Electrolysis of Titanium Oxide to Titanium in Molten Cryolite Salt

by

Bennett Chek Kin Yan

A thesis submitted in conformity with the requirements for the degree of Master of Applied Science
Graduate Department of Materials Science and Engineering
University of Toronto

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2016

Abstract

Cost-effective production of titanium is becoming a challenge being tackled in the metallurgical and sustainability sector and technological advancements are required to effectively separate the metal from its oxide. The existing methods of Ti production are extremely energy intensive and slow. This proof-of-concept study investigated the feasibility of separating and capturing Ti from TiO₂ through electrolysis after it has been dissolved in a cryolite bath at 1050°C. XRD and SEM/EDS results verified that TiO₂ is only partially reduced. However, addition of Al assisted in the precipitation of Ti in the form of TiAl and TiAl₃. Parameters such as electrolysis time, concentration of TiO₂, and electrolysis potential were explored. The experiments that were run for 4h, with TiO₂ <15wt% of the total bath gave promising results as there was intermetallic formation without the excessive evaporation of cryolite.
Acknowledgments

I would like to sincerely thank Professor Mansoor Barati for giving me the opportunity to work on this project, his guidance and patience was greatly appreciated. This experience has given me a taste of what research is really like and an increased appreciation for the sciences and the challenges faced in academia.

I would also like to give thanks the members of the Sustainable Materials Processing Research Group for lending an ear whenever I needed and providing suggestions to my problems. Initially, we were just colleagues, but through the process, we have become great friends.

Furthermore, I would like to thank the Materials Science Department for the facilities and financial support.

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<th>Description</th>
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<tbody>
<tr>
<td>FFC</td>
<td>Fray-Farthing-Chen</td>
</tr>
<tr>
<td>OS</td>
<td>Ono and Suzuki</td>
</tr>
<tr>
<td>PRP</td>
<td>Preform Reduction Process</td>
</tr>
<tr>
<td>EMR</td>
<td>Electronically Mediated Reduction</td>
</tr>
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</table>
Chapter 1

1 Introduction

Titanium is the ninth most abundant element in the earth’s crust at an average of 0.565% in the form of rutile (TiO$_2$) and ilmenite (FeTiO$_3$)[1]. The metal is light, strong, stiff, corrosion-resistant, and can be advantageous at a wide range of temperatures. It is used in the aerospace industry (aero-frames, engines, etc.) due to its high tolerance for different working condition[2, 3] (temperature, creep, strength-weight ratio, etc.). It is also found in the biomedical industry where titanium is alloyed with other elements like aluminum and vanadium (Ti6Al4V)[4]; this particular alloy is used for medical devices that are implanted in the body for structural support like the hip joint or knee joints. If the cost of Ti can be reduced, its uses can be greatly widened to numerous other applications such as automobile parts, home appliances, utensils, and even roofing material. The production cost reduction has been the objective of many research works in the past few decades.

Currently, research is being done to develop a new method of extracting Ti to replace the current Kroll process. The current technology for mass production of Ti consists of two steps. First, the ore goes through a process called chlorination which reacts impure titanium oxide with chlorine to form titanium chloride which can then be purified by fractional distillation at lower temperatures[5, 6]. The second step is called the Kroll process, which is presently the most widely used method of extracting titanium. In this step, TiCl$_4$ (g) is reacted with Mg(s), making titanium metal in a sponge form and magnesium chloride (MgCl$_2$(g)). The MgCl$_2$(g) is then recycled back into the system[7]. The titanium sponge is then crushed and ground into titanium powder[8].

A new process called the Fray-Farthing-Chen (FFC) Cambridge Process is being developed that would eliminate the need to reduce the rutile with chlorine while maintaining a high grade titanium metal and saving energy costs. This new process uses a molten salt bath of CaCl$_2$ as electrolyte and pellets of TiO$_2$, which are insoluble, placed at the cathode. Electrochemical reactions take place in the salt bath that dissociates the TiO$_2$ between 900$^\circ$C and 1000$^\circ$C. The O$_2$ reacts with the carbon anode to form CO$_2$ while at the cathode the Ti$^{4+}$ forms Ti(s). This process produces titanium of 99% purity, but is not without its issues; due to the low current efficiency,
the overall efficiency is reduced by half when trying to obtain a purity of 99%. Moreover, the process is time consuming due to the rate limiting step being the removal of oxygen in the solid phase[9]. There have been other variations of the FFC process which include the PRP, EMR, and OS processes, but they are all in the development phase and are not available commercially[8, 10, 11]. Also, all these processes produce Ti powders which require further treatment to form ingots.

The research that was conducted in this thesis was a proof-of-concept study directed at obtaining Ti by electrolysis in the form of an alloy, at temperatures below 1100 °C. In this approach, instead of dissociation of solid TiO₂ at the cathode, it is dissolved in a molten salt. Also, the cathode will be a low melting point metal or alloy into which Ti is deposited. The advantages of electro-deposition from molten salt into a liquid alloy includes a much faster reaction, easy removal of oxygen, and product that can be cast or further refined. The process would be easily scalable; it would have the potential of being a continuous process, because the feed could be added in the top while the melt could be tapped at the bottom without further treatment. These are expected to result in a more economical processing route for production of Ti and its alloys. This exploratory study is meant to demonstrate the concept of extracting Ti from dissolved TiO₂ through electrolysis in a molten bath with the intent of providing direction for future studies in this field.

The main scope of this study investigated:

- The feasibility of electrodepositing pure Ti from TiO₂ in a molten cryolite bath
- The minimum potential required to electrolyse TiO₂
- The addition of Al in the TiO₂ cryolite bath to assist in capturing the Ti in the bath
Chapter 2

2 Titanium

Titanium is the fourth most abundant metal on earth, after aluminum, iron and magnesium[12]. However, it is commonly found in the form of ilmenite (FeTiO$_3$) or rutile (TiO$_2$). The strong affinity of Ti towards elements like C, N, S, and O, makes its extraction very difficult and energy intensive, driving the cost up [13, 14], which can vary from $8/kg to $20/kg[15] depending on the cost of electricity, materials, and labor[16].

Titanium is the next revolutionary metal. For the same strength as steel, Ti is 60% lighter[17]. Furthermore, it is stiff, corrosion-resistant, and can maintain its properties in a wide range of temperatures. These are just some attributes that make this a very desirable material in many applications. However, due to the high production cost, Ti and its major alloys are only used in the aerospace and other high end products.

Titanium shares many similarities with aluminum, in characteristics and processing methods. Both have been considered precious metals at one point; aluminum was considered as precious as platinum up until the Bayer process was introduced. The process, enabling mass production of alumina which was then reduced to aluminum using electricity, brought the price of the metal from $1200/kg[18] down to $2.00/kg as of 2015[19]. Before the Bayer process, aluminum was produced via chlorination, generating aluminum chloride which was then reduced with an alkali metal such as potassium and sodium[1]. This approach is very similar to the current method of producing titanium (Kroll Process), so it is expected that if this metal follows a similar processing trend to aluminum, should a more efficient method of its extraction be discovered, the price of titanium should subsequently fall to a point where it can proliferate the manufacturing industry.

2.1 Ti Metal and Alloys: Properties and Applications

Titanium sponge is the primary form that is being produced in industry to date. The sponge is melted and alloyed with other elements such as Al or Fe to form plates and ingots. Depending on
the purity and the quality of the desired titanium, different melting sequences are applied to obtain a desired composition [1].

One industry that has seen prominent use of this metal/alloy is the aviation industry. The aerospace applications require high strength to mass ratio as well as being able to withstand varying temperatures, from sub-zero to 600°C [2, 17]. It is used in aircraft engines, body frames, and even body panels [2]. Titanium and its alloys have also been used in the manufacture of high-end sports equipment such as bicycle frames and golf clubs because of its low density compared to steel, and its stiffness compared to aluminum, as well as some other properties that this metal provides. These titanium frames/shafts tend to be quite expensive due to the cost of the metal and meticulous process techniques required during fabrication [20].

2.1.1 Ti-6Al-4V

Titanium alloy is also used in biomedical application for skeletal frames due to its biocompatibility and mechanical properties being closer to bone over stainless steel [4]. One such alloy is the Ti-6Al-4V alloy. However, a problem with long term use of Ti-6Al-4V implants is the possible toxic effects of Al and V when they are released into the body, so development of a safer alternative titanium alloy is under investigation.

2.1.2 Commercially Pure Ti

Commercially pure metal (Cp-Ti) is readily used in the biomedical industry for dental applications due to its mechanical (Table 2-1) and osseointegration properties[21]. Cp-Ti comes in different grades, dependent on the impurities (usually a combination of oxygen and iron).

<table>
<thead>
<tr>
<th>Property</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yield Strength (MPa)</td>
<td>170</td>
<td>275</td>
<td>380</td>
<td>483</td>
<td>795</td>
</tr>
<tr>
<td>Ultimate Tensile Strength (MPa)</td>
<td>240</td>
<td>345</td>
<td>450</td>
<td>550</td>
<td>860</td>
</tr>
<tr>
<td>Elongation (%)</td>
<td>24</td>
<td>20</td>
<td>18</td>
<td>15</td>
<td>10</td>
</tr>
<tr>
<td>Elastic Modulus (GPa)</td>
<td>103-107</td>
<td>103-107</td>
<td>103-107</td>
<td>103-107</td>
<td>114-120</td>
</tr>
</tbody>
</table>

*adapted from ASTM f67 (Grade 1 to 4) an F136 (Grade 5)
2.1.3 Ti-6Al-7Nb
Ti-6Al-7Nb is another promising alloy that is finding its way into the biomedical sector [22]. Studies by Iijima et al.[23] have found this alloy to be more wear resistant than Cp-Ti, which would make this material excellent for dental applications. Reports from Khan et al. [24] and Synthes® [22] have shown that Ti-6Al-7Nb would serve as a better dental prostheses than Ti-6Al-4V due to the better wear and corrosion properties in acidic environments.

Titanium is a versatile material that has potential to be used in a variety of different applications such as automobiles, sport equipment, and even domestic products such as utensils and building materials but one of the barriers against its use is the high production cost. Addressing this issue is the subject of this thesis as well as many other investigations in various institutes.

2.2 Production Methods

2.2.1 Hunter Process

The Hunter Process was the first industrial method of producing titanium. This process was invented in 1910 by Matthew A. Hunter and the process involved generation and reduction of titanium chloride (TiCl$_4$) with sodium (Na) according to Reactions (2.1) and (2.2).

\[
\text{Chlorination:} \quad \text{TiO}_2 + 2\text{Cl}_2 + C \rightarrow \text{TiCl}_4 + \text{CO}/\text{CO}_2 \quad (2.1)
\]

\[
\text{Reduction:} \quad \text{TiCl}_4 + 4\text{Na} \rightarrow \text{Ti} + 4\text{NaCl} \quad (2.2)
\]

The titanium oxide ore would initially be chlorinated to form TiCl$_4$ (g), and then Na would be introduced into the system under an inert environment. This process takes place at temperatures around 1065°C. The final products would be NaCl and Ti which would have to be chipped out, crushed, leached, and washed [12]. This batch process was slow and tedious, and was later replaced by a more economical method that used recyclable magnesium (Mg) in place of sodium, known as the Kroll Process.

2.2.2 Kroll Process

The Kroll Process was developed by William J. Kroll in Luxembourg in 1959 and is currently the most widely used method for producing titanium. Figure 2.1 shows a schematic diagram of this process which converts rutile and ilmenite to TiCl$_4$ (g) by reacting the oxide with carbon and chlorine gas at ~ 1000 °C, according to Reaction (2.1). Gaseous titanium tetrachloride is purified
through fractional distillation, and then directed to the reduction retorts, where it is reacted with Mg\textsubscript{(l)} to form titanium dendrites and MgCl\textsubscript{2(l)}. Vacuum is then applied to the retort to remove the MgCl\textsubscript{2(l)} and excess Mg\textsubscript{(l)}, leaving titanium dendrites which have to be removed mechanically from the reactor and ground into titanium powder [12].

\[
\text{TiCl}_4 + 2\text{Mg} \rightarrow \text{Ti} + 2\text{MgCl}_2 \tag{2.3}
\]

The operating temperature for this titanium production method is around 800°C-850°C.

**Figure 2.1 Schematic Diagram of the Kroll Process[25]**

Though this process has been the industry standard for many decades, there are many drawbacks to this technology that make it less than optimal; the use of toxic chlorine gas, the expensive magnesium to reduce the chlorinated titanium, the long solid state diffusion process that takes place to reduce the titanium \textit{(i.e.} low productivity), mechanical removal of the titanium sponge produced, and need for further processing to obtain titanium ingots. These have prompted many researchers to seek new techniques for production of titanium. Kroll himself predicted that because of the inherit drawbacks of the process, it would be replaced in 5-10 years after inception [26], but this has yet to be realized after over 50 years.
2.2.3 FFC Process (Electrodeposition)

The Fray-Farthing-Chen (FFC) process is currently the closest technology to commercialization out of the many other processes under development. This process was developed by Derek Fray, Tom Farthing, and George Chen at the University of Cambridge. The method is based on electrochemical decomposition of titanium oxide, and as seen in Figure 2.2, uses metal oxide preforms at the cathode, usually thin discs, and graphite anodes in a molten CaCl$_2$ bath as electrolyte at 950°C[27]. At a constant voltage of 2.9V-3.1V the metal oxide would be reduced allowing the oxygen ions to diffuse through the metal and travel through the calcium based melt to the carbon anode, where it would then form CO/CO$_2$ [27-29].

![Scheme of FFC Cambridge Process](image)

**Figure 2.2 Schematic of processing steps for the FFC Cambridge process[30]**

The general reaction occurring at the cathode is[30]:

$$\text{MO}_x + x\ e^- \rightarrow \text{M} + x/2\ \text{O}^{2-}$$  \hspace{1cm} (2.4)

This process has proven to be less environmentally hazardous than the Kroll Process because of the use of molten salt instead of chlorine gas [29]. High purity titanium pellets with low oxygen content are produced with this method (<1000ppm) but processing of a batch takes upwards of
24-48 h [1]. Like most titanium processes, the major disadvantage to this process is that its productivity is limited by a reaction involving solid state diffusion as shown in Figure 2.3. The advantages over the conventional Kroll process is that it is simpler, with less processing steps, and less energy intensive which makes the overall product more economical [31].

![Diagram of FFC process](image)

**Figure 2.3 Progression of the metallized phase into the pellet in the FFC process[30]**

According to Ma et al. [32], an advantage of the FFC process is that the reduction is independent of the feed material. This group used titanium-rich slag, titania dust from the factory floor, and metatitanic acid as feed material and this process still produced titanium with low levels of oxygen (<3000ppm). They ran their experiments using similar parameters as the FFC group (2.9-3.1V; 900°C) but only for 12 h instead of 24-48 h, which would explain the higher oxygen levels in their results. Ma also reported that the current efficiency was dependent on the pellet thickness and porosity, and the oxide particle size. The specific energy consumption in their experiments was 33 kWh/Kg Ti, which was less than the conventional Kroll process (50kWh/Kg Ti)[27].

Liu et al. [33] performed a study on the effect of the electrolysis voltage and determined the optimal cell voltage for electrolysis of titania in molten calcium chloride to be 2.6-3.1V. Initially, they performed electrolysis at low voltage (1.5-1.7V) and found that the TiO₂ would reduce to Ti₂O but not Ti. They concluded that the cell voltage was not enough to reduce the CaO, so no Ca was available to react with the oxygen from the Ti₂O. When they worked with higher voltages (2.1-3.1V), determined by the decomposition of CaO and CaCl, they found that the oxygen level would decrease rapidly when voltage was in the range of 2.1-2.6V and then show little change from 2.6-3.1V. As shown in Table 2-2, complete reduction occurs from 2.1V, but sufficient over-potential is required to remove the last remains of oxygen from the metal.
Table 2-2 Effect of electrolysis voltage on residual oxygen in reduced pellets[33]

<table>
<thead>
<tr>
<th>Raw Material</th>
<th>Voltage (V)</th>
<th>Duration (h)</th>
<th>Content of O (wt%)</th>
<th>Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti$_2$O</td>
<td>1.5</td>
<td>8</td>
<td>-</td>
<td>Ti$_3$O</td>
</tr>
<tr>
<td>Ti$_2$O</td>
<td>1.5</td>
<td>30</td>
<td>-</td>
<td>Ti$_3$O</td>
</tr>
<tr>
<td>Ti$_2$O</td>
<td>1.7</td>
<td>8</td>
<td>-</td>
<td>Ti$_3$O</td>
</tr>
<tr>
<td>Ti$_2$O</td>
<td>2.1</td>
<td>4</td>
<td>0.11</td>
<td>Ti</td>
</tr>
<tr>
<td>Ti$_2$O</td>
<td>2.6</td>
<td>4</td>
<td>0.06</td>
<td>Ti</td>
</tr>
<tr>
<td>Ti$_2$O</td>
<td>3.1</td>
<td>4</td>
<td>0.09</td>
<td>Ti</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>2.6</td>
<td>4</td>
<td>0.26</td>
<td>Ti</td>
</tr>
</tbody>
</table>

A study from Nie et al.[34] shows similar results to Liu’s work, where TiO$_2$ reduction is seen to be a multi-stage process and that applying different cell voltages at different times can improve the current efficiency and better control of the reaction products. Table 2-3 presents the theoretical decomposition voltages for multiple states of titanium oxide. Rather than allowing all reactions to take place at once, if the cell voltage is controlled, the oxide can be manipulated and pushed to the final product in a step-wise scheme.

Table 2-3 Theoretical decomposition voltage of reaction formulas[34]

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$E^\circ$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti$_3$O$_5$(s) + ½ O$_2$ = 3 TiO$_2$(s)</td>
<td>1.74</td>
</tr>
<tr>
<td>Ti$_3$O$_3$(s) + ½ O$_2$ = 2 TiO$_2$(s)</td>
<td>1.61</td>
</tr>
<tr>
<td>TiO$_2$(s) + ½ O$_2$ = TiO$_2$(s)</td>
<td>1.91</td>
</tr>
<tr>
<td>Ti(s) + O$_2$ = TiO$_2$(s)</td>
<td>2.13</td>
</tr>
<tr>
<td>3 Ti$_2$O$_3$(s) + ½ O$_2$ = 2 Ti$_3$O$_5$(s)</td>
<td>1.33</td>
</tr>
<tr>
<td>3 TiO$_2$(s) + O$_2$ = Ti$_3$O$_5$(s)</td>
<td>2.10</td>
</tr>
<tr>
<td>3 Ti(s) + 5/2 O$_2$ = Ti$_3$O$_5$(s)</td>
<td>2.24</td>
</tr>
</tbody>
</table>

2.2.4 Ginatta Process

Ginatta wrote a paper on a unique process that he developed with his company GTT on titanium electrowinning [26] where they used titanium chloride as the starting material. When compared to the other new and developing processes, this eliminates the step of converting the chloride into the pure titanium oxide first. This process used a halide electrolyte to dissolve the TiCl$_4$ and employed a “multilayer cathodic interphase” to have a clean, yet easy to separate, contact with the electrolyte and the Ti cathode[1], as seen in Figure 2.4. The multilayer interphase consisted of ions of K, Ca, Ti, Cl, F, and elemental Ca and K. The TiCl$_4$ would be injected into this multilayer interphase; titanium species react with these ions and elements to form different oxidation states in the different layers and eventually forming a molten Ti pool at the cathode.
The operating temperature of this titanium electrowinning process is between 1650°C-1800°C, which is higher than the melting temperature of titanium (1643°C), allowing the titanium to be tapped in liquid form and this also eliminates many problems that are associated with the lower temperature (<900°C) extraction techniques such as solid state diffusion. The advantages of this liquid state extraction process, as mentioned by Ginatta [26], include:

- Complete separation of metal from the electrolyte thus eliminating cleaning steps.
- Easier control of electrochemical process parameters; as compared to solid state formation, the liquid cathode will provide a consistent surface for conduction whereas in the solid state processing techniques this property fluctuates.
- Due to liquid deposition, the distance between electrodes can be minimized as there is no need to accommodate for crystal growth.
- The geometry of the cathode/anode setup for liquid electrolysis is more desirable than that of solid state electrolysis (horizontal vs. vertical respectively).
- Faster reaction rates (gas phase of TiCl₄ vs. solid phase of TiO₂)
- Forming a solid shell of Ti at the bottom of the bath so that the titanium can hold the electrolyte, eliminating the problem of liquid containment material.
- Release of chlorine gas at the anode that does not react with the carbon anodes; hence no anode consumption and significant economic benefits.
- Zone refining effect at as the ingot is produced, where the impurities have larger solubility in the liquid than the solid.
Figure 2.4 Schematic diagram of Multilayer cathodic/anodic interphase showing how TiCl₄ reacts in each layer to gradually reduce to liquid Ti at the bottom of the cathode [28]
This process is not without its challenges; firstly, a chlorination plant would have to be operating in the same vicinity as this plant, as transporting TiCl$_4$ would not be an easy task. Furthermore, the multilayer interphase is not easy to reproduce and maintain. Also, maintaining the desired temperature profiles (Figure 2.5) is challenging. With the operating temperature of 1700$^\circ$C, energy consumption could be substantial. Further, the gas released at the anode (Cl$_2$) has to be captured and transported safely. Also, titanium would have to be re-melted to create alloys, as alloying in the cell would be difficult. Lastly, recycling scrap would require chlorination of the Ti scrap before it is fed in as feed material for the process.

![Figure 2.5 Thermal zones in the proposed titanium electrowinning process][35]

2.2.5 OS process (Calciothermic Reduction)

The Ono and Suzuki (OS) process was developed by Ono and Suzuki from the Kyoto University [1, 31, 36], using the proven concept of calciothermic reduction to reduce TiO$_2$ to pure titanium. The TiO$_2$ reacts with Ca dissolved in a CaCl$_2$ melt forming CaO and Ti metal [31]. This reaction occurs thermodynamically at elevated temperatures because CaO is a more stable oxide than TiO$_2$ and given that in this system, there are Ca$^{2+}$, O$_2$ and Ti elements, it is more favorable for the Ca to react with the O$_2$ forming CaO, leaving Ti precipitates. The potential that is added into
this system reduces the Ca on the cathode and O₂ at the carbon anode in the form of CO/CO₂. Therefore, the reactions are:

Anode: \[ C + 2 \text{O}^{2-} = \text{CO}_2 + 4e^- \]  
Cathode: \[ \text{Ca}^{2+} + 2e^- = \text{Ca} \]

The voltage applied was between 1.66-3.2V; the limits were fixed by decomposition voltages of CaO and CaCl₂, respectively, to allow dissociation of CaO without losing any CaCl₂. Both CO₂ and CO evolve at the carbon anode[36].

Ono and Suzuki [36] found that there was an optimal concentration of TiO₂ and CaO in the melt because large amounts of CaO in the system allows for higher currents and subsequently faster formation of Ca which is beneficial. However, as the content of CaO increases, the dissolution rate for the removal of CaO from the TiO₂ decreases. Therefore, optimal levels of TiO₂ are required to control the CaO concentration for higher currents while not hindering dissolution rate. The optimal levels are shown in Figure 2.6.

![Figure 2.6 Optimal ratio of Ca-CaO and CaCl₂][36]

The inventors also tried stirring the melt to accelerate the reaction, but what they found was that though the Ca would react with the TiO₂, the CO/CO₂ that formed at the anode would re-react with Ca and form CaO, leaving the TiO₂ partially reduced to Ti₂O [36].
2.2.6 PRP

Okabe et al., [37] from the University of Tokyo, used the concept of calciothermic reduction to create a Preform Reduction Process (PRP) method, which uses calcium vapors to reduce titanium oxide. This method is similar to the OS process in that it uses CaCl₂ as a flux to facilitate the reduction, but also has its own unique merits because it employs calcium vapor to react with preforms made of TiO₂, CaCl₂ and binder. Before reduction occurs, the preforms are sintered to remove any unwanted moisture and binder at 1073K. The preforms are then placed in a stainless steel vessel at constant temperature ranging from 1073K to 1273K and sealed with TIG welds to prevent oxygen from entering the system, shown in Figure 2.7.

![Figure 2.7 Schematic of PRP reduction method [37]](image)

There are three major steps to this process:
1. Preform fabrication
2. Reduction by calcium vapor
3. Leaching of the final product

The purity of the final product was more than 99%. The advantages to this process include the ability to control the purity and morphology and as well as the flexible scalability[37].

2.2.7 EMR

In another interesting study performed at the University of Tokyo, Park et al.[38] used electronically mediated reactions (EMR) to reduce the titanium. The EMR process differs from
other processes because titanium is reduced by electrons released from a reductant alloy[10] and
there is no physical contact between the TiO$_2$ and the alloy. The technique uses CaCl$_2$ as the
medium for electron transfer and the alloy used in the study was Ca-Ni. The operating
parameters are very similar to the other processes in that the salt bath was at 900°C in an argon
atmosphere[10]. Titanium of high purity was obtained with this process, at 99.5%.

2.2.8 Co-deposition with Fe

The method explored by Takenaka et al. [13] attempts to directly electrodeposit iron and
titanium as an alloy over the conventional method of taking titanium sponge from the Kroll
process and mixing it into the iron melt. In their experiment a CaF$_2$-CaO electrolyte was used
with FeO and TiO$_2$ added as a source for Fe and Ti for the alloy. They kept a constant ratio of
CaO and TiO$_2$ at 1.5 while varying the FeO-TiO$_2$ ratios. They found the optimal ratio of FeO-
TiO$_2$ to be 0.90, which produced a metal with about 50wt% Ti while other ratios resulted in Fe
with very little Ti content, as shown in Figure 2.8.

![Figure 2.8 Dependence of Ti content in deposit on molar ratio of FeO/TiO$_2$ in bath][13]

Takenaka et al. were able to achieve good cathodic current efficiency when they ran an
electrolysis with a large current and cathodic over-potential which they later suggested was
needed to co-deposit Ti and Fe kinetically[13]. The bath temperature and composition seemed to
have a significant influence on the kinetics of the electrolysis. They also mentioned that in
previous studies when they attempted Ti electrolysis in just a CaF$_2$-CaO bath, changes in the bath composition varied the state of the Ti ions which in turn potentially affected the extent to which Ti ions could be reduced. With the addition of FeO into the mix, the ratio of CaO-TiO$_2$ and the ratio of TiO$_2$-FeO should both be considered simultaneously when optimizing this system[13].

2.2.9 Cost and Energy Consumption

As stated earlier, titanium has a strong affinity for F, O, N, and C, hence production has to be under vacuum or inert (e.g. argon) environment to avoid contamination of the metal. According to a study in 1999, done by the US Department of Energy and Oak Ridge National Laboratory on the relative cost to produce a 1 inch Ti alloy plate, the largest share of the cost is fabrication, followed by magnesium reduction at 47% and 25% respectively[1], Figure 2.9. In a study by Vuuren et al.[39], they have reported that titanium powder can cost anywhere from $18/kg to $440/Kg depending the quality and composition in different parts of the world.

![Relative cost to produce 1" Ti alloy plate](image)

**Figure 2.9 Relative cost to produce 1" Ti alloy plate[1, 40]**

The cost of titanium is very closely related to the energy cost. The large differences in the estimated cost of Ti are mostly due to the wide range of energy cost, as well as the product purity. The areas of the greatest cost are magnesium recycling which electrochemically reduce MgCl$_2$ to Mg and Cl$_2$(g) and the fabrication process that requires melting titanium sponge and alloying to specifications. Though the Kroll process is the dominant method of Ti production, the
inherent inefficiencies make this process undesirable. A study by Norgate et al.[41] found the energy for producing titanium through the Kroll and FFC Cambridge process to be 361 and 317 MJ/kg ingot in 2006, respectively. However, the information gathered for the FFC Cambridge process was on a small scale, that the energy cost could be reduced by 10-15% if the process is practiced in industrial scale. As shown in Figure 2.10, the energy needed to produce a kilogram of titanium is very similar to the energy required to produce a kilogram of magnesium. Theoretically, if a method of producing titanium eliminates the need for Mg, energy and cost savings would make the process more economical and environmentally friendly.

![Figure 2.10 Energy requirement for magnesium and titanium production [41, 42]](image)

Lastly, if titanium could be produced as a preform, the potential savings from shaping the titanium would be enormous because currently titanium parts are milled from ingots. This would reduce the amount of scrap titanium and further reduce the buy-to-fly ratio[43].

2.3 Cryolite-based Electrolysis of Metal Oxides

The method of Ti production investigated in this study endeavored to electrodeposit Ti and Ti-Al from a cryolite-TiO$_2$ bath, in a fashion similar to the Hall-Heroult process for the production of Al. The existing knowledge pertaining to this system is summarized in this section.

2.3.1 Hall-Heroult Process for Al Electrowinning

There are two main steps involved in the extraction of aluminum, the Bayer process for purification of the ore and the Hall-Heroult process for reduction of aluminum oxide by
electrolysis. In the Bayer process, the ore is reacted with sodium hydroxide and the aluminum is recovered from the ore in the form of aluminum hydroxide as seen in Reaction (2.7). Two products come out of this process, the hydroxide and the gangue material in the form of a sludge known as red mud. Red mud is a strong basic slurry that can be very harmful to the environment. It contains iron oxides, silica, and some metals such as residual aluminum and titanium oxide [44]. The hydroxide is separated from the red mud by precipitation, as shown in (2.8). Next, the aluminum hydroxide is calcinated at ~850–900°C forming alumina and water, reaction (2.9). The alumina is then dissolved in molten cryolite and electrolyzed to produce aluminum in the Hall-Heroult process.

\[
\text{Bauxite dissolution: } \text{Bauxite} + \text{NaOH} \rightarrow \text{Na}^+ + \text{Al(OH)}_4^- + \text{red mud} \quad (2.7)
\]

\[
\text{Precipitation: } \text{Na}^+ + \text{Al(OH)}_4^- \rightarrow \text{NaOH} + \text{Al(OH)}_3 \quad (2.8)
\]

\[
\text{Calcination: } 2 \text{Al(OH)}_3 + \text{heat} \rightarrow \text{Al}_2\text{O}_3 + 3 \text{H}_2\text{O} \quad (2.9)
\]

The Hall–Heroult process employs electrolysis to separate the oxygen from the aluminum. The overall reaction is:

\[
\text{Al}_2\text{O}_3 + \text{C} \rightarrow \text{Al} + \text{CO}/\text{CO}_2 \quad (2.10)
\]

The electrolyte is fluoride based (Cryolite- Na$_3$AlF$_6$) with additives such as AlF$_3$ and CaF$_2$ that are meant to decrease the operating temperature, control solubility of the alumina and manipulate the density of the bath. It takes roughly four tonnes of bauxite ore to produce two tonnes of alumina which then goes through further processing to make one tonne of aluminum. This just shows that producing aluminum is associated with producing a considerable amount of waste materials [45].

### 2.3.2 Solubility of TiO$_2$ in Cryolite

For electrolysis of oxides of reactive metals such as Al and Mg, molten salts are commonly used because of their solubility for the oxides and large decomposition potential so that the metal oxide is reduced before the salt. The molten salt of choice for the Hall-Heroult process is cryolite which is a low-cost material that can be mined or synthesized. Considering that titanium and aluminum are similar in characteristics such as decomposition voltage and solubility in cryolite,
it may be plausible to extract titanium from titania in a molten cryolite bath. The most important difference between the proposed method here with other processes such as FFC is that with the use of a fluoride (cryolite) as opposed to chloride electrolytes, titania dissolves in the bath, so this could lead to faster reaction rates as liquid deposition is much quicker than solid state deposition. A paper by Jentofsten et al. [46] discussed the solubility of TiO$_2$ in cryolite-alumina melts and reported the solubility by measuring the amount of dissolved Ti, in this case 3.1wt % corresponding to 5.2wt% TiO$_2$ at 1020°C. The total Ti content was measured against the total oxygen in the alumina saturated cryolite melt, as shown in Figure 2.11. Their values were in good agreement with Madhavan et al. [47] and their study of titanium oxide in cryolite at high temperatures (1020°C and 1050°C respectively).

![Figure 2.11 Solubility of Ti content verses oxygen content in cryolite-alumina melt in equilibrium at 1020°C [46]](image)

Madhavan et al. [47] also found that there was a small eutectic point around 8.75 mole %, seen in Figure 2.12, where the liquidus temperature drops to 981.5°C and then increases quickly again[47]. This information is useful for optimizing a bath composition to lower the operational temperature of the bath. The discrepancy between the two curves, shown in Figure 2.12, is likely due to the impurity of the cryolite.
Figure 2.12 Liquidus curve for TiO$_2$ in Na$_3$AlF$_6$-Al$_2$O$_3$ system [47]

2.3.3 Solubility of Al$_2$O$_3$

The Hall-Heroult method relies on dissolution of alumina into cryolite so that when a potential is applied across the bath, the oxygen ions are attracted to the positive carbon anode and react to form CO$_2$ which gets released. The Al$^{3+}$ ions reduce on the cathode, precipitating out into aluminum and since the operating temperature is higher than the melting temperature of aluminum (900°C and 660°C respectively), aluminum precipitate will be in liquid form that can be tapped from the bottom of the bath. What has enabled mass production of aluminum at low cost is dissolution of alumina in the melt, allowing liquid deposition at temperatures less than half of the alumina melting temperature.

The solubility of alumina in cryolite was studied by Thonstad et al. [48] where they measured time dependency of dissolved alumina in cryolite to determine the saturation concentration at a given temperature. As seen in Figure 2.13, they found that alumina dissolved quite rapidly in
cryolite and at ~1050°C (1058°C) the dissolved alumina reached almost 13wt% before reaching a plateau. This large amount of dissolved alumina improves the electrolysis rate when reducing to aluminum.

![Dissolution kinetics of alumina in cryolite](image)

**Figure 2.13 Dissolution kinetics of alumina in cryolite[48]**

The ternary phase diagram of Na₃AlF₆-AlF₃-Al₂O₃ in Figure 2.14 shows the liquidus temperature of cryolite-15 wt% alumina to be about 1025°C; at 11wt% alumina the temperature is 950°C. Addition of AlF₃ decreases these temperatures, so by adjusting the amount of additives the operating temperature can be controlled to be as low as 850-900°C.
2.3.4 Phase Diagrams of Ti-O and Al-Ti

The Ti-O phase diagram in Figure 2.15 shows that titanium has several oxidation states with the most oxidized form being titania (TiO$_2$). As the ratio of Ti/O increases, phases with lower oxidation state (Ti$_2$O$_3$, Ti$_3$O$_5$, and Ti$_4$O$_7$) become more stable. Figure 2.16 shows that between 58-68 at% Oxygen is where most of the other oxidation states occur. The phase diagram also shows that the titanium and titanium oxides will always be in solid state because typical cryolite based electrolysis of ~ 1000 °C is well below the melting temperatures of metal or oxides. In order to allow liquid-phase electrolysis, titanium oxides have to be in dissolved form. Also, Ti can be deposited into a liquid alloy phase rather than pure metal so that an all-liquid system is possible. Aluminum would be a good choice as an alloying element because of its abundance and low cost. Ti-Al alloys have many applications so the product can be used directly to turn alloys to specifications.
Figure 2.15 Ti-O phase diagram [50]

Figure 2.16 Enlargement of Ti-O phase diagram from 58-68 at% Oxygen [50]
Figure 2.17 shows the Ti-Al phase diagram where the liquid phase is on the aluminum rich side at <1000 °C. This window maybe small (0-0.05 mol % Ti), but it would be enough to try and extract the titanium in liquid phase. If for example, a temperature of 1000 °C is used, Ti and Al in the liquid phase will form TiAl₃ and if there is sufficient Ti in the melt, the concentration will gradually move towards a Ti-Al phase.

Figure 2.17 Ti-Al phase diagram[51]
2.3.5 Problem Statement

A review of the literature confirms that there are new developments made in the field of titanium production, but there are still many challenges to produce titanium more efficiently. Processes like the FFC and OS process, which are closest to commercialization, have been able to produce pure titanium with acceptable oxygen content, but the current efficiency and production rate are both very low. These new methods of titanium production are dependent on reduction of titanium oxide through a process that involves solid state diffusion. Inherently, the process is slow, resulting in high energy consumption and low productivity. If there were a method to convert the titanium oxide to metal via liquid phase reactions, the potential to increase efficiency and production levels may be unlocked. The method proposed in this thesis investigates dissolution of titanium oxide in a molten salt, followed by electrolysis of the salt to deposit Ti either as a pure metal or into Al as Al-Ti, to address the above issue.
Chapter 3

3 Experimental Aspects

3.1 Objectives

The overall objective of the research is to investigate the feasibility of depositing Ti from a TiO₂-cryolite melt as pure Ti or an alloy of Ti-Al. This chapter describes the experimental procedures, materials and equipment used in this work.

3.2 Materials

A variety of materials were used for different purposes, with the details of each material provided in Table 3-1.

Table 3-1 Details of the materials used

<table>
<thead>
<tr>
<th>Material</th>
<th>Source</th>
<th>Grade/Purity</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlCl₃</td>
<td>ACROS Organics™</td>
<td>98.5%</td>
<td>Extra pure, anhydrous, powder</td>
</tr>
<tr>
<td>TiO₂</td>
<td>DuPont™</td>
<td>93%</td>
<td>Ti-Pure ®R-706</td>
</tr>
<tr>
<td>TiO₂</td>
<td>Henan Billions Chemical Co. LTD</td>
<td>≥98.5%</td>
<td>BLR-501</td>
</tr>
<tr>
<td>Na₃AlF₆</td>
<td>Rio Tinto Alcan</td>
<td>Na:Al Ratio : 3.3</td>
<td>Used as is</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Impurities: &lt;0.6 wt%</td>
<td></td>
</tr>
<tr>
<td>Aluminum Pellets</td>
<td></td>
<td>99.99%</td>
<td>0.64g - 0.7g/pellet</td>
</tr>
<tr>
<td>Argon</td>
<td>Linde</td>
<td>Grade: 4.8 (≥99.998%)</td>
<td>N₂ ≤ 10 ppm</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>O₂ ≤ 3 ppm</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>H₂O ≤ 5 ppm</td>
</tr>
<tr>
<td>Graphite rod (GR)</td>
<td>Graphtek LLC</td>
<td>GR008G</td>
<td>Superfine grain, high density extruded graphite rod; 9.5mmOD x 605mm L</td>
</tr>
<tr>
<td>Graphite crucible (GC)</td>
<td>Graphtek LLC</td>
<td>GR001CC</td>
<td>57.1mmOD x 41.3mmID 86.4mm Deep (95.3mm High)</td>
</tr>
<tr>
<td>Molybdenum rod and wire</td>
<td>Espimetals</td>
<td>3N8 (&lt;200 ppm K+Cr+Cu+Fe+Ni)</td>
<td>Rod: 9.5mmOD x 160mm L Wire: 2mmOD x 600mm L</td>
</tr>
<tr>
<td>Gypsum lid</td>
<td>Bondex</td>
<td>CaSO₄ : 15-25% CaCO₃ : 75-85% SiO₂ : 0-1%</td>
<td>57.1mm D x 10mm H</td>
</tr>
<tr>
<td>Cement lid</td>
<td>Super Kastite 3000</td>
<td>Al₂O₃ : 55.7% SiO₂ : 38.4%</td>
<td>57.1mm OD x 20mm</td>
</tr>
</tbody>
</table>
Graphite was chosen as the material for crucibles and electrode (in some experiments) because of its inert properties in molten salt at the operating temperatures (~1100°C). Initially, the crucibles were flat bottomed, but a mini bowl shape was drilled into the bottom of the crucibles shown in the schematic diagrams in Figure 3.1.

![Figure 3.1 Graphite crucible with mini bowl cut (Diameter 0.03m, depth of 0.005m)](image)

Figure 3.2 is an aerial perspective of the graphite crucibles. The purpose of this was to allow for easier collection of the metal/alloy at the bottom of the cell, as the crucible was acting as the cathode in the experiments involving liquid Al.

![Figure 3.2 Bottom of crucible drilled to facilitate collection of the alloy](image)

In some experiments, molybdenum rods and wires were used as cathode or lead wire to cathode because of its excellent high temperature strength and also resistance to the corrosive salt environment. The rod was used as the tip of the electrode where it was connected to a thinner lead wire at top.
3.3 Analytical Techniques

3.3.1 X-ray Diffraction (XRD)

XRD was one of the techniques used to identify the compounds present in the materials. A Rigaku MiniFlex 600 with a SC-70 Detector was used to analyze the samples. The samples were analyzed using CuKα radiation (\( \lambda = 1.54056\)Å) with a Ni filter. The beam power was set to 40kV and 15mA. XRD spectrums were obtained at scan speed of 1.2° per minute using 0.03° step-size in the Bragg’s angle range (2θ) of 10-90°.

Difficulties arose when compounds exhibited strong and sometimes overlapping peaks, such as cryolite. With cases like these, a broader Bragg’s angle range was scanned from 10-140° to see if there are any distinct diffraction peaks that could be used for identification of various phases. Removing cryolite from the sample (metal/alloy) could potentially improve the results but often the cryolite is embedded in the metal matrix, making it difficult to clean and analyze.

3.3.2 Scanning Electron Microscopy (SEM)

A Hitachi SU3500 SEM with Back Scatter Electron detection (BSE) and Energy Dispersive X-Ray Spectroscopy (EDS) capabilities combined with Oxford AZtec X-Max50 SDD X-ray analyzer was employed for obtaining microstructural and compositional information in micro scale. When taking micrograph images, the beam voltage was set at 20kV at a working distance between 10-40mm depending on the scale of the image; 10 mm for images captured in the micro scale, and 40 mm for the images in the millimeter scale. The samples, as shown in Figure 3.3, were fixed in epoxy resin and coated with carbon to ensure that there was no charging during SEM works. Analysis was conducted under vacuum.

Figure 3.3 Samples mounted in epoxy resin and carbon-coated for SEM/EDS
The EDS tool uses the same machine at the beam voltage of 20kV with a working distance of 10mm to obtain elemental composition of a target area/phase. The X-ray detector employed was an Oxford Instruments X-Max 80mm². This machine which houses a polymer window is able to detect elements as light as oxygen in vacuum. Also, high resolution images with spatial resolution of up to 3nm at 30 KV can be obtained in high vacuum if needed, where this research required resolution in the mm and µm range.

The BSE detector improves the image contrast when elements with different atomic numbers are present due to the elastic energy of the backscattered electrons as compared to the secondary electrons (SE) image seen Figure 3.4. The BSE image shows heavier elements as brighter regions.

![Figure 3.4 SEM (left) and BSE (right) images of cross section of a sample. BSE shows greater contrast when identifying metal alloy embedded in cryolite](image)

### 3.4 Experimental setup

A vertical alumina tube furnace was used to perform the tests at high temperature. The 70mm OD (66mmID) x 700mm L tube was heated resistively using molybdenum silicate heating elements and a type B thermocouple was used to measure the furnace temperature. The top and bottom of the tube were sealed with rubber stoppers fitted to holes in aluminum caps covering the tube ends. The caps are cooled with cold water running through copper piping that is coiled around the cap. The sample would be charged from under the furnace and then sealed. Electrodes would run into the crucible through the stopper, and clipped to the lead wires as shown in Figure 3.5.
Figure 3.5 View of the furnace from top; a) Mo rod attached to carbon crucible and carbon anode; b) Attaching the power source to the electrodes; c) Heated vertical tube furnace.

The furnace tube was purged continuously with argon at the flowrate of 80mL/min to avoid oxidation of the metal and graphite. A schematic of the furnace assembly is shown in Figure 3.6.

Figure 3.6 Schematic diagram of the vertical tube furnace
Four different combinations of electrodes were used in the experiment, varying in material and surface area (Figure 3.7). The different electrode geometries were used to pass more current, thus increasing the amount of metal deposited. Initially, two carbon rods of the same dimension were used; followed by an increase of surface area when one of the electrodes was switched to a coiled molybdenum wire. Later, the surface area was reduced back to the initial ratio (1:1) but a molybdenum rod was used. Molybdenum cathodes were chosen because of their high melting temperature and ability to resist the corrosive environment of cryolite. Furthermore, forming titanium on graphite would generate TiC whereas Mo would be inert towards Ti. Lastly, the surface area was increased again, but using the same material. The carbon crucible was turned into an electrode.

Figure 3.7 Electrode arrangements from left to right (anode-cathode); carbon rod- carbon rod; carbon rod – molybdenum coil; carbon rod- molybdenum rod; carbon rod-molybdenum wire connected to carbon crucible

3.4.1 Heating Regime

The sample was charged in the furnace and sealed before the start of experiment and was allowed to cool in the furnace after electrolysis. The dwelling time during which electrolysis was carried out ranged from 4h to 24h. Heating and cooling had to be done slowly so that the alumina working tube did not crack due to thermal stresses. Figure 3.8 shows the temperature profile of a 4h melt. The temperature profile inside the tube and along the vertical axis was measured using a K-type thermocouple to identify the hot zone and temperature uniformity. The furnace controller
recorded a temperature 50 °C higher than the actual temperature measured. The temperatures reported in this thesis are those measured by the controller-independent thermocouple.

![Temperature profile](image)

**Figure 3.8** Temperature profile experienced by a sample for 4 h dwell time.

### 3.4.2 Procedure

Four sets of experiments were carried out. In the first set, to investigate deposition of solid Ti, mixtures of Na$_3$AlF$_6$ and TiO$_2$ were used as the electrolyte. In the second set, aluminum was added to allow formation of a liquid cathode onto which Ti is deposited as an alloy. The third set, co-deposition of Ti and Al from a Na$_3$AlF$_6$-TiO$_2$-Al$_2$O$_3$ melt was investigated. Finally, in the fourth set of experiments, a small amount of Al was added to the above mixture to allow formation of an initial liquid pool onto which both Ti and Al can be deposited. The total mass of material in each experiment ranged from 120 to 150 g, limited by the size of crucible, as shown in Figure 3.9; the pre-melt material would reach the brim of the crucible. The composition range of the mixture in each set of experiments is provided in Table 3-2.

| Blend of materials in wt %; total mass of sample 120g-150g |
|----------------------------------|-----------------|--------|--------|
| | Na$_3$AlF$_6$ | TiO$_2$ | Al | Al$_2$O$_3$ |
| Set 1 | 92-96% | 4-8% | --- | --- |
| Set 2 | 82-85% | 5-10% | 5-12% | --- |
| Set 3 | 65.1% | 12.9% | --- | 22% |
| Set 4 | 81% | 5.7% | 1.2% | 12.1% |
The crucible was covered with lids to minimize the evaporative losses of the salt during the process. Initially, gypsum lids were made about 10mm thick, Figure 3.10, covering the top with a hole in the middle for the carbon anode. Gypsum was chosen because of its low electrical conductivity and resistance to high temperature. However it was noticed that the material was severely attacked by the salt fumes, perhaps in part because it was not cured (sintered) at high temperature before use.

As an alternative, high temperature cement containing alumina and silica was used to make a cap about 20mm thick, seen in Figure 3.11. This time, the cap was dried and sintered prior to use. This cap maintained its integrity throughout the electrolysis process.
Figure 3.11 High temperature cement cap; cap was heat treated to drive off water before use to reduce chances of dissolving

3.4.2.1 Deposition of Ti from Na₃AlF₆-TiO₂

The first set of experiments attempted to deposit pure titanium from only titania (TiO₂) dissolved in cryolite (Na₃AlF₆). The titania amount ranged from 4.86 wt% to 7.94 wt%, which was determined based on the saturation point of titania in cryolite which was about 5.2 wt% at 1020 °C according to [46]. A test was done right under the saturation level and another was done with excess reactant to maintain the saturation level if the titania is reduced through the electrolysis. Figure 3.12 is an example of titiana mixed in cryolite after the electrolysis process; the mix did not wet the surface of the crucible and could be taken out easily when cooled. The specimen was about ⅓ of the original height of the crucible.

TiO₂ was only partially reduced to lower oxidation states, without formation of any pure Ti, although the applied potential was large enough for dissociation of TiO₂. It was hypothesized that Ti is reduced to metal but upon release of oxygen or CO₂ at anode and due to the small spacing between he electrodes, the metal reacts back to oxide. Therefore, if a reactive metal such as Al was kept at the cell, it could dissolve Ti before it gets oxidized. Al would have another important role that it will react with oxygen more preferentially than Ti, protecting Ti from oxidation. The third role of Al would be forming a liquid cathode so that the kinetic barriers associated with solid deposition are reduced.
3.4.2.2 Addition of Aluminum (Na$_3$AlF$_6$-TiO$_2$-Al)

Several variables were investigated in these experiments, such as the reaction time in the absence of a potential (Figure 3.13), applying a potential to the melt (Figure 3.14), and the ratio of TiO$_2$-Al. In some experiments, alloys of Ti-Al were formed, consisting of Al$_3$Ti, AlTi and AlTi$_3$; in others TiO$_2$ was only partially reduced similar to the previous set of experiments.

Figure 3.12 Cryolite and titania mixture do not wet the crucible; easy removal after solidification

Figure 3.13 Samples with no potential added; metallic skin forms at the bottom of melt
Figure 3.14 Sample with potential of 3V using a carbon rod as anode and carbon crucible as cathode; a) is of the melt closer to the anode and contains TiAl; b) is of the bottom of the sample, and contains TiAl as well as TiAl₃.

3.4.2.3 Replacing Aluminum with Alumina (Na₃AlF₆-TiO₂-Al₂O₃)

The aluminum was substituted with alumina to determine the possibility of reducing the alumina to aluminum, like that of the Hall-Heroult process, and then reacting with titania to form a titanium alloy. The amount of alumina added into the melt was at the maximum solubility for alumina (~15 wt%).

3.4.2.4 Addition of both Al and Al₂O₃ (Na₃AlF₆-TiO₂-Al-Al₂O₃)

In the last set of experiments, aluminum and alumina were both added in the bath. The assumption was that the aluminum would start the aluminothermic reduction and the alumina would provide the extra aluminum needed to reach a complete reaction. The amounts of titania, aluminum, and alumina were based on the final product TiAl₃ where 10% of the aluminum came from the initial melt and the rest from the alumina.
Chapter 4

4 Results and Discussion

Four sets of experiments were carried out, one with the goal of depositing pure solid Ti metal from a cryolite-TiO$_2$ melt, and the others aiming to deposit Ti into a liquid cathode of Al. The effects of several parameters were examined with the overall objective of extracting Ti from TiO$_2$.

Analytical techniques such as XRD, SEM/BSE and EDS were used extensively to gather information on the reaction products. In the first set of experiments, titanium was only partially reduced from TiO$_2$ to Ti$_3$O$_5$ or Ti$_4$O$_7$ and in some cases even Ti$_2$O and TiO, but pure Ti was not obtained regardless of the applied voltage and electrolysis time. Attempts to deposit titanium into aluminum were made and TiAl$_3$ was formed. In some experiments, the XRD analysis showed that AlTi was also generated.

In this chapter, the results will be presented and discussed with emphasis on the effect of changing various parameters on the extent of reaction and nature of reaction products.

4.1 Electrolysis of Na$_3$AlF$_6$-TiO$_2$ Melts

The solubility of titanium oxide in cryolite is ~5.2wt% at 1020°C as discussed in earlier sections; therefore experiments were run around the solubility limit. In the initial experiments the amount of TiO$_2$ varied from 4 - 8wt% and the specimens were held at 1050°C for 4h. The mix was uniform and did not stick to the crucible; the sample was easily removed when cooled. There was very little difference between the melts with various titania content. No trace of the TiO$_2$ powder was present in the mix; appearing that it was all dissolved in the cryolite. Visual examination did not show any metallic particles either. As the wt% of TiO$_2$ was kept constant, the carbon anode was consumed when the bath size 120g but not with a bath of 20g because there was a greater amount of total TiO$_2$. The consumption of carbon indicates oxygen removal from the system and the formation of metallic Ti or oxides of titanium with lower oxygen content than TiO$_2$. 
4.1.1 Effect of electrode type

Graphite and molybdenum were chosen as electrode materials due to their high melting temperatures, 3550 °C and 2623 °C respectively. Initially, both the cathode and anode were graphite, but later Mo wire was used in the shape of a coil as the cathode for a greater surface area. On the graphite cathode no titanium was formed, only cryolite was stuck on the electrode. The crucible was cut open after cooling and dendritic formation of cryolite was present. The middle of the sample was hollow due to solidification shrinkage.

![Figure 4.1](image)

**Figure 4.1 TiO₂ cryolite melt; 120g bath, hollow center, little wetting on crucible wall**

The cathode was then changed to a molybdenum wire in coil form; this resulted in similar dendritic formation on the cathode. This phase was analyzed using XRD and it was confirmed to be mainly cryolite with little TiO₂. Later the cathode was changed from wire to rod and found that the dendritic formation was independent of the shape. Also, despite applying a range of potential between 1 and 3 V, no Ti formation was observed, only partial reduction of TiO₂ took place as will be discussed later.

The anode material was not changed, only graphite was used. In the first experiment, the anode was not consumed visibly, probably due to the small melt size, *i.e.* smaller amount of oxide reduced, or insufficient potential. In the later tests with higher current and potential, the anode was consumed but it was not possible to determine the extent of reactions as the off gas was not analyzed.
4.1.2 Applied potential

The potential range was chosen based on the minimum theoretical decomposition of TiO$_2$ to be 2.13V at 900°C stated by Nie et al.[34] and operating conditions utilized by the FFC Cambridge process between 2.8V-3.2V[32]. The effect of cell potential was investigated by varying the applied voltage between 1V and 3V. Little change was noticed until potentials higher than 2V, where consumption of graphite anode was visible. The potential was controlled and the current was allowed to be the response variable. The potential and current had a linear relationship, at 1V, the current was 3A, 2V corresponded to 6.5A and 3V yielded about 10A. The current was not steady; it would slowly drop over time, which could be an indication of the reduction in conductivity of melt due to compositional change (conversion of TiO$_2$ to other oxides, evaporative loss of cryolite, etc), formation of gas bubbles on the anode leading to greater interface resistance, or both.

Samples of the solidified melt from vicinity of the cathode were recovered after the experiment and subjected to XRD for phase analysis. The sample was crushed and cleaned through dissolving the cryolite with aluminum chloride (AlCl$_3$). Ti$_3$O$_5$ and Ti$_4$O$_7$ were found in the material as shown in Figure 4.2. In other areas of the specimen, Ti$_5$O$_9$ was found as well as trace amounts of sodium titanium oxide (Na$_{0.23}$TiO$_2$) as shown in Figure 4.3 and Figure 4.4. It proved very difficult to completely remove the Na$_3$AlF$_6$, as the peaks would still appear in some of the XRD spectrums.
Figure 4.2 XRD spectrum of Na₃AlF₆-TiO₂ sample; found partially reduced titania (Ti₃O₅ and Ti₄O₇); Na₃AlF₆ was removed with AlCl₃ and rinsed before analysis.

Figure 4.3 XRD spectrum of TiO₂-Na₃AlF₆ melt; unable to completely remove cryolite.
It is evident that complete reduction of Ti did not take place. As expected from the Ti-O phase diagram, the reduction should be sequential, from one oxide to another with lower O/Ti ratio. The presence of all these oxides together indicates that kinetic barriers are at play. Furthermore, the fact that no Ti metal was detected despite using potentials as high as 3V, shows either inadequate potential or re-oxidation of the metal by reaction with evolved gases at the anode. A thermodynamic calculation shows that the decomposition potential of pure liquid TiO$_2$ at the electrolysis temperature of 1050°C is 1.83V given by Equations (4.1) and (4.2):

$$\text{Ti} + \text{O}_2 \rightarrow \text{TiO}_2 \quad \Delta G_{1323K}^o = -705,773 \text{ J/mol}$$  \hspace{1cm} (4.1)

$$\Delta G^o = -nFE$$  \hspace{1cm} (4.2)

where:

$n=$ # of electrons exchanged

$F=$ Faraday constant ($9.6485 \times 10^4$ C mol$^{-1}$)

$E=$ Reduction potential at desired temperature
Noting that TiO$_2$ was in dissolved form, and in the range of 8 - 41 mol% with the average amounts being 12 - 18 mol%, added potential is required ranging from 0.02-0.07V, given by Equation (4.3):

$$\Delta E = \frac{RT}{nF} \ln a_{TiO_2}$$  \hspace{1cm} (4.3)

where:

- $R$ = Universal gas constant (8.314 JK$^{-1}$ mol$^{-1}$)
- $T$ = Temperature (K)
- $a_{TiO_2}$ = Activity of TiO$_2$

There is no data to estimate the $a_{TiO_2}$ so as a rudimentary calculation, an ideal behavior was assumed, so that $a_{TiO_2} = X_{TiO_2}$ with $X_{TiO_2}$ being the mole fraction of titania in the melt. The calculation shows that the theoretical decomposition potential with this approximation would be in the range of 1.85 to 1.90 V. For electrolysis of Al, an overpotential of 0.5V[52] is employed to overcome other resistances such as contacts and connectors, interface resistance, and polarization. If a similar overpotential is assumed, the cell voltage should be in the range of 2.35V to 2.4V to allow conversion of TiO$_2$ to Ti. Also, in previous studies, the FFC process used voltages of 2.6-3.1V because of their calcium chloride salt bath. It was high enough so that it would be able to reduce titania without decomposing the calcium chloride. Therefore, given the information provided, 3V was chosen for the cryolite bath here. The fact that TiO$_2$ was not reduced to Ti metal under this potential implies that the re-oxidation hypothesis discussed above is a likely scenario; Ti is generated but immediately reacts with the evolved gases at anode to form oxides of lower oxidation states than TiO$_2$.

4.1.2.1 Addition of Al (Na$_3$AlF$_6$-TiO$_2$-Al)

Aluminum has a very high affinity for oxygen and forms a more stable oxide than titanium at any given temperature. The reason for adding Al was to allow capturing the evolved oxygen to prevent it from re-oxidizing Ti. However, this also means that Al may reduce TiO$_2$ directly, without a need to apply any potential. The effect of an applied potential would be to drive the
equilibrium to larger constant, \textit{i.e.} greater extent of TiO$_2$ reduction. In this section, the effect of Al addition with and without an applied potential is discussed.

### 4.1.3 No applied potential (Aluminothermic Reduction)

This set of experiment was conducted in the presence of Al metal in the system and without applying any potential to the cell. According to the Ellingham diagram (Appendix A) and the Gibbs free energy of formation of oxides given in Equations (4.1) and (4.4), Al metal can reduce TiO$_2$ to generate Ti metal and Al$_2$O$_3$ so the reaction should irreversibly proceed until equilibrium between the components is reached. Therefore, it can be argued that the reaction is primarily chemical and not electrochemical because no potential is required for it to occur.

\[
\frac{4}{3} \text{Al} + \text{O}_2 \rightarrow \frac{2}{3} \text{Al}_2\text{O}_3 \quad \Delta G^\circ_{1323K} = -1,169,633 \text{ J/mol} \quad (4.4)
\]

The role of any applied potential in this case would be to drive the reaction further so that the equilibrium is shifted towards less TiO$_2$ in the salt and more Ti as metal. At large enough potential, Al$_2$O$_3$ from the electrolyte should also be reduced back to metal.

Two experiments were conducted with the TiO$_2$/Al ratio maintained at 1:2 and temperature at 1050$^\circ$C while varying the hold time to 4 and 15 hrs. The 15 h run had more cryolite powder build-up inside the furnace tube and less in the crucible because of evaporation of the salt. However, for the metal formation, the results were very similar; a two-phase alloy was formed at the bottom of the crucible. Aluminothermic reactions occur very rapidly and it has been reported to complete their reactions in the first $\frac{1}{2}$ hr of the experiment[53]. The SEM in Figure 4.5 shows a metal shell (#2, #4) followed by layer of hard cryolite (#3) and a mix of metal and cryolite in the center(#1). There was also hard cryolite on the outside of the shell (#5). A BSE image showed better contrast of the different areas in the sample.
Figure 4.5 Product in the absence of an applied potential; metallic shell trapping cryolite and Al rich core inside

Figure 4.6 is a magnified version of the metallic shell where the two images show the same area, with Figure 4.6a) showing a secondary electron (SE) image and Figure 4.6b) showing a backscattered electron (BSE) image. Cryolite was detected on the outer most layer, represented by #1, followed by a shell structure (#2) and a Al rich core mixed with cryolite in #3, Figure 4.6.

Figure 4.6 Magnified image of the metallic layer (a) SE Image (b) BSE Image

Different regions of the product were analyzed in greater detail in Figure 4.7 using the SEM/EDS; the results are provided in Table 4-1.
As seen, the brighter region in Figure 4.7a, being the metal shell, consists of three other phases; a gray matrix, bright dendritic phases, and small round inclusions. EDS analysis reveals that these phases are an Al rich alloy, TiAl₃, and cryolite inclusions.

The EDS analysis also found Al₂O₃ embedded in the core of the sample (bottom left corner of Figure 4.7b, darker regions) which is presumably produced by the aluminothermic reduction. Traces of silica were also found in the area likely due to transfer from grinding and polishing procedures. The overall reaction for the formation of TiAl₃ is expressed by Equation (4.5):

\[
13\text{Al} + 3\text{TiO}_2 \rightarrow 2\text{Al}_2\text{O}_3 + 3\text{TiAl}_3
\]  

(4.5)

The Al rich phase is designated by the elemental composition where there is 50wt% remaining Al after assuming that Al has reacted with all other detected elements such as Ti and O.
Figure 4.7 EDS of specimen with no potential; Image b is magnified #2 and image c is #5; elemental composition given in Table 4-1
The reaction could potentially be controlled by limiting the amount of available Al, to only generate Ti metal, but recovery of such metal would be extremely difficult as it will be in the form of small solid particles dispersed in the molten salt. On the other hand, excess Al in the system gives rise to the formation of TiAl₃, as seen above. In the EDS analysis, when factoring the minor elements that were detected in some of the area such as oxygen and silica (all less than 10 wt%) the remaining elements, Ti and Al would make up the intermetallic area; the reported values for Ti was approximately 39wt% -50wt% with the balance being Al. Taken into account the wt% of the elements in intermetallic alloys provided in Table 4-2, the alloys that would be present in the sample would be a combination of TiAl and TiAl₃ with the bulk of the material being TiAl₃. The XRD analysis have been reporting the presence of Al1.1-Ti0.9, which is in agreement with the EDS results, but phase diagrams do not show this phase. The phase diagram does however show that at the given composition of materials that were used, it does seem viable that both TiAl and TiAl₃ are present.

<table>
<thead>
<tr>
<th>Table 4-2 Weight percentage of individual elements within the intermetallic compound of Ti-Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt% Ti</td>
</tr>
<tr>
<td>TiAl</td>
</tr>
<tr>
<td>TiAl₃</td>
</tr>
<tr>
<td>Ti₃Al</td>
</tr>
</tbody>
</table>

Even though reduction of titania with aluminum is thermodynamically favorable, adding a potential pushes the reaction forward towards greater extent of reduction. Therefore, the next step was to see how the same system would react to an applied potential.

4.1.4 Electrolysis (Applied Potential)

For these experiments, the aluminum at the bottom of the bath was intended to act as the cathode, so any reduced Ti would dissolve in it and is not reoxidized by the evolving gases. As described earlier, Al reduces TiO₂ chemically as well and the applied potential is expected to only promote the reaction. A potential of 3-3.1V was applied, leading to a starting current of 10-12A that would slowly decrease as the experiment continued. The current drops to 0A after 3h because the anode would lose contact with the bath due to consumption and the anode had to be lowered into the melt again.
It was found that applying the potential would change the shell-like formation of the metallic alloy to small particles dispersed in cryolite, see Figure 4.8. There were varying quantities of titanium to aluminum in the metallic alloy depending on the materials mix, suggesting that different ratios of aluminum pellet and titanium oxide could affect the product composition. The effects of Ti:Al ratio in the system, as well as electrolysis time were investigated and will be discussed in the following sections.

4.1.4.1 Increasing Ti:Al Ratio

The ratio of Ti to Al increased from 15wt% to 40wt% and 70wt% respectively in the three experiments, identified as “a”, “b” and “c”, as shown in Table 4-3. In the presence of aluminum, the titanium oxide (TiO₂) changed composition (Ti₂O₃ or TiO and even Ti₂O, Figure 4.8) and reacted with aluminum, forming TiAl₃ or Al₁.1-Ti₀.9 (XRD) as will be seen later (Figure 4.18). With higher ratios of aluminum, more TiAl₃ would be found in the system. TiAl would be found in the system along with TiAl₃ in the first two experiments. This follows the Al-Ti phase diagram, with the increase of Ti content in the system; the alloy would shift from TiAl₃ to TiAl at constant temperature. The following three experiments were carried out for 4h at 1050°C.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>“a”</th>
<th>“b”</th>
<th>“c”</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti:Al ratio</td>
<td>15:85</td>
<td>40:60</td>
<td>70:30</td>
</tr>
<tr>
<td>Wt% TiO₂</td>
<td>5.79</td>
<td>9.93</td>
<td>27.3</td>
</tr>
<tr>
<td>Wt% Al</td>
<td>11.6</td>
<td>5.10</td>
<td>4.24</td>
</tr>
<tr>
<td>Wt% Na₃AlF₆</td>
<td>82.6</td>
<td>85.0</td>
<td>68.4</td>
</tr>
<tr>
<td>mol% TiO₂</td>
<td>8.09</td>
<td>17.3</td>
<td>44.0</td>
</tr>
<tr>
<td>mol% Al</td>
<td>47.9</td>
<td>26.3</td>
<td>19.1</td>
</tr>
<tr>
<td>mol% Na₃AlF₆</td>
<td>44.0</td>
<td>56.4</td>
<td>39.5</td>
</tr>
</tbody>
</table>

For experiment “c”, 27.3 wt% of TiO₂ was added into the melt, and the top surface of the melt was rough compared the other experiments (Figure 4.8b vs. Figure 4.8c), suggesting that the bath may have been oversaturated and did not reach a fully liquid state. This data coincides with Madhavan et al.[47] who stated that there was a eutectic point present at 6 wt% (8.75 mol%) of TiO₂ around 981.5°C and the liquidus temperature increases drastically thereafter. The data provided gave values up to 8 wt% (~15mol%), showing a liquidus temperature of 1040°C.
Based on this, extrapolations show that the composition in first two experiments would fall above liquidus line, but the third experiment would still be in a mixed solid-liquid state. Therefore, in experiments “a” and “b”, TiO₂ could fully dissolve in the cryolite and react with aluminum. It can be seen in experiment “a”, there exist a large chunk of material at the bottom of the melt that was mounted in epoxy. The white layer was cryolite that could not be removed with AlCl₃. The XRD analysis showed that along with cryolite, TiAl₃, TiC, and TiO was also detected. The SEM was also employed for analysis and it was found that high levels of titanium were present at the bottom of the sample and other parts of the sample had Al₂O₃ and equal atomic percentages of Ti and Al. A plausible conclusion of detecting high amounts of Ti without carbon could relate to the limitation of the machine and that the sample had to be carbon coated to ensure no charging of the sample, so any carbon peaks were negated from the EDS.

In experiment “b”, two sections were analyzed in the XRD. As shown in Figure 4.9, a section of the bath was taken because it resembled an agglomerate of a metallic phase and also the pellet like shape was taken from the bottom of the bath.
The globule was analyzed with XRD and found to be $\text{Al}_{1.1}\text{-Ti}_{0.9}$ and cryolite, Figure 4.10. The pellet was also analyzed with XRD and showed $\text{TiAl}_3$, $\text{Ti}_3\text{O}_5$, $\text{TiF}_3$ and $\text{Al}_{1.1}\text{-Ti}_{0.9}$ as seen in Figure 4.11. The pellet at the bottom of the bath was approximately 1 cm in diameter, which was significantly smaller than the material at the bottom of experiment “a” (~2 cm in diameter). This would likely be explained because experiment “b” had less Al to start than experiment “a”, so there less areas that were Al rich. Furthermore, experiment “b” had a higher ratio of $\text{TiO}_2$, which could make the bath more viscous, helping explain the globule observed in experiment “b”.

The most significant difference between experiments “a” and “b” was the increase in $\text{TiO}_2$ content from 5.79 wt% to 9.93 wt% and a decrease in the Al content from 11.6 wt% to 5.1 wt%, while keeping the cryolite level at about 85 wt%. These changes to the bath shows what occurs when either $\text{TiO}_2$ or Al become the limiting reagent. In experiment “a”, when the $\text{TiO}_2$ was limited, there was $\text{TiAl}_3$ denderites in Al rich shell around Al, $\text{Al}_2\text{O}_3$ and $\text{TiAl}$ core with no $\text{TiAl}_3$ globules suspended in the cryolite bath. In experiment “b”, there was less Al to react with the $\text{TiO}_2$, so it appears that the Al had to diffuse in the cryolite to react with Ti that was dissolved in the bath, but did not have a high enough density to fall back to the bottom of the melt. The globule was very porous. It was noticed that experiment “b” still had a pellet at the bottom of the
bath that resembled the layer at the bottom of experiment “a” suggesting that there might have been some Al remaining unreacted. These observations are in agreement with experiment “c” as well, as no pellet was found at the bottom of the bath and no TiAl$_3$ was present in the bath.

Figure 4.10 XRD spectrum of "square" sample from experiment "b"; area #1 in Figure 4.9

Figure 4.11 XRD spectrum of pellet in experiment "b"; area #2 in Figure 4.9
In experiment “c”, the TiO₂ content was increased to 27.3 wt% and the Al was kept around 5 wt%, making sure that the Al would be the limiting reagent. The results showed partially reduced Ti in the form of TiO and Ti₂O₃ (Al doped). Furthermore, the XRD also picked up Al₂O₃. There was no trace of TiAl₃ or any form of TiₓAlᵧ. When the crucible was cut, three different regions with different color and texture were present (see Figure 4.12) with no metallic phase at the bottom of the bath as compared to the other experiments.

![Crucible with three regions](image)

**Figure 4.12** Experiment “c”, Excess TiO₂ in bath; only partially reduced titania in the form of TiO and Ti₂O₃; anode is not consumed.

The XRD results for Figure 4.12 showed that the top section which exhibited a dark blue color analyzed for trace of Ti₂O₃ (Figure 4.13), and the middle section that was a brownish color was found to be TiO (Figure 4.14). There was a bottom section, that was a duller brown color which consisted of Al, TiO and Al₂O₃ (Figure 4.15).

The XRD results suggest a gradient of oxygen in the crucible from top to bottom (where Al is) so that the top layer contained Ti₂O₃, the middle layer had TiO, and the bottom layer had TiO and Al. No metallic Ti was produced in this experiment to form Ti-Al alloy, persuambly because of insufficient Al in the system. The Al peaks of the XRD pattern are weak, indicating small amounts of remaining Al. Therefore, it can be argued that the Al could not fully engage in the reactions and when it did, it was consumed to capture oxygen from partial reduction of TiO₂ to
Ti$_2$O$_3$ and TiO. In this experiment, excess amounts of TiO$_2$ and semi-liquid state may have led to a highly viscous electrolyte, that does not facilitate complete and rapid reactions, hence the oxygen gradient and residual Al.

**Figure 4.13** XRD pattern of material recovered from top of crucible (blue region)

**Figure 4.14** XRD pattern of material recovered from mid region of crucible (brown region)
Overall, when comparing experiments “a” and “b” to experiment “c”, it is obvious that a respectable ratio is required to observe solid formations in the bath. Also, with higher ratios of Al to Ti, there are higher chances of forming TiAl alloys (TiAl, TiAl₃, Al₁.₁-Ti₀.₉) rather than oxides (Al₂O₃). The trend of the reactions was that with decreasing amounts of Al compared to TiO₂, it is evident that a minimum amount of Al is required to obtain TiAl₃ because the Al will react with the oxygen before the Ti, as seen in the case of experiment “c” where no TiAl₃ was formed and as for increasing the amount of TiO₂, the most significant change was seen where the TiO₂ was increased from 9.9 wt% to 27.3 wt% and no metallic formation was found. In experiment “c”, distinct phases were present as there were different colored powders at different heights of the bath as the Al was slowly working through the bath, and gradually reacting with titania. The level at which the reactants were reduced seems to suggest that the bath may not have been completely molten and solid state diffusion may have been involved. Longer times may be required to allow for reaction to complete. Also, with the high titanium oxide content, it shifted the melting point to a temperature past the operating temperature (needs to be a semicontinuous process). Experiments “a” and “b” were somewhat different because Al was in
excess in the bath and the dissolved Ti would be diffusing to the Al to form the intermetallic compound. Therefore, an optimum amount of titania and aluminum is needed to achieve a good working melt to be able to see intermetallic formation. The next step was to investigate the possibility of extending the electrodeposition time in the melt.

Initially, experiments were run for 4h because when experiments were run for longer periods of time (15h), the cryolite would evaporate and condense on the furnace side walls. Caps were devised as a method to contain the evaporated cryolite. Figure 4.16 is an analysis of an experiment that used a gypsum lid. In the end, it was found that the gypsum lid collapsed into the bath and introduced Ca in the bath, shown in #1 of Figure 4.16. Area #1 was analyzed to be mostly Na₃AlF₆ and CaF₂.

![Figure 4.16 Cross section of crucible showing points of interest for XRD analysis; shows area of reactions](image-url)
The areas in the melt were analyzed with the XRD, where Figure 4.17 and Figure 4.18 are XRDs of the samples taken from areas #2 and #3 respectively. In Figure 4.17, it can be shown that there were many different phases of Ti₅Al₂ present in the melt. This XRD was representative of the samples collected at the bottom and the side walls of the crucible. It was hard to identify the exact composition of the metal alloy, as the peaks of different alloys are very similar and some of them overlapping, but the XRD was able to confirm that a metal compound was present. The peaks for Ti₅Al₂ (AlTi, AlTi₃, TiAl₃, Al₁₁.1-Ti₀.9, Al₆Ti₁₉) are very close to one another with some peaks overlapping. However, when the sample was analyzed with EDS, the percentages of the elements present resemble closely to Al₁₁.1-Ti₀.9.

![XRD Spectrum](image)

Figure 4.17 Representation of findings in the melt; different phases of AlₓTiₙ in and around the melt mixed with cryolite and calcium byproducts from the plaster
Figure 4.18 found the floating globule in the cryolite to be mostly TiAl and Al$_2$O$_3$. This globule, represented by #3 in Figure 4.16 was located near the bottom of the melt and not contacting the carbon anode rod or carbon crucible cathode. The CaF$_2$ is from the cryolite melt reacting with the plaster coating on the side walls.

![XRD spectrum](image)

**Figure 4.18** XRD spectrum of reflective gray globule in Figure 4.16 b; showing the formation of AlTi and Al$_2$O$_3$

4.1.5 Replacing Aluminum with Alumina (Na$_3$AlF$_6$-TiO$_2$-Al$_2$O$_3$)

This experiment was performed in an attempt to co-deposit Al and Ti. By replacing aluminum from the last experiment with aluminum oxide, it can be assured that any alloy formed would be produced from the metal obtained from aluminum electrolysis and that it would be possible to reduce both oxides together. This experiment was run at 3V for 24h with the following current response profile.
The current started at 10A and fluctuated for five minutes before stabilizing and then slowly dropping. The physical constraints of the experimental setup meant that the anode would have to be lowered further into the melt when the anode was consumed. The indicator used to identify that the anode was being consumed was the current dropping over time. The first time the anode was lowered was 210 min into the experiment and it was moved approx. 25 mm into the melt. The second time the anode was moved another 25 mm at 560 min into the experiment. The third time, the anode could not be lowered anymore and it was noticed that the current increased. It was found that, after the experiment, the cryolite would creep up the sidewalls of the crucible and there would be very little bath left for the reaction to occur. The last 800-900 min of electrolysis may have been unnecessary because looking at the current profile and the end result of the bath; the cryolite had run up the sidewalls of the crucible leaving very little left at the bottom of the bath for reduction to occur. This case did not result in a metal alloy pellet at the bottom of the bath, but powders of different colors embedded in the cryolite, as seen in Figure 4.20. These sections were analyzed with XRD and it was found that there was mostly TiO and alumina in cryolite, Figure 4.21. The color of the powder was similar to the experiment with excess titania from above.

Figure 4.19 Variations of current with time
Figure 4.20 A section from the bottom of the crucible showing powders embedded in cryolite; powders were analyzed to be TiO and Al$_2$O$_3$

It is clear that in this experiment, similar to the case of Al-free run, only partial reduction of TiO$_2$ has taken place. If any Ti or Ti-Al were formed, they would be finely dispersed in the melt and in such low quantities that could not be detected. Al was added in the next set of experiments to facilitate forming a pool of metal that would collect such particles.

Figure 4.21 XRD pattern of reflective veins in molten salt bath
### 4.1.6 Addition of both Al and Al$_2$O$_3$ (Na$_3$AlF$_6$-TiO$_2$– Al-Al$_2$O$_3$)

Since the previous set of experiments did not generate an alloy or metal, either a large overpotential is required to reduce the alumina or an initial amount of aluminum may be required to collect any deposited metal and keep it from dispersing in the melt. In this experiment, ten percent of the total aluminum present in the bath was in the form of pellets and the rest was from alumina powder. The level of alumina and titania were based on their solubility limits, just enough was added to ensure everything was soluble without excess amounts which would be caught in the slag and potentially increase the melting temperature. The Al and Ti contents were similar to the conditions of experiment “a” where approximately 6 wt% TiO$_2$, 11 wt% Al (where 90% comes from alumina) and a balance of Na$_3$AlF$_6$.

Figure 4.22 is representative of how the materials in the bath interact. In Figure 4.22a, the white substance is cryolite and the space that it occupies is where the cathode was placed during the experiment. The fact that it is possible to see the cathode impression, may suggest a viscous bath. In Figure 4.22b, the crucible was cut into ⅛ and there were fine metallic particles present on top of the reformed Al pellet, which may suggest that the titania did react with the pellets.

The metallic phase was easier to detect with the BSE rather than with the conventional SEM, shown in Figure 4.22c. SEM/EDS was done on these particles and it was proved to be TiAl particles based on the composition shown in Figure 4.24. This will be discussed in a later section.

Figure 4.22d is an SEM image of the bottom of the melt where there was an outline of the original Al pellet. A BSE image and EDS was taken of the outline and it was found to be cryolite but with a different structure, as shown in Figure 4.22f. This outline may have been caused by the difference in melting temperature of cryolite and aluminum because the aluminum would be in the molten state at 660°C whereas pure cryolite would melt at 1012°C meaning that there would be a liquid drop in solid cryolite as the crucible is cooling.

The dark regions on the SEM/BSE, as seen in Figure 4.22e are voids filled with epoxy during the mounting process showing that the bath was actually very porous.
Figure 4.22 a) Top layer of cryolite and built-up around the anode area; b) Cross-section cut, found aluminum pellet that was partially reacted and left an outline of the original size of pellet; c, d, e) BSE images of image b) showing the aluminum pellet and the alloy distribution within cryolite; f) Close up of the outline around aluminum pellet.
The alloy phase in the sample was located about half a centimeter above the aluminum pellet and spanned about 4mm high, as seen in Figure 4.22c, with the particles sizes from 5µm-100µm shown in Figure 4.23, spread sparsely across in disc shape around the anode. The particles got slightly sparser further away from the bottom of the bath. The alloy that formed was easy to crush into powder form when dry, meaning that the particles were not sintered together, but all nucleated individually. Both XRD and EDS confirmed that the metallic substance was TiAl (Figure 4.25); the EDS gave the percentage of each element, which was consistent with TiAl in Figure 4.23. Ti₃Al was also found with the XRD in the more dense area, but that was only found near the walls in the crucible rather than in the bulk during EDS analysis.

![Image](image_url)

**Figure 4.23 AlTi particles embedded in cryolite ranging from 5µm-100µm in diameter**

EDS was performed on the metallic area labeled # 1 in Figure 4.23 and elemental makeup of the area was representative of TiAl, as shown Figure 4.24. Further analysis using XRD was performed and AlTi₃ and TiAl were found in the sample. The darker regions are of cryolite marked by #2.
Figure 4.24 EDS analysis of the bright phase in Figure 4.23

For XRD, the metallic area was cut into two sections, the top half which was sparser and a bottom half which was denser. The TiAl was found in the sparse areas and AlTi$_3$ was found in the denser areas, as per the XRDs in Figure 4.25 and Figure 4.26, respectively. Al$_2$O$_3$ was found in both samples along with cryolite. The alumina in the sample would explain the oxygen that was detected in the XRD samples.

Figure 4.25 XRD pattern of metallic-looking particles.
Figure 4.26 XRD pattern of the dense region of the sample.

The EDS shown in Figure 4.27 revealed the weight percentage of the elements being close to Ti₃Al near the walls in the crucible by # 3 in Figure 4.28 where there is a 10-12µm layer of on the wall of the crucible.

Figure 4.27 EDS of Ti₃Al build up on the sidewall of crucible; percentage of Ti and Al are closer to Ti₃Al than TiAl
The amount by the sidewall was too small to collect but it should be noted that the titanium did not react with the carbon and remained as Ti₃Al. Oxygen was also detected on the crucible side walls, which could mean that there was Al₂O₃ and Ti₅O₇ present. It is more plausible that Al₂O₃ is present over Ti₅O₇ because of higher affinity for O by Al than Ti. The other regions of the EDS were of carbon, broken off TiAl and cryolite in #1, #2, and #4 respectively.

![Electron Image 6](image)

**Figure 4.28** Titanium/aluminium/oxygen collected as a very thin layer ~10-12 µm thick along the crucible wall

### 4.1.7 Relation of Products to the Phase Diagram

Alloys of aluminum and titanium (Al₃Ti, Al-Ti) can be formed at 1050°C, as shown by the arrow in the phase diagram in Figure 4.29. For all mixtures containing Al and TiO₂, the final product showed Al₃Ti and different forms of titanium oxide. The ratio of Ti to Al was 60 wt% to 40 wt% which would yield AITi if the reactions went to equilibrium. Some samples showed AITi which is mostly likely explained by the middle of the phase diagram where AITi is present. As the
concentration of Ti increases, TiAl₃ is slowly converting to TiAl after going through different intermetallic phase of TiₓAlₙ. Given that TiAl, TiAl₃ and Al₁.1-Ti₀.9 phases all exist in the XRD patterns; it is evident that the bath did not fully reach equilibrium because according to the phase diagram presented, if the experiment reached equilibrium, there would only be TiAl present, according to the composition of the bath. TiAl₃ and other intermetallic alloys present in the bath prove that reactions are still occurring and that this is a kinetically slow process, which would indicate that solid state reactions are occurring after the initial formation of TiAl₃.

Figure 4.29 Al-Ti Phase Diagram[51]
Chapter 5

5 Conclusion

The possibility of producing pure titanium from titanium oxide through molten salt electrolysis was studied. Cryolite ($\text{Na}_3\text{AlF}_6$) was the preferred molten salt because of its ability to dissolve titanium oxide making liquid state diffusion possible at lower operating temperatures ($1050^\circ\text{C}$) and it is a well-studied salt. If this process is successful, it would be beneficial to convert Al processing plants to include TiO$_2$ refining. TiO$_2$ was the starting material of choice because currently 90% of all titanium recovered from the ore is in this form and is used as additives in paint. This makes for a good candidate for further refining.

Initially, the bath composition was only cryolite and TiO$_2$ and later Al and Al$_2$O$_3$ was added to the bath in an attempt to co-deposit the metals from their oxides. The bath was charged into a resistance tube furnace in an argon environment and heated to $1050^\circ\text{C}$ for 4hr and 15hr. A potential was applied across conducting rods to allow for electrolysis to occur. The main composition of bath was approximately 85wt% Na$_3$AlF$_6$, 5-10wt% TiO$_2$, and balance of Al. There was one exception where 27 wt% TiO$_2$ was used, which reduced the Na$_3$AlF$_6$ content leaving the Al at approximately 5 wt%. The experiments were then allowed to cool and samples were taken from it and cleaned with AlCl$_3$ to remove Na$_3$AlF$_6$ before analysis with XRD and SEM/EDS. Based on the studies performed, the following conclusions were reached:

- Pure titanium could not be obtained during electrolysis as titanium has a high affinity for oxygen and only partially reduced titanium oxide phases (Ti$_x$O$_y$) were found with XRD
- Aluminum was added to the bottom of the bath to act as the cathode and to capture the reduced Ti atoms before it re-reacted with the oxygen; titanium aluminum compounds are found in the bath (TiAl$_3$, TiAl, and Ti$_3$Al) along with alumina (Al$_2$O$_3$)
- Saturation limit exist for TiO$_2$ where the bath melting temperature will be higher than the operating temperature and Ti and Al will not react with one another (27wt% TiO$_2$ was used in this study);
- Electrolysis of both Ti and Al simultaneously was attempted with no success of recovering Al from Al$_2$O$_3$. 
Chapter 6

6 Future Work

This preliminary and exploratory research showed that alloys of Al-Ti with varying ratio of Ti/Al could be generated when Al metal is present in the system. Very little quantitative work was carried out as the purpose of this study was for proof-of-concept rather than optimization. The following studies are suggested as future steps in further advancing our understanding of this method of Ti production.

1. Elements more noble than Ti be used as alloy-maker (such as Cu) to eliminate the reducing effect associated with Al, so one can see only the effect of trapping Ti in an alloy. In other words, the true capability of the electrolysis process in reducing TiO$_2$ can only be investigated in the presence of no other metal, or metals more noble than Ti.

2. It would be interesting and desirable to separate Al and Ti in this alloy to increase the Ti/Al ratio so it can be used as a master alloy directly, or ideally generate pure Ti. One could for example attempt an electro-refining process in which the alloys (e.g. TiAl$_3$) are placed at an anode of a motel salt based cell; by applying a small potential and depending on the melt composition, one metal would precipitate in cathode, and the other settle below the anode. There has been an attempt to recover the Ti onto a Ti cathode in the cryolite melt, but more studies have to be done to find the underlying effect as the Ti was dissolved in the cryolite.

3. Possibility of producing Ti or its alloys from molten slags, such as CaO-TiO$_2$ is a valuable investigation. With slags, the operating temperature could be substantially higher as evaporation of electrolyte is not issue, meaning that liquid cathodes with much greater Ti concentrations or even possibly pure liquid Ti could be generated. For example, a system containing Fe-Ti or Cu-Ti as liquid cathode in the presence of a CaO-TiO$_2$ electrolyte is suggested as a starting point.
References


Appendix A Ellingham Diagram[54]