be:

$$\text{Volume} = \frac{\text{mass}}{\text{density}} = 1 \text{ kg}/2750 \text{ kg/m}^3 = 3.64 \times 10^{-4} \text{m}^3$$

Let us assume the uniform distribution of AlB₁₂ particles in the Al-B master alloy, then 75 wt% excess and 150 wt% excess addition of boron will have 6.14 \times 10^{-4} \text{ m}^2 and 8.78 \times 10^{-4} \text{ m}^2 surface areas of AlB₁₂. The calculated surface area of AlB₁₂ is simply the 75% and 150% more than the stoichiometric addition of boron.
D4: Calculations of melt stirring

D4.1 Induction stirring

Stirring energy of molten aluminium was calculated using following parameters:

Properties of Aluminium

- Density (900°C) = 2.3 Kg/m³
- Melting point = 660 °C
- Electrical conductivity (700°C) = 2.8 – 4.2 x 10⁶ A/Vm = /Ω.m
- Dynamic viscosity (700°C) = 1.29 x 10⁻³ NS/m²
- Kinematic viscosity = 0.56 x 10⁻⁶ m²/s
- Specific heat (800°C) = 1133 W/Kg.K
- Magnetic permeability of free space (μ₀) = 1.26 x 10⁻⁶ Henry/m

Crucible Dimensions

- A4 Morgan crucible was employed with following dimensions:
  - TOD: 114 mm (100 mm taken), Height: 141 mm, BOD: 76 mm
- Melt height in crucible: 95 mm

Furnace parameters

- Power output: 8.4 kW
- Voltage: 609 V
- Frequency: 20.2 kHz

Calculation of induction stirring

Relationship between melt velocity and coil current has been given by (Chang et al., 1978, Szekely et al., 1977) which has been presented below:

\[ V = J \frac{\sigma}{\rho} L^2 \mu_0 \]  

(D.1)

Where in above equation, \( V \) is melt velocity, \( J \) is coil current, \( \sigma \) is electrical conductivity of aluminium melt, \( f \) is frequency of furnace, \( \rho \) is melt density, \( L \) is
characteristic length (crucible diameter is our case) and $\mu_0$ is magnetic permeability of free space. Coil current can be computed from given power and voltage employed during the melting of Al and is presented below;

$$P = VI$$  \hspace{1cm} (D.2)

The coil current will be $8400/609 = 13.80$ A. Now change in melt velocity as a function of characteristic length is calculated from the given parameters. It comes up as,

$$V = 3.34L^2$$  \hspace{1cm} (D.3)

Here $L$ is the radial distance which will be $D = 100$ mm ($r = 50$ mm), now the velocity of melt will be:

Velocity of Al melt will be Avg. $V = 0.835$ cm/sec

It has been shown by (Sundberg, 1978) that the average velocity is about 0.5 times of actual melt velocity:

$$V(\text{averages}) = 0.5V(\text{actual})$$  \hspace{1cm} (D.4)

$$V(\text{Actual}) = 0.835 / 0.5 = 1.67$$ cm/sec

The Stirring energy can be calculated ifAvg. velocity is given by following relationship (Engh, 1992)

$$\varepsilon^{\circ} = \frac{V^{3}_{\circ}}{I}$$  \hspace{1cm} (D.5)

The characteristic length in this case is 0.05 m (50 mm), so the value of $\varepsilon^{\circ}$ Will be;

$$\varepsilon^{\circ} = (0.0167)^3 / 0.05 = 9.315 \times 10^{-5} \text{ m}^2/\text{sec}^3 \cdot a$$

$$\varepsilon^{\circ} = 9.315 \times 10^{-5} \text{ m}^2/\text{sec}^3 \ast 1000 \text{ kg}$$

$$\varepsilon^{\circ} = 9.315 \times 10^{-2} \text{ W/ton}$$

\textit{D4.2 Mechanical Stirring}

The mechanical stirring of melt was carried out using rotator. The rotator was attached with mechanical stirrer which has a digital controller. Torque and spindle
rotation (rpm) is displayed on the digital screen. The power input due to mechanical
stirrer can be calculated as (Engh, 1992):

\[
\text{Power input (watt)} = \text{Torque (N.m)} \cdot \pi \cdot \text{rpm}
\]  
(D.6)

The specific stirring energy \( \varepsilon^o \) into bath = power (W)/mass of melt

Table D-1. Stirring of melt using mechanical rotator

<table>
<thead>
<tr>
<th>rpm</th>
<th>Frequency (rps)</th>
<th>Torque (N.m)</th>
<th>Power (W)</th>
<th>Stirring energy (W/tonne)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>1.67</td>
<td>0.0535</td>
<td>0.5623</td>
<td>5.62 x 10^{-4}</td>
</tr>
<tr>
<td>150</td>
<td>2.5</td>
<td>0.0545</td>
<td>0.858</td>
<td>8.6 x 10^{-4}</td>
</tr>
<tr>
<td>350</td>
<td>5.83</td>
<td>0.0635</td>
<td>2.33</td>
<td>2.33 x 10^{-3}</td>
</tr>
<tr>
<td>550</td>
<td>9.17</td>
<td>0.065</td>
<td>3.75</td>
<td>3.75 x 10^{-3}</td>
</tr>
</tbody>
</table>

D4.3 Gas stirring

The stirring energy input into molten melt by gas bubbling with top lance can be
calculated by Equation C4.17. Brimacombe et al. (1990) reported the work of
Nakanishi et al. who derived theoretical expression for \( \varepsilon^o \) for top blown gas
(Brimacombe et al., 1990).

\[
\varepsilon^o = 0.0453Q^oDU^2Cos^2\theta / wX
\]  
(D.7)

\( Q^o \) = Gas flow rate = 2.94 x 10^{-5} m^3/sec = 1.764 LPM

\( D \) = Nozzle diameter = 10 mm = 0.01 m and radius = 0.005 m

Area of nozzle opening = \( \pi r^2 = 8.53 \times 10^{-5} \) m^2

\( U \) = Velocity = \( Q/A = 0.345 \) m/sec

\( \theta \) = Angle of top lance = 90°

\( w \) = 1kg = 0.001 tonne

\( X \) = lance height = 52 mm = 0.052 m
\[ \varepsilon^o = (0.0453 \times 2.94 \times 10^{-5} \text{m}^3/\text{sec} \times 0.01 \times (0.345)^2 \text{ m/sec} \times \cos(90)^2)/ (0.052 \times 0.001) \]

\[ \varepsilon^o = 3.058 \times 10^{-3} \text{ W/ton} \]

**Appendix E: Industrial trials**

**E1. First trial**

Table E-1. Details of events during first industrial trial

<table>
<thead>
<tr>
<th>NZAS Trial number one</th>
<th>18/07/2012</th>
</tr>
</thead>
<tbody>
<tr>
<td>Furnace L</td>
<td>F3</td>
</tr>
<tr>
<td>Batch number</td>
<td>87954</td>
</tr>
<tr>
<td>furnace empty</td>
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<table>
<thead>
<tr>
<th>Event</th>
<th>Time(abs)</th>
<th>Time (relative)</th>
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<th>time</th>
<th>note</th>
<th>other</th>
<th>time</th>
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<td>17</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Cruc2</td>
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<td></td>
<td></td>
</tr>
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<td>Cruc3</td>
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<td>TS1A27</td>
<td>27.5</td>
<td>top</td>
<td></td>
<td></td>
</tr>
<tr>
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<td>27.00</td>
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<td>28</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cruc5</td>
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<td>34.00</td>
<td>TS1A36</td>
<td>36</td>
<td>top</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cruc6</td>
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<td>TS1A37</td>
<td>37</td>
<td>bottom</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>TS1A43</td>
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<td>top</td>
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<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>TS1A44</td>
<td>44</td>
<td>bottom</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>TS1A54</td>
<td>54</td>
<td>top</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>TS1A55</td>
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<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
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<tr>
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<td></td>
<td></td>
<td>TS1A72</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>TS1A73</td>
<td>73</td>
<td>bottom</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Stirring start</td>
<td>45</td>
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<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Stirring end</td>
<td>48</td>
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</tr>
</tbody>
</table>

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Figure E-1. Change in concentration of boron during first trial
Figure E-2. The concentration of V at top and bottom of furnace during first trial

Figure E-3. Overall drop in V concentration during first trial
Figure E-4. Concentration drop of V, Ti, Zr and Cr during first trial

E2. Second trial

Table E-2. Details of events during second industrial trial

<table>
<thead>
<tr>
<th>Event</th>
<th>Time (abs)</th>
<th>Time (relative)</th>
<th>Sample</th>
<th>time</th>
<th>note</th>
</tr>
</thead>
<tbody>
<tr>
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<td>0.00</td>
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<td>9.5</td>
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<tr>
<td></td>
<td></td>
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<td>TS2A10</td>
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<td></td>
</tr>
<tr>
<td>Cruc2</td>
<td>9:10</td>
<td>25.00</td>
<td>TS2A25</td>
<td>17</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>TS2A26</td>
<td>17.5</td>
<td></td>
</tr>
<tr>
<td>Cruc3</td>
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</tr>
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<td>TS2A39</td>
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<td>Cruc4</td>
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<tr>
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<td></td>
<td></td>
<td>TS2A58</td>
<td>58</td>
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</tr>
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<td>Cruc5</td>
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<td></td>
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<td>Ts2A71</td>
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</tr>
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<td>Cruc</td>
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<td>80.00</td>
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<tr>
<td>8</td>
<td>10:25</td>
<td>100.00</td>
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<td>12</td>
<td>10:54</td>
<td>129.00</td>
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</table>
Figure E-5. The observed concentration of V during second trial

Figure E-6. The concentration of B during second trial
Figure E-7. The concentration of Fe, V and B in second trial

Figure E-8. The change in concentration of V, Ti, Zr and Cr during second trial
E3. Mapping

Figure E-9. Elemental mapping of inclusions in 17 minute sample taken during first trial
E4. Point analysis of inclusions

Figure E-10. Point analysis of different inclusions in 17 minute sample taken during first trial
Appendix F: Error analysis

In this appendix, error analysis is described. Error is described as the difference between the measured and actual values of a physical quantity. In laboratory, measurement of each physical quantity is associated with certain error. The common known errors are systematic, random and careless. Systematic errors are built within the instruments (design or calibration) and are very difficult to detect during repetition of experiments. Random errors show a spread in results during the repetition of experiments. They may arise from uncertainties in the measuring devices. Random errors could be minimised by repeating the experiments several time, calculating average, mean and standard deviation values. The general formula for calculating average or mean value is written as:

\[ X_{\text{Av}} = \frac{1}{n} (X_1 + X_2 + X_3 + \ldots + X_n) \quad (F.1) \]

Where \( n \) is the number of repeated measurements.

Standard deviation (\( S_X \)) is used to measure experimental error. The general formula for standard deviation is given by:

\[ S_X = \sqrt{\frac{1}{n-1} \left[ (X_1 - X_{\text{Av}})^2 + (X_2 - X_{\text{Av}})^2 + (X_3 - X_{\text{Av}})^2 + \ldots + (X_n - X_{\text{Av}})^2 \right]} \quad (F.2) \]

The final results are then written as:

“Final results” = “Average value” \( \pm \) “Standard deviation” with same units

If final results are based on the summation or abstraction of two or more quantities, the error for quantities \( X, Y \) and \( Z \) could be written as:

\[ \delta Z = \delta X + \delta Y \quad (F.3) \]

The error in the case of product can be written as:
Careless errors are due to personal observation and could be eliminated by repeating the experiment couple of times. The propagation of the random error in the final equation can be written as:

\[
\frac{\delta Z}{Z} = \frac{\delta X}{X} + \frac{\delta Y}{Y} \quad (F.4)
\]

\[
Z = X + Y \quad (F.5)
\]

\[
\delta Z = \sqrt{\delta X^2 + \delta Y^2} \quad (F.6)
\]

\(\delta Z\) will be propagated error in the Z quantity in the final summation of \(X\) and \(Y\).

In this study, errors in the results were identified from the preparation of master alloys (weighing and composition), temperature measurements (manual and melting facilities), and recording of reaction time. The post experimental treatment errors were identified from the characterisation techniques (EDX, ICP-AES, EPMA, and spectroscopy). In the following section, errors analyses of each step have been described.

**F1. Preparation of master alloys**

Aluminium master alloys were weighed using three figures (after decimal point) balance. The variation in the initial weights of Al-V, Al-B and Al-Zr master alloys were determined and found to be within the error of \(\pm 1.0\) g. The error propagation calculations in the case of Al-V-B alloys showed an error of 1.73% and 2.0% for Al-Zr-V-B alloys. Such a small error will not have significant effect on the final composition of elements and interfacial area of AlB\(_{12}\) because their concentrations within the master alloys were 15wt%, 10wt%, 4wt% and 1wt% for Zr, B and V respectively. These errors of 1.73% and 2.0% will be further divided during making 1000 g of alloys.

Experiments were carried out using similar aluminium master alloys. The compositions of V, Zr and B in their source master alloy were determined using spectrometer. It found the concentration of elements were within an error of \(\pm 0.3\) wt%. During the preparation of alloys for investigation, the required compositions
were adjusted considering an error of ±0.3 wt%. It could be suggested that the composition of final alloys were within experimental error.

F2. Temperature measurements

During the current study, K-type thermocouple was used for melting of alloys in induction, resistant pot furnace and for the calibration of vertical tube furnace. The temperature readings were recorded using multimeter. K-type thermocouples have following uncertainties:

- Temperature below 1000°C: ±0.1°C
- Temperature above 1000°C: 1.0°C

The temperature control in the case of alloys preparation in induction furnace was not accurate and was found in the range of ±10°C. Temperature in the range of 750°C±10°C was maintained manually by regulating the furnace power.

Vertical tube resistant furnace was calibrated using K-type thermocouple sheathed with alumina tube. Temperature was recorded at a distance of 2 cm by inserting the thermocouple in the vertical tube. An isothermal hot zone of 10 cm was determined where sample (25 g) was placed within alumina crucible. It was expected that the variation of temperature within the isothermal zone and alumina crucible was within ±2°C.

The temperature control in the case of resistant pot furnace was within the range of ±1°C. K-type thermocouple sheathed with alumina tube was directly inserted into molten aluminium and attached with temperature control. This gives the maximum temperature variation of ±1°C. However, temperature drop of 5°C±2°C were recorded during each sampling cycle. The fall of temperature in the case of Al-B master alloy addition into molten Al-V alloy was 25°C±5°C for stoichiometric and 40°C±5°C for 75wt% excess boron alloys. The experimental set temperature was regained in 3±1 minutes for stoichiometric and 5±1 minutes for 75wt% excess boron alloys.
F3. Reaction time measurements

The error associated with the sampling time was also calculated. It was found that the error was ±20 sec for 2, 4, 6, 8 and 10 minutes and ±15 sec for 15, 30, 45 and 60 minutes samples taken after the addition of Al-B master alloy.

F4. Characterisation techniques errors

EDX analysis

The bulk compositions of V, Zr, Al and B in the alloys were determined using energy dispersive x-ray spectrometry. It was calculated that the compositions of V, Zr and Al was within an error of ±5% but the error associated with B was ±20%. The composition of boron was calculated from the number of counts in the EDX spectrum.

EPMA analysis

The compositions of V, Al and B were also determined using electron probe x-ray micro-analyser with wavelength dispersive spectrometer (WDS). The standard used Al and O was Al₂O₃, BN for B and V for V during EPMA analysis. The average accuracy of the EPMA measurements was estimated to be within ±1% of element concentration.

ICP-AES analysis

The error from ICP instrument was also evaluated by repeating the similar experiments for several times. The concentration of V and Zr in solution with aluminium was determined by dissolving samples in HCl solution. The error associated with ICP-AES instrument was found to be ±1. The error from solution preparation and concentration of acid could also contribute in the final error of ICP-AES analysis. If ±5% error is assumed from manual handling, the error propagation will be ±5.01 in final elemental concentrations.
AlB\textsubscript{12} interfacial area calculations

Interfacial area of AlB\textsubscript{12} particles was calculated using image processing software (ImageJ). Representable SEM images of Al-B master alloys were analysed and surface area of AlB\textsubscript{12} particles was calculated in used in kinetics investigation (Chapter 6). The error associated with surface area calculation could be from analysing number of particles in SEM images processed using ImageJ. It was observed that this package overestimate the number of particles by dividing larger into smaller particles. This error was estimated to be ±5% based on the observation of original SEM and processed images as shown in Figures C3.1 and C3.2.

The other possible error could originate from non-uniform distribution of AlB\textsubscript{12} particles in the Al-10wt% B and Al-4wt% B master alloys. Three SEM images analysed showed large deviation from mean values of estimated areas as shown in Table C3.1. It was expected the mean surface area of AlB\textsubscript{12} used for the current study was within an error of ±25%.

It could be concluded from the error analysis of different step that the majority of them are within the acceptable limits. The main error that can affect the mass transfer coefficient and activation energy of early stage of reaction is AlB\textsubscript{12} surface area.