Alternative Al production methods: Part 1 - a review of indirect carbothermal routes

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Abstract
The production of Al from its ores at present relies on the Bayer (alumina production) and the Hall-Heroult (Al production) process. The cost associated with alumina production and apparent disadvantages of the Hall-Heroult process have led to intensive research to find alternative routes for Al production. The direct carbothermal reduction process has been thoroughly investigated as an alternative technique. Another alternative includes the indirect carbothermal reduction route where alumina (or aluminous ores) is first reduced to intermediate Al compounds before reduced further to Al. The present study reviews and provides systematic thermodynamic analyses of alternative Al production routes. In this paper (Part 1), a comprehensive review of alternative Al production techniques focusing on the indirect carbothermal reduction routes is presented. These include carbochlorination, carbonitridation and carbosulphidation routes for the formation of intermediate Al compounds, followed by various Al extraction processes.

Keywords
indirect, carbothermal, Al, production, routes, methods, alternative, part, 1, review

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Alternative Al Production Methods:

Part I – A Review of Indirect Carbothermal Routes

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ABSTRACT

The production of aluminium from its ores at present relies on two processes: the Bayer process (alumina production), and the Hall-Heroult process (aluminium production). The cost associated with the alumina production and apparent disadvantages of the Hall-Heroult process have led to intensive research to find alternative routes for aluminium production. The direct carbothermal reduction process has been thoroughly investigated as an alternative technique. Other alternatives include the indirect carbothermal reduction process where alumina (or aluminous ores) is reduced to intermediate Al-compounds before further reduced to extract aluminium. The current study reviews and provides systematic thermodynamic analyses of alternative aluminium production routes. In this paper (Part I), a comprehensive review of alternative aluminium production techniques focusing on the indirect carbothermal reduction routes is presented. These include carbochlorination, carbonitridation and carbosulphidation routes for the formation of intermediate Al-compounds, followed by aluminium extraction processes.

Keywords: carbothermal reduction of alumina, carbochlorination of alumina, carbonitridation of alumina, carbosulphidation of alumina, thermal dissociation, electrolysis, disproportionation
1. Introduction

Aluminium is the most abundant metallic element in the Earth’s crust (about 8%) and the second most widely used metal next to steel. The production of aluminium has increased by nearly four times in the last three decades\(^1\). Pure aluminium cannot be found in nature because of its high affinity to oxygen. In general it is found in a variety of minerals combined with various elements such as silicon, oxygen, phosphates, fluorine, and hydroxides\(^2-5\). In the last century a number of methods have been developed to extract aluminium from its ores. The current commercial production method relies on two energy-intensive processes developed in the late 1800s: the Bayer process which produces pure alumina from bauxite ore, and the Hall-Heroult electrolysis process which produces aluminium metal from alumina. The cost of the Bayer process represents about 27% of the cost of aluminium production\(^6\) and the Hall-Heroult process uses about three quarters of the total energy requirement, though these numbers vary depending on the specifics of the ores and sources of energy used.

The Bayer process is the principal industrial technique to refine bauxite to pure alumina. There has been little changes to the basic process since the first plant opened in 1893\(^7\). In this process, bauxite containing typically 10-30 wt% Fe\(_2\)O\(_3\), 4-8 wt% SiO\(_2\), and 2-5 wt% TiO\(_2\) as major impurities\(^8\) is dried, ground, digested in sodium hydroxide under pressure. Impurities are separated by filtration, before an alumina hydroxide is precipitated and calcined to produce commercial alumina. The relatively high purity alumina produced from the Bayer process is then transferred to the Hall-Heroult electrochemical cell for electrolysis.

The Hall-Heroult process was patented in 1886\(^9\) and the basic process layout remains unchanged except for the form of the carbon anode\(^10\). There has been significant improvement in the process over last hundred years, through increasing cell size, greater automation and control, and improved control of emissions. Tarcy et al.\(^11\) provides an outline of the improvements in a recent review, showing that the overall energy usage per kg of metal has decreased from typically over 30 kWh/kg Al in 1914 to below 14 kWh/kg Al by 2000.

In the Hall-Heroult process aluminium metal is extracted through electrolysis of purified Al\(_2\)O\(_3\) dissolved in NaF-AlF\(_3\) (cryolite) solution according to the following overall reactions:

\[
0.5 \text{(Al}_2\text{O}_3) + 0.75 \text{C} \rightarrow \text{Al}(l) + 0.75 \text{CO}_2(g) \quad (1)
\]

\[
0.5 \text{(Al}_2\text{O}_3) + 1.5 \text{C} \rightarrow \text{Al}(l) + 1.5 \text{CO}(g) \quad (2)
\]

In this process, liquid aluminium is produced at the bottom of the cell and CO and CO\(_2\) gases are evolved from the bath. The Hall-Heroult process also generates greenhouse gasses such as
CF₄ and C₂F₆ from the carbon electrode and reactions with liquid cryolite (Na₃AlF₆). Per fluorocarbons (PFCs) may also form during the so-called anode effect when the electrolyte becomes depleted in alumina. In general, the process has high capital costs, low productivity compared to other metallurgical processes and consumes significant energy (from 12.9 to 15 kWh/kg Al). The production of each kg of Al consumes between 0.4 to 0.5 kg of carbon in the form of anodes and in total, aluminium production contributes to 2.5% of the world anthropogenic CO₂ equivalent emissions. This value will vary from plant to plant as it depends on energy source, the details of the cell and quality of the feed materials.

The apparent disadvantages of the Hall-Heroult process have led to numerous researches to develop alternative routes throughout the 20th and early 21st centuries. The most important alternatives that have been envisaged include modified Hall-Heroult process utilising inert anodes, direct carbothermal reduction of alumina, and indirect carbothermal reduction of alumina (e.g. formation of AlCl₃ intermediate followed by Al extraction in the Alcoa process).

In this Part 1 paper, a comprehensive review of various aluminium production methods, focusing on the indirect carbothermal reduction routes, is presented. There have been a number of major review papers on Al production routes. In 1964, Stroup provided a detailed review on the carbothermal production processes of aluminium. Russell provided another major review on various new technologies in 1981, including review and progress on the development of Alcoa processes. The current paper briefly reviews the recent development in direct carbothermal routes followed by systematic reviews of different indirect carbothermal reduction routes. In the Part 2 of the paper, systematic thermodynamic analyses of selected indirect carbothermal reduction routes are presented. These include evaluation of Gibbs free energy formation and equilibrium calculations of various intermediate Al-compounds formation and extraction of aluminium from these compounds.

2. Direct Carbothermal Reduction Processes

The direct carbothermal reduction of alumina to aluminium has potential for greater productivity, lower capital investment, less consumption of electric power, and lower overall greenhouse gases emission, compared to the Hall Heroult process. It is well established that direct carbothermal reduction of iron oxide, through blast furnace technology, offers far greater productivity and energy efficiency than any comparable electrolytic process. It is this desire to duplicate the merits of pyrometallurgy processing to aluminium that has driven interest in carbothermal reduction of alumina. The overall reactions for carbothermal reduction of alumina can be presented as:
\[
\text{Al}_2\text{O}_3(s) + 3\text{C}(s) = 2\text{Al}(s) + 3\text{CO}(g) \quad (3)
\]

\[
\text{Al}_2\text{O}_3(s) + 3\text{CH}_4(g) = 2\text{Al}(s) + 3\text{CO}(g) + 6\text{H}_2(g) \quad (4)
\]

These two reactions are thermodynamically favoured above 2057°C and 1497°C, respectively\textsuperscript{19}. Although these reactions look simple, in practice these are difficult to achieve with high Al yield. The reaction steps are not straight forward as the aluminium oxide forms intermediate and volatile sub-compounds during the process. During cooling down of the products, mixture of carbide and oxycarbide can form due to reactions between the products. The chemistry and thermodynamics of the Al-C-O system have been studied extensively\textsuperscript{16-17, 19, 21-32}.

Recent developments in carbothermic production of aluminium have evolved in the direction of a two-stage process. Cochran and Fitzgerald\textsuperscript{33} invented a stack-type reactor in which Al\textsubscript{2}O\textsubscript{3} and C was reacted in a high-temperature upper reaction zone and produced liquid mixture of Al\textsubscript{2}O\textsubscript{3} and Al\textsubscript{4}C\textsubscript{3} which was then transferred to a lower reaction zone for Al extraction. Alcoa and Elkem companies thoroughly investigated carbothermic production of aluminium using the stack-type reactor\textsuperscript{34-40}(ARP-Advanced Reactor Process). Alumina was carbothermally reduced in the first reaction compartment of a vessel to produce a 50% Al\textsubscript{2}O\textsubscript{3}-50% Al\textsubscript{4}C\textsubscript{3} slag melt at approximately 2000°C. Further reaction took place between alumina and aluminium carbide in the second compartment at approximately 2200°C to produce an aluminium-carbon alloy. The reactions associated with each stage are given below:

\[
3 \text{ Al}_2\text{O}_3(s) + 9 \text{ C}(s) = (\text{Al}_4\text{C}_3.\text{Al}_2\text{O}_3) \text{ (l) + 6 CO}(g) \quad T = 2000^\circ\text{C} \quad (5)
\]

\[
(\text{Al}_4\text{C}_3.\text{Al}_2\text{O}_3) \text{ (l) = 6 Al (l) + 3 CO}(g) \quad T = 2200^\circ\text{C} \quad (6)
\]

The ARP included a method for vapour recovery for recycling the aluminium and aluminium sub-oxide vapours generated. Fruehan \textit{et al.}\textsuperscript{38} studied the mechanism and reaction rate of Al\textsubscript{2}O\textsubscript{(g)}, Al\textsubscript{(g)} with carbon source. They found that the rate of formation of Al\textsubscript{4}C\textsubscript{3} from Al\textsubscript{2}O and Al gases in CO is controlled by diffusion of the reactant gases through the Al\textsubscript{4}C\textsubscript{3} product layer. The two-zone method was also researched by Persson\textsuperscript{41}, and Dougan and Southam\textsuperscript{42}. Dmitriev and Karasev\textsuperscript{43} proposed an induction shaft furnace for Al\textsubscript{4}C\textsubscript{3} production from alumina. Then aluminium was extracted by electrolysis in the lower zone of the furnace.

Other recent developments include the vacuum carbothermic reduction currently being developed under the ENEXAL project\textsuperscript{44}. This process uses an electric arc furnace (EAF) with integrated shaft attachment. The EAF is the main reactor where liquid aluminium is produced and the shaft acts as condenser for the Al and Al\textsubscript{2}O vapours. By carrying out the process under vacuum, the formation of aluminium rich vapour will be favoured over liquid aluminium. The process can also be carried out at lower temperatures, e.g. 1500°C at 10 Pa
pressure. Preliminary experimental study has been carried out using a solar furnace to demonstrate the process. At temperatures 1027 to 1727°C and pressures 350 to 1200 Pa, Al (up to 19%) along with Al₄C₃ and Al₄O₄C can be produced upon condensation. It is unclear whether yield can be improved and whether the proposed process has potential for commercialisation.

Sayad-Yaghoubi proposed a carbothermic process for the production of aluminium carbide by injection of carbon and Al₂O₃ into superheated aluminium (> 1400°C). The reaction between the injected carbon with molten aluminium followed:

\[
4 \text{Al(l)} + 3 \text{C(s)} = \text{Al}_4\text{C}_3(l) \quad T > 1400^\circ\text{C} \quad (7)
\]

The formed Al₄C₃ attaches to Al₂O₃ and forming a mixture of Al₄C₃ - Al₂O₃. Aluminium was then extracted from this mixture in a separate zone through reaction given in Eq.6 at temperatures about 1700°C to 2000°C. This was done by maintaining a sufficiently low gas pressure in the second zone, e.g. by extracting the CO gas. Sayad-Yaghoubi also proposed various types carbonaceous materials (such as CH₄ and other hydrocarbons) and additional reactants (such Al scrap and dross).

Despite the developments to date and significant scientific and financial investment of resources, no processes based on direct carbothermal reduction have been successfully developed to full plant scale. Direct carbothermal processes have to date suffered generally from problems with yield, associated with the formation of other compounds other than aluminium.

3. Indirect Carbothermal Reduction Processes

Researchers and industry have also directed their attention to multi-stage process, in particular indirect carbothermal reduction of alumina. These types of processes involves two or more steps where in the first step (Stage 1) alumina or aluminium ores are converted to intermediate Al-compounds. The intermediate Al-compounds are then further reduced to aluminium metal in subsequent steps (Stage 2). This is schematically shown in Figure 1.

The following sub-sections review the various indirect production processes of aluminium, focusing on the carbochlorination, carbosulphidation and carbonitridation routes for the Stage 1 followed by various Al extraction techniques in the Stage 2.
3.1 Carbochlorination Route

This route involves the formation of aluminium chloride intermediate compounds from reactions of alumina and/or aluminous ores with carbon and chlorine sources. The production of volatile metal halides (including aluminium trichloride) from alumina has been known for many years, but most of the processes have difficulties in terms of operation and control. One of the earliest patented works in the production of aluminium trichloride was from Ferguson et al.\textsuperscript{50}, where they developed a continuous process using fluidised-mixture reactor. In the case of carbochlorination of alumina, the process can be represented by the reactions,

\begin{align}
\text{Al}_2\text{O}_3(s) + 3 \text{ C}(s) + 3 \text{ Cl}_2(g) &= 2 \text{ AlCl}_3(g) + 3 \text{ CO}(g) \quad (8) \\
\text{Al}_2\text{O}_3(s) + 3 \text{ CO}(g) + 3 \text{ Cl}_2(g) &= 2 \text{ AlCl}_3(l) + 3 \text{ CO}_2(g) \quad (9)
\end{align}

The chlorination temperature is in the range of 400 to 1000\textdegree C depending upon the reacting agents. There have been a number of studies on the chlorination of alumina investigating the effect of various kinetic parameters (chlorination media, partial pressure of gaseous components, particle shape and size and reactor design) on the reactions in the temperature range between 427 and 1027\textdegree C\textsuperscript{51-54}. Unless a high purity alumina source is used, other elements that are generally present such as iron, silicon, and titanium are also chlorinated and must be separated from the aluminium trichloride. Yuan et al.\textsuperscript{55} carried out study of carbochlorination of alumina in vacuum and reported that AlCl\textsubscript{3}(g) is formed at temperatures 1430 to 1580\textdegree C at pressures 40 to 150 Pa.

Grob and Richarz\textsuperscript{56} attempted to chlorinate alumina in kaolinitic clay in Cl\textsubscript{2} and CO gas mixtures. They found that the reactivity of alumina in the raw material increases when the material is first pretreated using ammonium sulphate (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4}(g) or sulphur trioxide SO\textsubscript{3}(g). At temperatures below 727\textdegree C, the chlorination rates were found to be comparable to those
reported for using pure gamma alumina as starting material. However above 727°C, SiCl₄ formed and interacted with alumina, leading to a decrease in the rate of aluminium chlorination.

Huapin et al.⁵⁷ produced aluminium trichloride from alumina through reaction with carbon and chlorine in alkali metal halides and alkaline earth metal halides molten salt baths (AlCl₃-NaCl-LiCl) between 400 and 950°C. Becker et al.⁵⁸ used a mixture of high purity activated carbon and alumina heated in bubbling chlorine between 500 and 775°C and was able to obtain 100% conversion to AlCl₃ vapour.

In 1971 Toth⁵⁹ patented a two-stage process for aluminium production where in the 1st stage, alumina was reacted with manganese chloride in the presence of carbon at temperatures 900 to 1300°C producing aluminium trichloride and manganese, through the reaction:

\[
\text{Al}_2\text{O}_3(s) + 3 \text{MnCl}_2(l) + 3 \text{C}(s) = 3 \text{Mn}(l) + 2 \text{AlCl}_3(g) + 3 \text{CO}(g)
\]  

Wyndham et al.⁶⁰ and Lippman et al.⁶¹ (of Toth Al Corporation) used alumina based ores as the source for aluminium. In the case of alumina-silica ores, the reaction was carried out in the presence of sulphur to improve the halogenation. Sulphur acted as a catalyst and the process could be carried out a temperature as low as 400°C through this reaction:

\[
\text{Al}_2\text{O}_3.2\text{SiO}_2(s) + 7\text{C}(s) + 7 \text{Cl}_2(g) + \text{Sulphur} = 2 \text{AlCl}_3(g) + 2\text{SiCl}_4(g) + 7\text{CO}(g)
\]

T = 400 to 1000°C  

There are other processes for aluminium trichloride production, including various aluminium extraction techniques from the chloride. Table 1 summarises selected processes and technological development associated with the chloride route (both the Stage 1 and 2).

### 3.2 Extraction of Aluminium from Aluminium Trichloride

The common routes for extracting aluminium from its chlorides are through disproportionation and electrolysis reactions. Other routes include distillation and direct reduction with other metals.

**Disproportionation of Aluminium Halides (including Chlorides)**

Willmore⁶² (Alcoa) discovered that AlF₃ and several other fluorine compounds selectively distil aluminium at 900-1300°C. Klemm and Voss⁶³ indicated that this occurs because of a formation of a monovalent compound (in this case AlF) at a temperature around 1200°C. This compound was then disproportionated at a lower temperature of around 800°C according to the following reaction:
3 AlF\(_{(l)}\) = 2 Al\(_{(s)}\) + AlF\(_3\)\(_{(s)}\)  \hspace{1cm} (12)

In this process the aluminium condensed as a fine powder, mixed with solid AlF\(_3\). Therefore further process using molten-flux was necessary to separate and agglomerate the aluminium. It was then found that the above reaction also occurs with other aluminium halides. The halide formation has been the basis of aluminium production and refining process using various aluminium halides and other sub-compounds. Belyayev and Firsanova\(^{64}\) conducted a survey on various aluminium sub-compounds and concluded that subfluoride and subchloride provided the most potential for practical refining processes.

Gross\(^{65-66}\) in 1944 proposed a process using AlCl\(_3\) where AlCl\(_3\) vapour was passed through a bed of impure crushed aluminium alloy above 1000\(^{\circ}\)C and aluminium was extracted and condensed by disproportionation at 700\(^{\circ}\)C according to the reaction:

\[ 3 \text{AlCl}_\text{(g)} = 2 \text{Al}_{(l)} + \text{AlCl}_3\text{(g)} \]  \hspace{1cm} (13)

The reformed AlCl\(_3\) was not condensed and was recirculated through the reaction furnace. As only aluminium was condensed, further separation process from the AlCl\(_3\) was not necessary.

In the 60’s, Alcan developed an alternative process for production of aluminium which involved carbothermal reduction of aluminous ores followed by monochloride purification\(^{20}\). This work was stopped due to problems associated handling of chlorides which included stress-corrosion cracking and inefficiency in separating manganese impurities. In the 70’s Othmer\(^{67-68}\) proposed a separation of aluminium from aluminous ores (bauxite, clays, feldspar) through carbochlorination (to form AlCl\(_3\)) followed by disproportionation or halogenation in a flash condenser. One of the recent works associated with carbochlorination of alumina followed by disproportionation was from Yuan et al.\(^{55}\). They carried out the carbochlorination in vacuum and observed AlCl\(_{\text{(g)}}\) at temperatures between 1430\(^{\circ}\)C and 1580\(^{\circ}\)C and pressures from 40 to 150 Pa. The AlCl\(_{\text{(g)}}\) was then disproportionate into Al and AlCl\(_3\)\(_{\text{(g)}}\) below 660\(^{\circ}\)C. They were able to obtain Al metal with average purity of 95.32 wt%.

**Electrolysis of Aluminium Trichloride**

It has been claimed that aluminium chloride electrolysis method is attractive both from an economic and technical point of view\(^{69}\). Ishikawa and Ichikawa\(^{70}\) argued that the potential advantages of aluminium chloride salt electrolysis process include:

1. chloride salts are much less corrosive than fluoride salts which results a longer cell life;
2. the electrolysis process requires a closed system which limit the emission of gasses;
(3) chloride salts have higher conductivities compared to the fluoride salts resulting lower energy consumption, higher power and current efficiencies;
(4) the electrolysis process has a very broad operational range of aluminium concentration which results in no “anode effect”;
(5) it is possible to design an electrolytic process cell with bipolar electrodes which results in a much more compact cell with increased production potential per unit volume.

In the 70’s, Alcoa developed alternative processes to produce aluminium which focused in three major directions: (1) direct carbothermal reduction of alumina and (2) indirect carbothermal reduction of aluminous ores that involved carbochlorination, monochloride purification and (3) electrolysis of aluminium chloride\textsuperscript{20}. The general schematic of the process routes is shown in Figure 2.

![Figure 2](image)

**Figure 2** – A schematic diagram showing the process routes considered by Alcoa\textsuperscript{20}.

Russell \textit{et al.}\textsuperscript{18} from Alcoa developed an aluminium chloride electrolysis process using NaCl-LiCl (50:50 wt%) electrolyte at temperatures from 660 to 730°C. They suggested operation with 1 to 15 wt% concentration of AlCl\textsubscript{3} in the bath. The anode-cathode distance in the process was approximately 25mm. They were able to improve the current efficiency (up to 80%) and avoid the formation of sludge from the impurities using these proposed operating conditions. Dell \textit{et al.}\textsuperscript{71}, improved the process by developing a new design with bipolar electrodes. This allowed the process to operate with a lower anode-cathode distance (less than 19mm). Alcoa developed the aluminium trichloride electrolysis route in the 1970s to a commercial level but halted operations in the 1980s, because of difficulties associated with production and handling of pure aluminium trichloride\textsuperscript{72}.
Ishikawa and Ichikawa\textsuperscript{70} from Nippon Light Metal electrolysed AlCl\textsubscript{3} in a molten AlCl\textsubscript{3}-LiCl-NaCl salt bath at 700\textdegree C. Additions of LiCl, CaCl\textsubscript{2} or MgCl\textsubscript{2} salts to the bath improved the electrical conductivity and the current efficiency. They were able to obtain 90 to 100\% current efficiency. Cohen \textit{et al.}\textsuperscript{73} from Pechiney proposed a continuous process through carbochlorination of alumina to form AlCl\textsubscript{3} followed by electrolysis in AlCl\textsubscript{3}-alkali/alkali-earth metal halides electrolyte. One of the recent works on the electrolysis of AlCl\textsubscript{3} was from Sharma\textsuperscript{74} where aluminium was produced through electrolysis in a chloride-fluoride salt bath at 750\textdegree C. The electrolytes used include Na\textsubscript{3}AlF\textsubscript{6}-NaCl-NaF, Li\textsubscript{3}AlF\textsubscript{6}-LiCl-LiF, and K\textsubscript{3}AlF\textsubscript{6}-KCl-KF.

Wilkening\textsuperscript{75}, produced aluminium through electrolysis where the bath consists of alkali halides and/or alkali earth halides. A mixture of aluminium oxide and carbon was used as a feed material. Different arrangements of the electrolytic cell were also proposed in the work. Tomaswick\textsuperscript{76} from Alcoa electrolysed Al\textsubscript{2}O\textsubscript{3} directly in a bath containing AlCl\textsubscript{3} and an alkali metal chloride (NaCl, LiCl, KCl, MgCl\textsubscript{2}, CaCl\textsubscript{2}, BeCl\textsubscript{2}, BaCl\textsubscript{2}). The process was carried at 300\textdegree C and aluminium was extracted as a solid metal at the cathode in a frozen layer of the alkali metal chloride.

Other Al Extraction Methods from Aluminium Trichloride

There are other methods used to extract aluminium from AlCl\textsubscript{3}. One example is through direct reduction using another metal (e.g., manganese). Toth\textsuperscript{59} patented a two-stage process where in the 1\textsuperscript{st} stage, alumina was reacted with manganese chloride in the presence of carbon producing aluminium trichloride and manganese, as given in reaction in Eq. (10). The aluminium was extracted by reacting AlCl\textsubscript{3} with manganese in the 2\textsuperscript{nd} stage at a temperature sufficient to reduce AlCl\textsubscript{3} to Al, according to the following reaction:

\begin{equation}
3 \text{Mn(l)} + 2 \text{AlCl}_3(g) = 2 \text{Al(l)} + 3 \text{MnCl}_2(l) \quad T = 900 \text{ to } 1300\textdegree C \quad (14)
\end{equation}

The flowsheet of the process is shown in Figure 3. Terry \textit{et al.}\textsuperscript{77} modified the process and carried out the reaction at lower temperatures (180 to 600\textdegree C) and higher pressures (0.1 to 3.04 MPa) using solid manganese to form solid aluminium directly according to the reaction:

\begin{equation}
3 \text{Mn(s)} + 2 \text{AlCl}_3(g,l) = 2 \text{Al(s)} + 3 \text{MnCl}_2(s,\text{soln}) \quad (15)
\end{equation}
Figure 3 – A flowsheet of Toth process.²⁹
Table 1: Summary of previous major works/patents in the Chloride Route (*p refers to patent; 1st stage refers to production of intermediate Al chlorides; 2nd stage refers to extraction of Al from the chlorides)

<table>
<thead>
<tr>
<th>Year</th>
<th>Author</th>
<th>Reactions and Parameters</th>
<th>Process Information</th>
</tr>
</thead>
<tbody>
<tr>
<td>2002</td>
<td>Tomaswick <em>76p</em> (Alcoa)</td>
<td>$\text{AlCl}_3$ molten bath with NaCl, LiCl, KCl, MgCl$_2$, CaCl$_2$, BeCl$_2$, BaCl$_2$. $T = 300^\circ\text{C}$ preferably (150-200$^\circ\text{C}$). Conc. of alkali metal chloride = 10-50 mol%, Voltage &lt; 2.0 volts. Current density &gt; 0.2A/in$^2$. Electrolysis of $\text{Al}_2\text{O}_3$ in a low temperature bath containing $\text{AlCl}_3$ and an alkali metal chloride. The bath is at 300$^\circ\text{C}$ and solid aluminium is produced at the cathode in the frozen layer of the alkali metal chloride. (2nd Stage)</td>
<td></td>
</tr>
</tbody>
</table>
| 2000 | Sharma *74p* | \[
\begin{align*}
\text{AlCl}_3 + 3\text{NaF} &\rightarrow \text{AlF}_3 + 3\text{NaCl} \\
3\text{NaCl} &\rightarrow 3\text{Na} + 1.5\text{Cl}_2 \\
\text{AlCl}_3 + 3\text{LiF} &\rightarrow \text{AlF}_3 + 3\text{LiCl} \\
3\text{LiCl} &\rightarrow 3\text{Li} + 1.5\text{Cl}_2 \\
\text{AlF}_3 + 3\text{Li} &\rightarrow 3\text{LiF} + \text{Al} \\
\text{AlCl}_3 + 3\text{KF} &\rightarrow \text{AlF}_3 + 3\text{KCl} \\
3\text{KCl} &\rightarrow 3\text{K} + 1.5\text{Cl}_2 \\
\text{AlF}_3 + 3\text{K} &\rightarrow 3\text{KF} + \text{Al} \\
\end{align*}
\] Electrolytes: Na$_3$AlF$_6$-NaCl-NaF; Li$_3$AlF$_6$-LiCl-LiF; K$_3$AlF$_6$-KCl-KF; Temperature: 750$^\circ\text{C}$ | Electrolytic production of aluminium metal from aluminium trichloride using chloride-fluoride salts bath. Aluminium fluoride is separated from the bath and electrolytically reduced to metallic aluminium. (2nd Stage) |
<p>| 1990 | Wilkening <em>75p</em> (VAW Vereinigte Aluminium-Werke AG) | Electrolyte melt: &gt; 50% consist of NaCl-KCl, 10-40% at least of cryolite, alkali fluorides and alkaline earth fluorides; $\text{AlCl}_3$ 3-5%. $T = 680-850^\circ\text{C}$ Production of aluminium from alumina through electrolysis where the bath consists of alkali halides and/or alkali earth halides. Alumina is charged as briquette with carbon which also acts as anode. Bipolar electrodes designs are also used. (2nd Stage) | |
| 1986 | Cohen et al. <em>73p</em> (Pechiney) | $\text{Al}_2\text{O}_3(s) + 3\text{Cl}_2(g) + 3\text{C}(s) = 2\text{AlCl}_3(g) + 3\text{CO}(g)$ Chlorinating gas: Cl$_2$, CCl$_4$, C$_2$Cl$_6$, phosgene Electrolysis: Conc. of $\text{AlCl}_3$ in bath = 10-40 mol% $T = 450-900^\circ\text{C}$ | Al production method through carbochlorination of alumina, followed by electrolysis of aluminium trichloride in a molten salt bath containing at least one alkali/alkali earth metal halides. Flowsheet of a continuous process. (1st &amp; 2nd Stage) |
| 1986 | Rao et al. <em>8p</em> (Washington Res. Foundation) | Example for MgF$_2$ catalyst: $\text{MgF}_2(g) = \text{MgF}_2(g)$ $3\text{Al}_2\text{O}_3(g) + 2\text{MgF}_2(g) + 9\text{CO}(g) + 9\text{Cl}_2(g) = 2\text{MgAl}_2\text{F}_2\text{Cl}_9(g) + 9\text{CO}_2(g)$ $\text{MgAl}_2\text{F}_2\text{Cl}_9(g) = \text{MgF}_2(g) + 3\text{AlCl}_3(g)$ The use of catalysts for carbochlorination of $\text{Al}_2\text{O}_3$ at 750-950$^\circ\text{C}$. These include: alkali fluorides, alkaline earth fluorides, alkaline earth carbonates, alkaline earth chlorides, alkaline earth bromides, alkaline earth oxides, and their mixtures. (1st Stage) | |
| 1981 | Sinha <em>78p</em> (CSIRO Australia) | Dehydration $T = 300-400^\circ\text{C}$ Chlorination $T = 400-500^\circ\text{C}$ $2\text{AlCl}_3\cdot6\text{H}_2\text{O}(s) + 12\text{CO}(g) + 12\text{Cl}_2(g) = 2\text{AlCl}_3(g) + 2\text{CO}_2(g) + 24\text{HCl}(g)$ Gas Mixture: 40-50%/Cl$_2$, 30-50%/CO, 5-15%/CO$_2$, 5-15%/H$_2$ Development of a process to produce anhydrous aluminium chloride from aluminium chloride hexahydrate. The process involved dehydration and chlorination in a fluidized bed reactor. (1st Stage) |</p>
<table>
<thead>
<tr>
<th>Year</th>
<th>Authors</th>
<th>Process Description</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1981</td>
<td>Mueller et al.</td>
<td>Dilution Agents: quartz, corundum, MgO</td>
<td>Improved carbochlorination process of aluminous ores in a fluidized bed reactor by the addition of an inert solid dilution agent to the bed. (1&lt;sup&gt;st&lt;/sup&gt; Stage)</td>
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<tr>
<td>1981</td>
<td>Loutfy et al.</td>
<td>Al₂O₃·Fe₂O₃(s) + 6Cl₂(g) + 6C(s) = 2AlCl₃(g) + 2FeCl₃(g) + 6CO(g); T = 900-1200 K</td>
<td>Production of aluminium trichloride from aluminous material contains iron, titanium and silicon compound reacting with carbon and a chlorine-containing gas. Produced chloride gases are cooled down to 400 K or lower to condense the aluminium chloride and iron chloride gases then heated to 800K and passed into intimate contact with aluminium sulphide to precipitate solid iron sulphide. (1&lt;sup&gt;st&lt;/sup&gt; Stage)</td>
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<tr>
<td>1979</td>
<td>Ishikawa et al.</td>
<td>CaCl₂/MgCl₂(15-70wt%)-(83-15wt%)NaCl; with conc. AlCl₃ = 2-15wt%; T = 680-780°C; Current Density: 0.5-2.0 A/cm²</td>
<td>Production of aluminium by electrolysis of fused aluminium chloride together with an alkali metal halide. (2&lt;sup&gt;nd&lt;/sup&gt; Stage)</td>
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<td>1978</td>
<td>Harvey et al.</td>
<td>Al₂O₃·SiO₂(s) + 5C + 5Cl₂ = 2AlCl₃(g) + SiCl₄(g) + 5CO₂(g)</td>
<td>Production of aluminium chloride by reaction of aluminium oxide, carbon and chlorine. (1&lt;sup&gt;st&lt;/sup&gt; Stage)</td>
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<tr>
<td>1978</td>
<td>Lippman et al.</td>
<td>Bauxite/Cl₂(g) + 3Cl₂(g) + 3C(s) = 2AlCl₃(g) + 3CO(g)</td>
<td>Process for the production of pure aluminium chloride and alumina from aluminous ores through carbochlorination followed by chlorides separation and purification. (1&lt;sup&gt;st&lt;/sup&gt; Stage)</td>
</tr>
<tr>
<td>1978</td>
<td>Wyndham et al.</td>
<td>Al₂O₃·2SiO₂(s) + 7C(s) + 7Cl₂(g) + Sulphur = 2 AlCl₃(g) + 2SiCl₄(g) + 7CO(g)</td>
<td>Improved halogenation of aluminous ores by sulphur treatment; allowing low temperature processing. Sulphur acts as catalyst but no detailed mechanisms were presented. (1&lt;sup&gt;st&lt;/sup&gt; Stage)</td>
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<tr>
<td>1977</td>
<td>Pope</td>
<td>N/A</td>
<td>Development of a fluidised bed reactor for chlorination of alumina with multilayer lining. (1&lt;sup&gt;st&lt;/sup&gt; Stage)</td>
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<tr>
<td>1977</td>
<td>Holliday et al.</td>
<td>Fe₂O₃(s) (in bauxite) + 3 SO₂(g) + 7 CO(g) = Fe₂S₃(g) + CO₂(g)</td>
<td>Removal of iron from bauxite by reaction with SO₂/CO gas mixtures followed by chlorination. (1&lt;sup&gt;st&lt;/sup&gt; Stage)</td>
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<td>1977</td>
<td>Haupin et al.</td>
<td>Al₂O₃(s) + 3Cl₂(g) + 3C(s) = 2AlCl₃(g) + 3CO(g)</td>
<td>Production of aluminium chloride by reaction of aluminium oxide, carbon and chlorine. (1&lt;sup&gt;st&lt;/sup&gt; Stage)</td>
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<tr>
<td>Year</td>
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<td>Process Details</td>
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<td>1975</td>
<td>Terry <em>et al.</em> 77&lt;sup&gt;p&lt;/sup&gt; (Toth Al Corp.)</td>
<td>Molten bath: AlCl&lt;sub&gt;3&lt;/sub&gt;-NaCl-LiCl&lt;br&gt;Cl&lt;sub&gt;2&lt;/sub&gt; conversion to AlCl&lt;sub&gt;3&lt;/sub&gt;: 99%&lt;br&gt;T = 400-950°C&lt;br&gt;3Mn&lt;sub&gt;(s)&lt;/sub&gt; + 2AlCl&lt;sub&gt;3&lt;/sub&gt;&lt;sub&gt;(g,l)&lt;/sub&gt; = 3MnCl&lt;sub&gt;2&lt;/sub&gt;&lt;sub&gt;(s,soln)&lt;/sub&gt; + 2Al&lt;sub&gt;(s)&lt;/sub&gt;&lt;br&gt;Pressure range: 15-450 psi.&lt;br&gt;Temperature: 180-600°C; Time: ~2hrs&lt;br&gt;AlCl&lt;sub&gt;3&lt;/sub&gt; Flow Rate: 0.75-3.20 g/hr</td>
<td>A method of producing aluminium wherein aluminium chloride in liquid phase reacted with manganese in solid phase. The manganese reduces aluminium chloride and forms essentially elemental aluminium and manganese chloride. (1&lt;sup&gt;st&lt;/sup&gt; Stage)</td>
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<tr>
<td>1975</td>
<td>Dell <em>et al.</em> 77&lt;sup&gt;p&lt;/sup&gt; (Alcoa)</td>
<td>AlCl&lt;sub&gt;3&lt;/sub&gt;&lt;sub&gt;(l)&lt;/sub&gt; = Al&lt;sub&gt;(l)&lt;/sub&gt; + 1.5Cl&lt;sub&gt;2&lt;/sub&gt;&lt;sub&gt;(g)&lt;/sub&gt;&lt;br&gt;Electrolyte: 50-75% NaCl and 25-50% LiCl&lt;br&gt;Conc. AlCl&lt;sub&gt;3&lt;/sub&gt;: 1.5-10 wt%; T = 660-730°C&lt;br&gt;Design and development of electrolytic cell with intermediate bipolar electrodes. This allows the flow of bath melt and settling of Al metal. Anode-cathode distance/spacing of less than ¼ in. (2&lt;sup&gt;nd&lt;/sup&gt; Stage)</td>
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<td>1975</td>
<td>Othmer 68&lt;sup&gt;p&lt;/sup&gt;</td>
<td>3 AlCl&lt;sub&gt;3&lt;/sub&gt;&lt;sub&gt;(g)&lt;/sub&gt; = 2 Al&lt;sub&gt;(l)&lt;/sub&gt; + AlCl&lt;sub&gt;3&lt;/sub&gt;&lt;sub&gt;(g)&lt;/sub&gt;&lt;br&gt;2 AlCl&lt;sub&gt;3&lt;/sub&gt;&lt;sub&gt;(g)&lt;/sub&gt; + 6 S(l) = 2 Al&lt;sub&gt;(l)&lt;/sub&gt; + 3 S&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt;&lt;sub&gt;(g)&lt;/sub&gt;&lt;br&gt;T = 600-1000°C&lt;br&gt;Other reactions above 1500°C:&lt;br&gt;Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;(s) + S&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt;(g) + 3C(s) = 2 AlCl(g) + 3CO(g) + 3SO&lt;sub&gt;2&lt;/sub&gt;(g)&lt;br&gt;SiCl&lt;sub&gt;4&lt;/sub&gt;(g) + 2Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;(s) + 4C(s) = 4AlCl(g) + 4CO(g) + SiO&lt;sub&gt;2&lt;/sub&gt;(s)&lt;br&gt;AlCl&lt;sub&gt;3&lt;/sub&gt;(g) + Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;(s) + 3C(s) = 3AlCl(g) + 3CO(g)&lt;br&gt;T = 1000-1200°C&lt;br&gt;Removal of Fe impurities:&lt;br&gt;2AlCl&lt;sub&gt;3&lt;/sub&gt;&lt;sub&gt;(g)&lt;/sub&gt; + Fe&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;(s) = 2FeCl&lt;sub&gt;3&lt;/sub&gt;&lt;sub&gt;(g)&lt;/sub&gt; + Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;(s)&lt;br&gt;Disproportionation T = 700°C&lt;br&gt;3AlCl&lt;sub&gt;3&lt;/sub&gt;&lt;sub&gt;(g)&lt;/sub&gt; = 2Al&lt;sub&gt;(l)&lt;/sub&gt; + AlCl&lt;sub&gt;3&lt;/sub&gt;&lt;sub&gt;(g)&lt;/sub&gt;</td>
<td>Separation of Aluminium from aluminous ores (bauxites, clays, feldspar, etc) through the formation of volatile tri-halide, followed by disproportionation of tri-halide to metallic aluminium. (1&lt;sup&gt;st&lt;/sup&gt; and 2&lt;sup&gt;nd&lt;/sup&gt; Stage)</td>
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<td>1973</td>
<td>Russell <em>et al.</em> 18&lt;sup&gt;p&lt;/sup&gt; (Alcoa)</td>
<td>AlCl&lt;sub&gt;3&lt;/sub&gt;&lt;sub&gt;(l)&lt;/sub&gt; = Al&lt;sub&gt;(l)&lt;/sub&gt; + 1.5Cl&lt;sub&gt;2&lt;/sub&gt;&lt;sub&gt;(g)&lt;/sub&gt;; T = 660-730°C&lt;br&gt;Electrolyte: NaCl-LiCl&lt;sub&gt;2&lt;/sub&gt; (50:50 wt)&lt;br&gt;Conc. AlCl&lt;sub&gt;3&lt;/sub&gt; in bath 1-15 wt%; oxide impurities&lt;0.25 wt%; ACD: 1 inch, Current density: 10 A, Voltage: &lt; 5 V, Current Efficiency: 80%&lt;br&gt;Production of aluminium by continuous electrolysis of aluminium trichloride. Increase of current efficiency of the process (avoiding the formation of sludge) using proposed operating conditions (2&lt;sup&gt;nd&lt;/sup&gt; Stage)</td>
<td></td>
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<tr>
<td>1971</td>
<td>Toth 59&lt;sup&gt;p&lt;/sup&gt; (Applied Al Research Corp.)</td>
<td>Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;(s) + 3MnCl&lt;sub&gt;2&lt;/sub&gt;&lt;sub&gt;(l)&lt;/sub&gt; + 3C(s) = 3MnCl&lt;sub&gt;2&lt;/sub&gt;(l) + 2AlCl&lt;sub&gt;3&lt;/sub&gt;(g) + 3CO&lt;sub&gt;(g)&lt;/sub&gt;&lt;br&gt;3Mn&lt;sub&gt;(s)&lt;/sub&gt; + 2AlCl&lt;sub&gt;3&lt;/sub&gt;&lt;sub&gt;(g,l)&lt;/sub&gt; = 2Al&lt;sub&gt;(l)&lt;/sub&gt; + 3MnCl&lt;sub&gt;2&lt;/sub&gt;(l)&lt;br&gt;T = 900-1300°C</td>
<td>Production of aluminium by a two-steps process comprising the reaction of alumina with manganese chloride in the presence of carbon to form aluminium trichloride and manganese and the subsequent reaction of aluminium trichloride with manganese at a temperature sufficient to reduce aluminium trichloride to aluminium. (1&lt;sup&gt;st&lt;/sup&gt; and 2&lt;sup&gt;nd&lt;/sup&gt; Stage)</td>
</tr>
<tr>
<td>1948</td>
<td>Ferguson <em>et al.</em> 50&lt;sup&gt;p&lt;/sup&gt; (Standard Oil Development Co)</td>
<td>Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;(s) + 3C(s) + 3Cl&lt;sub&gt;2&lt;/sub&gt;(g) = 2AlCl&lt;sub&gt;3&lt;/sub&gt;(g) + 3CO&lt;sub&gt;(g)&lt;/sub&gt;&lt;br&gt;T = 649-816°C</td>
<td>Production of Al-chloride and Al-bromides. Development of a continuous process using a “fluidised mixture” type reactor (1&lt;sup&gt;st&lt;/sup&gt; Stage)</td>
</tr>
<tr>
<td>1939</td>
<td>Willmore 52&lt;sup&gt;p&lt;/sup&gt; (Alcoa)</td>
<td>3 AlF&lt;sub&gt;3&lt;/sub&gt;&lt;sub&gt;(l)&lt;/sub&gt; = 2 Al&lt;sub&gt;(l)&lt;/sub&gt; + AlF&lt;sub&gt;3&lt;/sub&gt;&lt;sub&gt;(g)&lt;/sub&gt;&lt;br&gt;T = 900°C-1000°C</td>
<td>Disproportionation of Al-halides, including Al-chlorides (2&lt;sup&gt;nd&lt;/sup&gt; Stage)</td>
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</table>
Another alternative aluminium production method that has received less attention is through the formation of aluminium sulphides (Al₂S₃ and AlS), as intermediate compounds. One of the first patented works on the carbothermic production of Al₂S₃ was by Haglund. Haglund produced a mixture of Al₂O₃ and Al₂S₃ from the reaction between Al₂O₃-containing ores, carbon as reduction agent, and sulphur sources in the form of FeS and ZnS. FeS was added in the form of a lump (mixed with uncalcined bauxite) where it was sink through the formed slag into the liquid iron alloy underlying the slag. Aluminium sulphide was formed as part of the reaction products, while aluminium was contained in the iron alloy.

In 1958, Weiss proposed a method for producing aluminium from a mixture of aluminous ores and Al₂S₃ reacted with carbon at temperatures above 1000°C at pressures below atmospheric pressure. The reaction resulted in vapors of aluminium subsulphide (such as Al₂S) which upon cooling disproportionated into aluminium sulphide (Al₂S₃) and aluminium precipitate. The reactions are given below;

\[
\begin{align*}
2\text{Al}_2\text{O}_3(s) + \text{Al}_2\text{S}_3(s) + 6\text{C}(s) &= 3\text{Al}_2\text{S}(g) + 3\text{CO}(g) \\
3\text{Al}_2\text{S}(g) &= \text{Al}_2\text{S}_3(g) + 4\text{Al}(s)
\end{align*}
\]

Weiss proposed the process to be carried out at 1000-1200°C at pressure below 5 mmHg. The process could be carried out at higher pressures if the temperature of the process is increased, e.g. at temperature above 2000°C, the process can be carried out at atmospheric pressure.

Loutfy et al. studied the thermodynamics of the carbo sulphidation of alumina and patented an aluminium production process in 1981. Aluminous ores were reacted with carbon and sulphur containing gas at temperatures 1027 to 1227°C to obtain molten aluminium sulphide (Al₂S₃) and CO gas according to the following reaction:

\[
\text{Al}_2\text{O}_3(s) + 3\text{C}(s) + 1.5\text{S}_2(g) = \text{Al}_2\text{S}_3(l) + 3\text{CO}(g)
\]

The Al₂S₃ was further heated at temperatures 1327 to 1627°C to produce aluminium monosulphide (AlS) and sulphur. Then AlS was cooled to a temperature 927 to 1097°C where it disproportionated to molten aluminium sulphide (Al₂S₃) and aluminium metal following the reactions:

\[
\begin{align*}
\text{Al}_2\text{S}_3(l) &= 2\text{AlS}(l) + \text{S}(g) \\
3\text{AlS}(l) &= \text{Al}_2\text{S}_3(l) + \text{Al}(l)
\end{align*}
\]

The Al₂S₃(l) produced from the reaction in Eq. 20 was then electrolysed to extract the aluminium. The flowsheet of the process is shown in Figure 4.
Sportel and Verstraten\textsuperscript{88} (of Corus Aluminium GmbH) produced Al\textsubscript{2}S\textsubscript{3} from $\gamma$-Al\textsubscript{2}O\textsubscript{3} using CS\textsubscript{2} gas at 850\textdegree C according to the following reactions:

$$\text{Al}_2\text{O}_3(s, \gamma) + 3\text{CS}_2(g) = \text{Al}_2\text{S}_3(l) + 3\text{CO}(g) + 1.5\text{S}_2(g) \quad (21)$$

$$\text{Al}_2\text{O}_3(s, \gamma) + 3\text{CS}_2(g) = \text{Al}_2\text{S}_3(l) + 3\text{COS}(g) \quad (22)$$

The carbon disulphide was produced by reacting methane with sulphur gas through the following reactions:

$$\text{CH}_4(g) + 2\text{S}_2(g) = \text{CS}_2(g) + 2\text{H}_2\text{S}(g) \quad (23)$$

$$3\text{H}_2\text{S}(g) + 1.5\text{O}_2(g) = 3\text{S}(g) + 2\text{H}_2\text{O}(g) \quad (24)$$

The process is preferably performed in the range 750 to 1100\textdegree C and 5x10\textsuperscript{5} to 35x10\textsuperscript{5} Pa. Typically a temperature of 850\textdegree C and 30x10\textsuperscript{5} Pa is applied if solid Al\textsubscript{2}S\textsubscript{3} is required\textsuperscript{88}. This temperature was proposed to avoid transformation of $\gamma$-Al\textsubscript{2}O\textsubscript{3} to $\alpha$-Al\textsubscript{2}O\textsubscript{3}. It was shown that the reaction rate between $\gamma$-Al\textsubscript{2}O\textsubscript{3} and CS\textsubscript{2(g)} is higher compared to reaction rate between $\alpha$-Al\textsubscript{2}O\textsubscript{3} and CS\textsubscript{2(g)}. It was proposed that the resulting Al\textsubscript{2}S\textsubscript{3} is then electrolysed to extract the aluminium. This route (carbosulphidation followed by electrolysis) is the basis of the Corus - Compact Aluminium Production Process (CAPP). The proposed flowsheet for this process is shown in Figure 5.
Xiao et al.\textsuperscript{89} studied the kinetics of the sulphidation of alumina with CS\textsubscript{2} gas at ambient pressure. They suggested that the optimum temperature for sulphidation of \(\gamma\)-Al\(_2\)O\(_3\) is around 850\textdegree}C. In the experimental conditions studied, they reported that the particle size of \(\gamma\)-Al\(_2\)O\(_3\) had no effect on the reaction rate. A maximum conversion ratio of about 40\% after 5 hours of reaction at the conditions studied was achieved.

Li et al.\textsuperscript{90} investigated the possibility of direct formation of aluminium monosulphide (AlS) by reacting alumina-carbon mixture with FeS according to the following reaction:

\[
\text{Al}_2\text{O}_3(s) + 3\text{C}(s) + 2 \text{FeS}(s) = 2\text{AlS}(g) + 3\text{CO}(g) + 2\text{Fe}(s) \quad (25)
\]

They suggested the above reaction can be carried out at temperatures as low as 407-597\textdegree}C at pressure range of 15 to 300 Pa.

Previous major works on the production of aluminium from alumina (or aluminous ores) through carbosulphidation reactions followed by various aluminium extraction process (Stage 1 and 2) are summarised in Table 2.

### 3.4 Extraction of Aluminium from Aluminium Sulphides

The literature review on the production of aluminium through carbosulphidation route revealed that the methods proposed to extract aluminium from its sulphides are disproportionation and electrolysis.

**Disproportionation of Aluminium Sub-Sulphides**

The basis of aluminium extraction by disproportionation is through dissociation of aluminium sub-sulphides to aluminium sulphide (Al\(_3\)S\(_2\)) and aluminium upon cooling (e.g. at temperature below the disproportionation temperature of associated sub-sulphides). Weiss\textsuperscript{85} suggested the disproportionation of Al\(_2\)S\(_6(g)\) sub-sulphide as per reaction given in Eq. (17) at pressure 5 mmHg and temperature of 1200\textdegree}C. Loutfy et al.\textsuperscript{86} proposed an extraction of liquid...
aluminium through disproportionation of AlS$_{(l)}$ sub-sulphide at temperature between 927 and 1097$^\circ$C following reaction in Eq. (20). Loutfy et al.$^{86}$ did not provide information on the pressure for the process. Thermodynamic analysis carried out by Rhamdhani et al.$^{91}$ showed that the reaction in Eq. (20) does not occur at ambient pressure. Although mentioned in a number of patents$^{85-86}$, there is a limited published work on the details of thermodynamics and kinetics of the disproportionation reactions of aluminium sub-sulphides. Further studies on the thermodynamics and kinetics of aluminium sub-sulphide disproportionation are needed for optimisation of the process.

**Electrolysis of Aluminium Sulphide**

The extraction of aluminium metal by electrolysis of aluminium sulphide in molten salts is attractive from the viewpoint of energy utilization. By improving the cell design and electrolyte composition, the theoretical energy consumption can be reduced to 8.41 kWh/kg Al which is considerably lower than the value of 14 kWh/kg Al in the current Hall-Heroult process$^{92}$. Aluminium sulphide (Al$_2$S$_3$(s)) has a lower theoretical decomposition potential, compared to Al$_2$O$_3$(s) and AlCl$_3$(l)$^{93}$. Al$_2$S$_3$(s) can be electrolytically decomposed in a molten cryolite between 727 and 927$^\circ$C$^{87}$ to produce molten Al and sulphur gas that can be recycled for CS$_2$ production.

The early works on the electrolysis of Al$_2$S$_3$ in a mixture of cryolite with NaCl were from German and Russian scientists (in 1930’s and early 1940’s). In these studies, a maximum current efficiency of 55% was reported$^{94-96}$. The overall reaction for electrolysis of Al$_2$S$_3$ in molten electrolyte follows:

$$\text{Al}_2\text{S}_3(\text{soln}) = 2\text{Al}(l) + 1.5\text{S}_2(g)$$

(26)

In the early 1980’s, Minh et al.$^{93,97}$ electrolysed Al$_2$S$_3$ to extract aluminium in an electrolytic bath containing alkali metal chloride and alkaline earth metal chlorides (MgCl$_2$-NaCl-KCl and MgCl$_2$-NaCl-KCl-AlCl$_3$). They carried out the process at 750$^\circ$C and found out that the limiting current density for the process was at the graphite anode. Within the current density range investigated (0.2-1.2 A/cm$^2$), current efficiencies of 75 to 85% were claimed. Minh et al.$^{98}$ further patented the work in 1984. In this work it was suggested that the process be carried between 700 to 800$^\circ$C, with the concentration of MgCl$_2$ in the electrolyte between 20 and 70 mol% with a balance of NaCl, KCl and AlCl$_3$. The solubility of the Al$_2$S$_3$ was about 3 wt% at 750$^\circ$C, but could be enhanced by the presence of MgCl$_2$ and AlCl$_3$ according to the following reactions:

$$\text{MgCl}_2(\text{soln}) + \text{Al}_2\text{S}_3(\text{soln}) = 2\text{AlSCl}(\text{soln}) + \text{MgS}(s)$$

(27)

$$\text{AlCl}_3(\text{soln}) + \text{Al}_2\text{S}_3(\text{soln}) = 2\text{AlSCl}(\text{soln})$$

(28)
In the 2000’s, Corus developed a process for Al extraction through electrolysis of Al₂S₃, as part of development of the CAPP process. Lans et al.⁹⁹-¹⁰⁰ electrolysed Al₂S₃ and obtained aluminium melt and sulphur gases at the anode according to reaction given in Eq.(26). A molten electrolyte of MgCl₂-NaCl-KCl (50:30:20 mol %) was used and cryolite (~10 wt%) was added to enhance the solubility of Al₂S₃ and increase the activities of Al and S in the melt. This resulted in an increase in the current density up to three times. This work was the basis of the Corus patent (Van Der Plas¹⁰¹) in 2004. Further studies were carried out by Xiao et al.⁹² to investigate in detail the mechanism of the process. It was concluded that the electrolytic process was governed by its ohmic drop. The production of sulphur bubbles at the anode was suggested to significantly affect the ohmic drop. Addition of cryolite changed the characteristic of the sulphur bubbles layer thus decreasing the ohmic drop. Increased Al₂S₃ solubility due to the cryolite addition resulted in a higher limiting current density. It was reported that a current efficiency of 62% can be achieved.

In 2006, Corus¹⁰² developed a continuous production process of aluminium from alumina. In the first stage, alumina was dissolved in a molten salt and a sulphur containing gas (in particular CS₂) was fed through the melt; this resulted in partial conversion of alumina to aluminium sulphide. Aluminium was then separated from aluminium sulphide in a multi-pole electrolysis cell. The process was carried out at temperatures 800-900°C, at pressures above 3x10⁵ Pa in a KCl-NaCl-(10wt%) cryolite mixture.
Table 2: Summary of previous major works/patents in the Sulphide Route (*p refers to patent; 1st stage refers to production of intermediate Al sulphides; 2nd stage refers to extraction of Al from the sulphides)

<table>
<thead>
<tr>
<th>Year</th>
<th>Author</th>
<th>Reactions and Process Parameters</th>
<th>Process Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>2007</td>
<td>Xiao et al. <em>92</em></td>
<td>( \text{Al}_2S_3 = 2\text{Al} + 1.5\text{S}_2(g) ) Electrolytes: MgCl_2-NaCl-KCl Temperature: 700°C Yield: 42%, Current Efficiency: 62% Energy Required: 13.4 kWh/kg</td>
<td>The electrochemical behaviour of Al_2S_3 in molten salt on a laboratory scale. Temperature and cryolite addition have a positive effect on the current density. (2nd Stage)</td>
</tr>
<tr>
<td>2006</td>
<td>Van Der Plas et al. <em>102</em> &lt;p&gt;Corus Aluminium)</td>
<td>Temp: 800-900°C Pressure: ( \geq 3 \times 10^5 ) Pa Salt mixture: KCl-NaCl-10 %wt. Cryolite Sulphidation gas: mainly CS_2</td>
<td>Continuous production of aluminium from alumina including a first step of converting alumina into aluminium sulphide (Al_2S_3) and a second step of separation of aluminium from aluminium sulphide in a separating reactor. In the first step, alumina is dissolved in a molten salt. Sulfur containing gas is fed through the melt. It is proposed that Al extraction is carried through electrolysis in multi-pole cell (1st &amp; 2nd Stage)</td>
</tr>
<tr>
<td>2004</td>
<td>Xiao et al. <em>99</em></td>
<td>( \text{CH}_4(g) + 2\text{S}_2(g) = \text{CS}_2(g) + 2\text{H}_2\text{S}(g) ) ( \text{Al}_2\text{O}_3(\gamma) + 3\text{CS}_2(g) = \text{Al}_2\text{S}_3 + 3\text{CO}(g) + 1.5 \text{S}_2(g) ) Al_2S_3 = 2Al + 1.5S_2(g) Sulphidation T = 850°C. Yield: 40%</td>
<td>Investigation of sulphidation kinetics of Al_2O_3 with CS_2 gas. The alumina with a higher specific surface area results in a higher sulphidation ratio. The particle size of γ-Al_2O_3 has no effect on the reaction ratio. (1st &amp; 2nd Stage)</td>
</tr>
<tr>
<td>2004</td>
<td>Van Der Plas <em>101</em> &lt;p&gt;Corus Technology BV)</td>
<td>Cathode: ( \text{Al}^{3+} + 3e^- = \text{Al} ) Anode: ( 2\text{S}_2^- = \text{S}_2(g) + 4e^- ) Overall: ( \text{Al}_2\text{S}_3 = 2\text{Al} + 1.5\text{S}_2(g) ) Electrolytes: MgCl_2-NaCl-KCl T = 700-800°C. Current Efficiency: 80%</td>
<td>Production of aluminium by electrolysis of Al_2S_3 in multipolar cell, using a molten chloride salt bath. The sulphur gas was collected and recycled to produce CS_2 which was used in the sulphidation step. MgCl_2 is added to the bath to increase solubility of Al_2O_3. Cryolite may also be added. (2nd Stage)</td>
</tr>
<tr>
<td>2003</td>
<td>Sportel et al. <em>88</em> &lt;p&gt;Corus Aluminium)</td>
<td>( \text{CH}_4 + 2\text{S}_2 = \text{CS}_2 + 2\text{H}_2\text{S} ) (T = 550-650°C) ( 2\text{Al}_2\text{O}_3 + 6\text{CS}_2 = \text{2Al}_2\text{S}_3 + 6\text{CO} + 3\text{S}_2 ) ( \text{Al}_2\text{S}_3 = 2\text{AlS} + \text{S} ); T = 1527-1627°C ( 3\text{AlS} = \text{Al}_2\text{S}_3 + 2\text{Al} ); T = 927-1097°C</td>
<td>Production of primary aluminium from alumina comprising the step of converting alumina into aluminium sulphide (Al_2S_3) and subsequently aluminium is separated from aluminium sulphide. γ-alumina is preferred for the reaction due to better kinetics. Three reactors were proposed: (1) for manufacturing CS_2, (2) for manufacturing Al_2S_3 from Al_2O_3 and CS_2, and (3) electrolysis cell for Al extraction (1st Stage)</td>
</tr>
<tr>
<td>1984</td>
<td>Minh et al. <em>98</em> &lt;p&gt;Dept of Energy of USA)</td>
<td>MgCl_2(soln) + Al_2S_3(soln) = 2AlSCl_2(soln) + MgS(s) Temperature: 700-800°C Voltage &lt; 2-3 V Conc. Al_2S_3 in bath 2-10 mol% Electrolytes: MgCl_2(20-70mol%)-NaCl-KCl MgCl_2-NaCl-KCl-AlCl_3(1-10mol%) Current Efficiency: 75-85%</td>
<td>Production of aluminium through electrolysis of Al_2S_3 utilizing an electrolytic bath containing alkali metal chloride and/or alkaline earth metal chloride to provide improved operating characteristics of the process. (2nd Stage)</td>
</tr>
<tr>
<td>1981</td>
<td>Loutfy et al. <em>87</em> &lt;p&gt;Dept of Energy of USA)</td>
<td>( \text{Al}_2\text{O}_3 + 3\text{C} + 3\text{S} = \text{Al}_2\text{S}_3 + 3\text{CO} ); T = 1027-1227°C ( \text{Al}_2\text{S}_3 = 2\text{AlS} + \text{S} ); T = 1327-1627°C ( 3\text{AlS} = \text{Al}_2\text{S}_3 + \text{Al} ); T = 927-1097°C</td>
<td>Aluminium ore is reacted with carbon and sulphur containing gas at elevated temperatures forming molten aluminium sulphide which is decomposed to aluminium sub-sulphide (AIS). Then aluminium monosulphide is cooled to below its disproportionation temperature to produce aluminium metal. Blended aluminous ores</td>
</tr>
</tbody>
</table>
and coke were used. (1st & 2nd Stage)

Note: Current thermodynamic analyses indicate that the proposed reactions of the 2nd stage of the process do not occur at the conditions specified.

<table>
<thead>
<tr>
<th>Year</th>
<th>Author</th>
<th>Reference</th>
<th>Reaction Expressions</th>
<th>Conditions</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1958</td>
<td>Weiss</td>
<td>N/A</td>
<td>[2\text{Al}_2\text{O}_3(s) + \text{Al}_2\text{S}_3(s) + 6\text{C}(s) = 3\text{Al}_2\text{S}_3(g) + 3\text{CO}(g)] [3\text{Al}_2\text{S}_3(g) = \text{Al}_2\text{S}_3(g) + 4\text{Al}(s)]</td>
<td>[T = 1000-1200{}^\circ\text{C} \text{ at } P &lt; 5\text{mmHg}] [T &gt; 2000{}^\circ\text{C} \text{ at } P = 0.1\text{MPa}]</td>
<td>Production of aluminium from aluminous ores by reactions of a mixture of aluminous ores, (\text{Al}_2\text{S}_3) and carbon. The reaction produce vapours of aluminium sub-sulphide which upon cooling produce aluminium sulphide and aluminium precipitate. (1st Stage and 2nd Stage)</td>
</tr>
<tr>
<td>1931</td>
<td>Haglund</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>Production of mixture of (\text{Al}_2\text{O}_3) and (\text{Al}_2\text{S}_3) by reaction between (\text{Al}_2\text{O}_3)-containing materials, reduction agents (carbon) and sulphur sources (FeS, ZnS). (1st Stage)</td>
</tr>
</tbody>
</table>
3.5 Carbonitridation Route

Selvaduray and Sheet\textsuperscript{103} and Haussonne\textsuperscript{104} provided a review on various methods for the synthesis of aluminium nitride. In general the methods can be classified into: carbonitridation reactions, direct nitridation, floating nitridation, CVD (chemical vapour deposition), vapour phase reactions, and reactions utilising organometallic precursors\textsuperscript{103}. Only the carbonitridation route will be described in this paper, as it is the route most relevant to industrial scale production of metal.

Carbonitridation of alumina and aluminous ores is a well-known process. It follows an overall reaction of:

\[
\text{Al}_2\text{O}_3(\text{s}) + 3\text{C}(\text{s}) + \text{N}_2(\text{g}) = 2\text{AlN}(\text{s}) + 3\text{CO}(\text{g}) \quad (29)
\]

Rather than for aluminium production, the original aim of the process was to produce aluminium nitride or to purify alumina from its ores. In the later case, for example in the Serpek\textsuperscript{105} process, a mixture of bauxite and coke is heated in an electric furnace in the presence of nitrogen to produce aluminium nitride. Aluminium nitride can then be hydrolysed through reaction with water to form pure alumina and ammonia. The reaction can be carried out even at ambient temperature\textsuperscript{106-107} but at slow reaction rates\textsuperscript{108}.

Considerable disagreement exists in the literatures concerning the detailed reaction steps for nitride formation. Hirai \textit{et al.}\textsuperscript{109} synthesized AlN\textsubscript{(s)} from Al\textsubscript{2}O\textsubscript{3}(s) and graphite at temperatures between 1500\textdegree C and 1700\textdegree C. They observed a small quantity of aluminium oxynitride, AlON, when alumina graphite mixture was heated at 1700\textdegree C\textsuperscript{109}. Their results indicated that the reaction rate was not affected by the grain size of graphite, pellet diameter and flow rate of N\textsubscript{2}; and they suggested that the diffusion of the reactant gas through the AlN\textsubscript{(s)} layer (formed around Al\textsubscript{2}O\textsubscript{3}(s)) was the rate determining step. Lefort and Billy\textsuperscript{110} argued that the rate determining step suggested by Hirai \textit{et al.} was unlikely as the apparent activation energy (~530 kJ/mol) was beyond what would be expected from a limiting gaseous diffusion. Lefort and Billy suggested that the rate limiting process was the combustion of carbon and suggested the following reaction steps:

\[
\text{Al}_2\text{O}_3(\text{s}) \rightarrow 2\text{Al}(\text{g}) + 1.5\text{O}_2(\text{g}) \quad (30)
\]

\[
3\text{C}(\text{s}) + 1.5\text{O}_2 = 3\text{CO}(\text{g}) \text{ (rate limiting step)} \quad (31)
\]

\[
2\text{Al}(\text{g}) + \text{N}_2(\text{g}) = 2\text{AlN}(\text{s}) \quad (32)
\]

The dissociation of alumina was suggested to be controlled by the very low partial pressure of oxygen in contact with carbon, and followed by fast nitridation of the aluminium vapor formed. Lefort and Billy recommended temperatures from 1550\textdegree C to 1600\textdegree C for the process.
Chen and Lin\textsuperscript{111}, studied a carbonitridation of alumina at temperatures from 1375\textdegree{}C to 1552\textdegree{}C and developed a kinetic model for the process. A mixed mechanism was proposed comprising reaction between Al\textsubscript{2}O\textsubscript{3}(s) and C(s) to form Al\textsubscript{2}O\textsubscript{2}(g) and CO\textsubscript{2}(g), followed by surface reaction between Al\textsubscript{2}O\textsubscript{2}(g) and N\textsubscript{2}(g) to form AlN\textsubscript{(s)}\textsuperscript{111-112}. They suggested that the formation of Al\textsubscript{2}O\textsubscript{2}(g) is the rate limiting step according to:

\[ \text{Al}_2\text{O}_3(s) + 2C(s) = \text{Al}_2\text{O}_2(g) + 2\text{CO}(g) \quad (33) \]

Aluminium monocyanide, AlCN\textsubscript{(s)}, can also form as described by Perieres and Bollack (Pechiney)\textsuperscript{113} according to

\[ \text{AlN}(s) + C(s) = \text{AlCN}(g) \quad (34) \]

A preferred temperature of 1700\textdegree{}C was recommended for nitride preparation as the formation of AlCN\textsubscript{(g)} increases above 1700\textdegree{}C, which explains the apparent decrease in nitride formation and the presence of aluminium carbide in the condensates\textsuperscript{113}. Aluminium monocyanide vapour can react with aluminium vapour forming solid encrustations of carbide and nitride.

Ide \textit{et al.}\textsuperscript{114} produced AlN\textsubscript{(s)} through carbonitridation of alumina at temperatures 1350\textdegree{}C-1450\textdegree{}C using CaF\textsubscript{2}(s) as catalyst. They reported that nitridation rate tended to increase with decreasing particle size of alumina and was affected by the history of the alumina used in the reaction. They observed the formation of intermediate compounds CaO\textsubscript{6}Al\textsubscript{2}O\textsubscript{3} (CA\textsubscript{6}) and CaO\textsubscript{2}Al\textsubscript{2}O\textsubscript{3} (CA\textsubscript{2}) and suggested that the process proceeded through the nitridation of the intermediate compounds from liquid phase system CaF\textsubscript{2}-CA\textsubscript{6}-CA\textsubscript{2}. Molisani and Yoshimura\textsuperscript{115} investigated the effect of various additives (0.5-3 wt\% of CaF\textsubscript{2}, Y\textsubscript{2}O\textsubscript{3}, Li\textsubscript{2}CO\textsubscript{3} and SrCO\textsubscript{3}) on the carbonitridation of alumina at 1300-1400\textdegree{}C. The addition of these additives (and their mixture combinations) was reported to reduce the synthesis temperature by a maximum of 200\textdegree{}C. They attributed this to the formation of aluminate phases that easy to vaporize at lower temperature.

Bartnitskaya \textit{et al.}\textsuperscript{116} studied the carbonitridation reaction at temperatures from 1800 to 1900\textdegree{}C in a static condition (closed system) under nitrogen atmosphere of 0.2 to 0.3 MPa. They obtained isometric AlN particles of 2 to 6 \textmu{}m as opposed to fibrous type particles usually obtained in reaction carried out in a stream of nitrogen gas. They suggested that in the case of reaction at a high nitrogen pressure, alumina dissociation is suppressed which exludes the possibility of reaction in the gas phase, hence the formation of isometric particles. Chowdhury \textit{et al.}\textsuperscript{117} synthesized nano size AlN\textsubscript{(s)} by nitridation of C-Al\textsubscript{2}O\textsubscript{3} composite particles at 1500-1600\textdegree{}C in an over pressure (0.4 MPa) flowing nitrogen gas. A mixture of fibrous and spherical particles was obtained.
Joo and Jung\textsuperscript{118} investigated the effect of CO content in the N\textsubscript{2}-CO gas mixture for carbonitridation reaction from 1000 to 1600°C. They used Al-hydroxosuccinate as precursor for the reaction. The carbonitridation reaction was found to be retarded with increasing content of CO in the mixed gas. They observed conversion sequence from $\rho$-Al\textsubscript{2}O\textsubscript{3} to $\gamma$-Al\textsubscript{2}O\textsubscript{3} to AlN\textsubscript{(s)} (or to $\delta$-Al\textsubscript{2}O\textsubscript{3}) depending on the CO content in the gas mixture. Qin \textit{et al.}\textsuperscript{119} prepared C-Al\textsubscript{2}O\textsubscript{3} composite particles from Al(NO\textsubscript{3})\textsubscript{3} \cdot 9H\textsubscript{2}O, CO(NH\textsubscript{2})\textsubscript{2}, and C\textsubscript{6}H\textsubscript{12}O\textsubscript{6} \cdot H\textsubscript{2}O and carried out the nitridation at 1000-1600°C in a flowing nitrogen gas. They reported a conversion to $\gamma$-Al\textsubscript{2}O\textsubscript{3} followed by direct conversion to AlN\textsubscript{(s)} upon nitridation. Complete conversion was observed at 1400°C.

Galvez \textit{et al.}\textsuperscript{108} produced AlN\textsubscript{(s)} using concentrated thermal radiation through reduction of Al\textsubscript{2}O\textsubscript{3} using activated C (and CH\textsubscript{4}) in a flowing nitrogen. The radiative fluxes used were equivalent to solar concentration exceeding 4500 kW/m\textsuperscript{2} and the reaction was carried out at 1827-2027°C. In the case of carbothermal-nitridation reaction (reaction given in Eq.28), the experimental data were fitted into a solid-solid reactions model with an apparent activation energy of 360 kJ/mol. In the case of reduction using CH\textsubscript{4} (methanothermal reduction), the overall reaction follows:

$$\text{Al}_2\text{O}_3\text{(s)} + 3\text{CH}_4\text{(g)} + \text{N}_2\text{(g)} = 2\text{AlN}\text{(s)} + 6\text{H}_2\text{(g)} + 3\text{CO}\text{(g)}$$

(35)

In this case, a low conversion (~10%) was observed. It was suggested that the diffusion is hindered by a carbon layer produced from the decomposition of CH\textsubscript{4}. The kinetics, however, may be enhanced by doping the alumina with metallic particles (such as Ni and Fe). Best results were obtained when Ni is used, where it acts as nucleation site for carbon filament growth.

Galvez \textit{et al.}\textsuperscript{120} also investigated the carbothermal reduction of alumina in nitrogen atmosphere at temperatures between 1500 and 1700°C. The kinetics were described as solid-solid reactions and fitted to Jander and Ginstling-Brounshtein models with activation energies of 815 and 757 kJ/mol, respectively. They also evaluated various types of carbon sources and reported that the reaction rates vary for different carbons (listed in decreasing order of reaction rates: petcoke, activated carbon, wood charcoal, and carbon black)\textsuperscript{121}.

Baik \textit{et al.}\textsuperscript{122} and Kuang \textit{et al.}\textsuperscript{123} produced aluminium nitride through carbonitridation using sucrose precursors. Zhang and Gao\textsuperscript{124} produced nanocrystalline aluminium nitride from $\delta$-Al\textsubscript{2}O\textsubscript{3} nanoparticles in flowing ammonia. They reported that the nanocrystalline $\delta$-Al\textsubscript{2}O\textsubscript{3} was converted into AlN\textsubscript{(s)} completely at temperatures 1350 to 1400°C within 5 hours in a single-step synthesis process. Xi \textit{et al.}\textsuperscript{125} synthesized AlN\textsubscript{(s)} by carbothermal reduction using a mechanically activated Al\textsubscript{2}O\textsubscript{3}. They showed that carbonitridation can be carried out at
temperature as low as 1100°C and completed thoroughly at 1250°C when milled Al₂O₃ (for 20 hours) was used.

There are two primary methods to prepare AlN powders in an industrial scale: (1) direct nitridation of Al with N₂ (2Al + N₂ = 2AlN), and (2) carbothermal reduction of Al₂O₃ with carbon black (or other carbonaceous sources) in the presence of N₂(g) at 1500-2000°C (reaction in Eq. 29). The former is beyond the scope of this paper. In terms of technological developments, a number of aluminium nitride production processes by carbonitridation in nitrogen or mixed gas atmosphere have been patented. A summary of these studies are presented in Table 3.

One of the first patents in the carbonitridation of alumina was from Shoeld in 1918 where he carried out the reaction at 1800-2000°C. In the 1960’s, Pechiney patented various carbonitridation processes. Perieres and Bollack produced AlN powder to 99% by roasting the produced AlN(s) from carbonitridation reaction in an oxygen-free atmosphere at 700-800°C to burn off the excess carbon. Clair developed a vertical-shaft counter-current reactor for continuous production of aluminium nitride, while Paris and Perieres used a mixed environment of nitrogen and hydrocarbon gas for carbonitridation of alumina at 1200-1700°C. The hydrocarbon gas was cracked to elemental carbon in a highly reactive state in uniform distribution throughout the aluminium oxide particle.

Kuramoto et al. produced AlN powder from alumina and carbon by firing the mixture at 1400-1700°C in nitrogen (or ammonia) gas atmosphere followed by heating at 600-900°C to improve the purity to 94%. Bolt patented a method to produce aluminium nitride films (and fibres) using precursors containing alumina and carbon.

In the 1990’s, a number of AlN(s) production processes were patented by various companies. Nakano et al. patented a process using very fine source materials (<5μm). Dunn et al. increased the purity of AlN(s) produced by carbonitridation by applying mechanical agitation. Most of the impurities remain in the outer zone of the pellet and a significant amount of the surface portion is removed to improve the purity of the final aluminium nitride product. Dorn et al. produced AlN(s) through calcinations of aluminium hydroxide-carbon mixtures at temperatures from 400 to 1000°C followed by nitridation from 1400 to 1700°C. Ravenel et al. patented a process for continuous production of aluminium nitride from 1350 to 2000°C using a moving bed reactor. Kotaka et al. patented a process to produce AlN(s) from γ-Al₂O₃ using mixtures of ammonia and hydrocarbons from 1200 to 1700°C and claimed to obtain purity of 99%.
3.6 Extraction of Aluminium from Aluminium Nitride

One of the ways to extract aluminum from aluminum nitride is through thermal dissociation. The thermal dissociation of aluminium nitride occurs at a temperature above 2400°C at 0.1MPa according to reaction:

\[ \text{AlN(s)} = \text{Al(g)} + 0.5\text{N}_2(g) \]  \hspace{1cm} (36)

The temperature of the dissociation can be reduced by operating the process at lower pressures or in a vacuum condition. Thermodynamic calculations\textsuperscript{91} showed that the dissociation temperature can be reduced to around 1700°C if the pressure is reduced to 0.1kPa.

The theoretical decomposition voltage of aluminium nitride to aluminium and nitrogen is 0.75V at 700°C. This is a lower decomposition voltage than that of AlCl\textsubscript{3}(l), Al\textsubscript{2}S\textsubscript{3}(s) and Al\textsubscript{2}O\textsubscript{3}(s) at the same temperature. From the thermodynamic point of view, electrolysis has a good potential to be used for extracting aluminum from aluminium nitride. One of the major challenges is to find the appropriate electrolytes that can dissolve the very stable AlN\textsubscript{(s)}. Bonomi et al.\textsuperscript{137} carried out a limited study on the solubility and the electrolysis of AlN in molten salt (Li\textsubscript{3}N-LiCl) bath at 660-700°C. The current efficiency for this system was 83% with a cathodic current density of about 1.5A/cm\textsuperscript{2}. No further results indicating the successful of the process have been presented. Goto et al.\textsuperscript{138} used the salt system of LiCl-KCl-Li\textsubscript{3}N to deposit AlN film onto Al substrate. Figure 6 shows the E-pN\textsuperscript{3-} diagram for the Al-N system in a LiCl-KCl eutectic melt at 450°C showing the region where Al solid is stable. Yan\textsuperscript{139} conducted a direct electrochemical reduction of AlN cathode in a CaCl\textsubscript{2}-NaCl melt at 1133K and observed a pure Al droplet. The yield however was low, i.e. 3-5%.
Figure 6 - A potential-pN³⁻ diagram for Al-N system of a LiCl-KCl eutectic melt in the presence of 10⁻³ cation fraction of Al³⁺ at 450°С.138
<table>
<thead>
<tr>
<th>Year</th>
<th>Author</th>
<th>Reactions and Parameters</th>
<th>Process Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>2008</td>
<td>Joo and Jung</td>
<td>$\text{Al}_2\text{O}_3 + 3\text{C} + \text{N}_2 = 2\text{AlN} + \text{CO}$ Temperature: 800-1600°C</td>
<td>The carbothermal reduction and nitridation (CRN) of alumina to aluminium nitride was investigated in a gas environment consisting of N₂ and CO. The CRN reaction of alumina is slowing with increasing content of CO in the mixed gas.</td>
</tr>
<tr>
<td>1998</td>
<td>Kotaka et al.</td>
<td>$\text{Al}_2\text{O}_3$: 300-1100°C Nitridation Temperature: 1200-1700°C Gas: Mixtures of NH₃ and hydrocarbons Purity: 99%</td>
<td>A method of manufacturing aluminium nitride by calcining $\gamma$-$\text{Al}_2\text{O}_3$ in ammonia and hydrocarbon gas to obtain aluminium nitride having both carbon content and an oxygen content of 1wt% of less.</td>
</tr>
<tr>
<td>1997</td>
<td>Ravenel et al.</td>
<td>$\text{Al}_2\text{O}_3 + 3\text{C} + \text{N}_2 = 2\text{AlN} + \text{CO}$ Temperature: 1450-1500°C. Time: 12 hrs Residual carbon, &lt; 700 ppm Oxygen Content &lt; 1.1%. Flow rate of granule: 4.4 kg/hr Flow rate of N₂: 12 kg/hr</td>
<td>A continuous process for production of aluminium nitride by the carbonitriding process of alumina.</td>
</tr>
<tr>
<td>1996</td>
<td>Ravenel et al.</td>
<td>$\text{Al}_2\text{O}_3 + 3\text{C} + \text{N}_2 = 2\text{AlN} + \text{CO}$ Exchange surface area/volume, 5-50 m⁻¹. C/ $\text{Al}_2\text{O}_3 = 3$ Granules Feed Rate: 5 kg/h. N₂ Feed Rate: 20 kg/h Yield: 100% Time: 12 hrs Temperature: 1350-2000°C.</td>
<td>Continuous production of aluminium nitride by carbonitriding of alumina in a moving bed reactor reaction zone comprising at least one conduit.</td>
</tr>
<tr>
<td>1993</td>
<td>Dorn et al.</td>
<td>Calcination of mixture at 400-1000°C Nitridation at 1400-1700°C (1-100 hrs)</td>
<td>Production of fine aluminium nitride by reaction between aluminium hydroxide with carbon in the presence of flowing nitrogen.</td>
</tr>
<tr>
<td>1992</td>
<td>Dunn et al.</td>
<td>$\text{Al}_2\text{O}_3 + 3\text{C} + \text{N}_2 = 2\text{AlN} + 3\text{CO}$ Temperature: 1650-1750°C. Time: 90 min Frequency: 1100 vibration/min. Yield: 97%wt.</td>
<td>Purification of aluminum nitride produced by carbothermal reaction of aluminium oxide, carbon and nitrogen. Significant amount of the surface portions are removed by mechanical agitation or mechanical abrasion to leave behind aluminium nitride pellets having significantly increased purity.</td>
</tr>
<tr>
<td>1991</td>
<td>Nakano et al.</td>
<td>$\text{Al}_2\text{O}_3 + 3\text{C} + \text{N}_2 = 2\text{AlN} + 3\text{CO}$ Temperature: 1500-1700°C. Time: 2-10 hrs, starting materials &lt; 5µm O, &lt;2 wt.% Fe, &lt;20 ppm</td>
<td>Production of aluminium nitride by firing and reacting alumina and carbon mixture in a nitrogen containing atmosphere.</td>
</tr>
<tr>
<td>Year</td>
<td>Author</td>
<td>Reference</td>
<td>Equation</td>
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<td>1989</td>
<td>Bolt (Du Pont)</td>
<td>Bolt, 1989</td>
<td>$\text{Al}_2\text{O}_3 + 3\text{C} + \text{N}_2 = 2\text{AIN} + 3\text{CO}$</td>
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<td>1986</td>
<td>Kuramoto et al. (Tokuyama)</td>
<td>Kuramoto et al., 1986</td>
<td>$\text{Al}_2\text{O}_3 + \text{N}_2 (\text{NH}_3) = 2\text{AIN} + 3\text{CO}$</td>
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<tr>
<td>1963</td>
<td>Paris and Perieres (Pechiney)</td>
<td>Paris and Perieres, 1963</td>
<td>$\text{Al}_2\text{O}_3 + 3\text{C} + \text{N}_2 = 2\text{AIN} + 3\text{CO}$</td>
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<tr>
<td>1961</td>
<td>Perieres and Bollack (Pechiney)</td>
<td>Perieres and Bollack, 1961</td>
<td>$\text{Al}_2\text{O}_3 + 3\text{C} + \text{N}_2 = 2\text{AIN} + 3\text{CO}$</td>
</tr>
<tr>
<td>1918</td>
<td>Shoeld (Armour Fert. Works)</td>
<td>Shoeld, 1918</td>
<td>$\text{Al}_2\text{O}_3 + 3\text{C} + \text{N}_2 = 2\text{AIN} + 3\text{CO}$</td>
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4. Concluding Remarks

Many researchers have pursued an alternative commercial method for aluminium production. Although carbothermal reduction of alumina or aluminous ores (direct or indirect) offers the potential for lower energy consumption and improved productivity, compared to existing process, none of these proposed processes have been successfully commercialized. In the case of direct carbothermal reduction of alumina/aluminous ores, a mixture of aluminium carbide and metallic aluminium is formed. Equilibrium studies show that the driving forces for both aluminium carbide and aluminium metal formation by carbothermic reduction of alumina are similar, therefore it is difficult to obtain high yield of pure aluminium. This route has other difficulties, including a high operating temperature and yield problems associated with aluminium vapour back reactions with carbon monoxide forming aluminium oxides and carbides. The recent technology in this area has shifted to a multi stage process, the Alcoa-Elkem process, where a slag of Al₂O₃-Al₄C₃ is first produced followed by extraction of aluminium.

In the case of multistage production of aluminum through the formation of intermediate compounds; there had been intense developments of the chloride route in the 60’s and throughout the 70’s with major players including Alcoa and Toth Al Corporation. At one stage, the Alcoa chloride process (carbochlorination followed by electrolysis) was used to produce Al commercially. This however was halted in the mid 80’s due to problems associated with production and handling of pure aluminium chloride and chlorine at high temperatures.

In the sulphide route, Al₂S₃(l) can be produced by carbosulphidation of alumina or aluminous ores. Aluminium metal can be extracted from Al₂S₃(l) by disproportionation and electrolysis processes. In the 2000’s, Corus developed a process for making aluminium through carbosulphidation followed by electrolysis. This, however, is not yet commercialised.

There is also the nitride route where AlNₙ(s) is produced from alumina-graphite mixture reacted at 1700°C in nitrogen containing gas. One of the major challenges is to find the economical route to extract Al from AlNₙ(s). The nitride is a very stable phase but can be dissociated to aluminium metal at above 2400°C at 0.1 MPa pressure. The theoretical decomposition voltage of aluminium nitride to aluminium and nitrogen is 0.75V at 700°C. It is the lowest compared to the decomposition voltage of AlCl₃(l), Al₂S₃(s) and Al₂O₃(s) at the same temperature. Therefore, electrolysis has potential to be used for extracting aluminum from aluminium nitride. However, to date no appropriate electrolytes are available to dissolve the very stable AlN.
In summary, direct carbothermic reduction has yet to be commercialized because of problems with extreme operating conditions and yield, whilst, two stage indirect carbothermic reduction using Cl, S, and N sources to form intermediates have been investigated but still require significant development. No systematic thermodynamic examination of all the options has been published in the literature.

5. Acknowledgement

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6. References


