

University of Wollongong

Research Online

Faculty of Engineering and Information
Sciences - Papers: Part A

Faculty of Engineering and Information
Sciences

1-1-2012

Thermodynamic assessment of aluminium production through carbosulphidation route

Nazmul Huda
Swinburne University of Technology

Muhammad A. Rhamdhani
Swinburne University of Technology

M A. Dewan
Csiro Materials Science And Engineering

Geoffrey A. Brooks
Swinburne University of Technology

B J. Monaghan
University of Wollongong, monaghan@uow.edu.au

See next page for additional authors

Follow this and additional works at: <https://ro.uow.edu.au/eispapers>



Part of the [Engineering Commons](#), and the [Science and Technology Studies Commons](#)

Recommended Citation

Huda, Nazmul; Rhamdhani, Muhammad A.; Dewan, M A.; Brooks, Geoffrey A.; Monaghan, B J.; and Prentice, L, "Thermodynamic assessment of aluminium production through carbosulphidation route" (2012). *Faculty of Engineering and Information Sciences - Papers: Part A*. 219.
<https://ro.uow.edu.au/eispapers/219>

Research Online is the open access institutional repository for the University of Wollongong. For further information contact the UOW Library: research-pubs@uow.edu.au

Thermodynamic assessment of aluminium production through carbosulphidation route

Abstract

Indirect carbothermal reduction of alumina for the production of aluminium has been claimed to be better compared to the existing Hall-Heroult process in-terms of energy usage, generation of perfluorocarbons and overall greenhouse gas emission. In the process, alumina is reduced to an intermediate compound which is then further reduced to Al. It has been shown from the previous thermodynamic study by the authors that high conversion of alumina can be obtained if it is reduced to Al-chloride, Al-nitride or Al-sulphide. This paper deals with detailed systematic thermodynamic analysis of the process through carbosulphidation route, where alumina is first reduced to Al_2S_3 in the presence of reductant and sulphur source. Various ratios of carbon to sulphur have been considered in this modelling study. In the second stage, Aluminium is extracted from the Al_2S_3 through thermal decomposition, disproportionation or electrolysis. The different thermodynamic and energy analysis of the second stage is also discussed in this paper.

Keywords

thermodynamic, assessment, route, carbosulphidation, production, aluminium

Disciplines

Engineering | Science and Technology Studies

Publication Details

Huda, N., Rhamdhani, M. A., Dewan, M. A., Brooks, G. A., Monaghan, B. J. & Prentice, L. (2012). Thermodynamic assessment of aluminium production through carbosulphidation route. Chemeca: Australasian Conference on Chemical Engineering (pp. 1-14).

Authors

Nazmul Huda, Muhammad A. Rhamdhani, M A. Dewan, Geoffrey A. Brooks, B J. Monaghan, and L Prentice

THERMODYNAMIC ASSESSMENT OF ALUMINIUM PRODUCTION THROUGH CARBOSULPHIDATION ROUTE

Nazmul Huda¹, M. A. Rhamdhani¹, M. A. Dewan², G. A. Brooks¹, B. J. Monaghan³, L. Prentice⁴

¹HTP Research Group, Swinburne University of Technology, VIC 3122, Australia

Contact email: Mhuda@swin.edu.au

²CSIRO Materials Science and Engineering, NSW 2070, Australia

³PYRO Research Group, University of Wollongong, NSW 2522, Australia

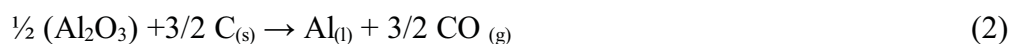
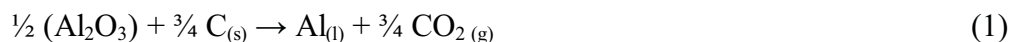
⁴CSIRO Process Science and Engineering, VIC 3169, Australia

ABSTRACT

Indirect carbothermal reduction of alumina for the production of aluminium has been claimed to be better compared to the existing Hall-Heroult process in-terms of energy usage, generation of perfluorocarbons and overall greenhouse gas emission. In the process, alumina is reduced to an intermediate compound which is then further reduced to Al. It has been shown from the previous thermodynamic study by the authors that high conversion of alumina can be obtained if it is reduced to Al-chloride, Al-nitride or Al-sulphide. This paper deals with detailed systematic thermodynamic analysis of the process through carbosulphidation route, where alumina is first reduced to Al₂S₃ in the presence of reductant and sulphur source. Various ratios of carbon to sulphur have been considered in this modelling study. In the second stage, Aluminium is extracted from the Al₂S₃ through thermal decomposition, disproportionation or electrolysis. The different thermodynamic and energy analysis of the second stage is also discussed in this paper.

INTRODUCTION

Aluminium is the most widely used nonferrous metal, second most widely used metal after steel in the world and is the third most abundant element in the earth's crust and constitutes 7.3% by mass (2012). The production of aluminium from its ore at present relies on two processes developed in the late 1800s: the Bayer process which produces pure alumina from bauxite ore, and the Hall-Heroult process which produces aluminium from alumina. In the Hall-Heroult process, Al₂O₃ is dissolved in a NaF-AlF₃ (cryolite) solution followed by direct current electrolysis according to the following reactions (Withers &Upperman, 1982)



The Hall-Heroult process for the production of aluminium has been used for well over a century (Gardner, Grojotheim et al., 1981). The process was patented in 1886 and fundamentally remain unchanged, except for the form of carbon anodes (Brooks, Cooksey et al., 2007). The Hall-Heroult process requires purified alumina which is produced through the Bayer process using bauxite ore, accounts for nearly all of the alumina production in the world (Sohn &Harbuck, 1986) and uses about a quarter of the total energy requirement (Murray, 1999). Most of this energy is thermal. The cost of the Bayer process represents about 27% of the cost of aluminium production (Murray, 1999), while the Hall-Heroult process uses about three quarters of the total energy. Most of this energy is electrical energy. Figure 1 shows in more detailed the apportionment of thermal and electrical energies for these two processes.

The commercial technology for aluminium production through Hall-Heroult process is far from perfect. The electrolysis of alumina requires high capital costs, large amounts of energy (12.9-15 DC kWh/kg Al (Namboothiri, Taylor et al., 2007), 0.186 GJ/kg Al (Halmann, Frei et al., 2007)) and is associated with a substantial environmental burden (Xiao, Van Der Plas et al., 2004). Apart from substantial CO₂ and SO₂ emissions from the production of electrical energy, the Hall-Heroult process generates greenhouse gas emissions such as CF₄ and C₂F₆ from carbon electrode and liquid cryolite (Na₃AlF₆) reactions. The greenhouse gas emission by the electrolytic Al production contributes to 2.5% of the world anthropogenic CO₂-equiv emission (Steinfeld & Thompson, 1994).

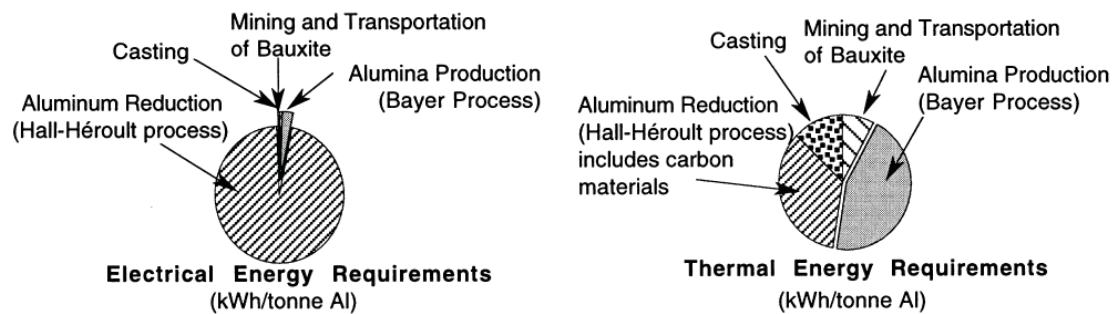


Fig 1: Distribution of thermal and electrical energy required for both the Bayer process and the Hall-Heroult process. The figures for the aluminium reduction step (Hall-Heroult) include the energy for the carbon materials on the thermal side. (OECD, 1976; Murray, 1999).

The obvious drawbacks of the Hall-Heroult process have led to numerous research efforts to find alternative routes for primary aluminium production throughout the 20th and early 21st centuries. The most important alternatives that have been envisaged include modified Hall-Heroult process utilising inert anodes (Kvande, 1999), the use of AlCl₃ as an intermediate step (Russell, Knapp et al., 1979) and the carbothermic reduction of alumina (Motzfeldt, Kvande et al., 1989). Alcoa vigorously pursued the electrolysis of aluminium chloride in the 1960s and 1970s and halted the operation in 1980s, reportedly owing to difficulties with production and handling aluminium chloride (Thonstad, Fellner et al., 2001).

INDIRECT CARBOTHERMAL REDUCTION (MULTI STAGE METHOD)

The indirect carbothermal reduction method includes at least two stages where alumina (or aluminium ores) is reduced to an intermediate compound by carbothermal reduction in the first stage followed by subsequent reduction of the compound to aluminium at later stages. The basic idea of the process is that by forming the intermediate compounds, the problems associated with the direct carbothermal reduction process can be avoided. The details of the process is shown schematically in Figure 2.

In the previous study, Rhamdhani et al. (Rhamdhani, Dewan et al., 2011) provided a comprehensive review of the various multistage indirect carbothermal processes. The comparison of these processes, in terms of the thermodynamics, were also presented (Dewan, Rhamdhani et al., 2011). It was shown that from thermodynamic perspective, high conversion in the step-1 can be achieved when alumina is reduced to Al-chloride, Al-sulphide or Al-

nitride. It was also shown that thermal dissociation and disproportionation may be suitable for extraction of Al from Al-chloride and Al-sulphide in the step-2. Electrolysis can also be used for processing of Al-chloride and Al-sulphide.

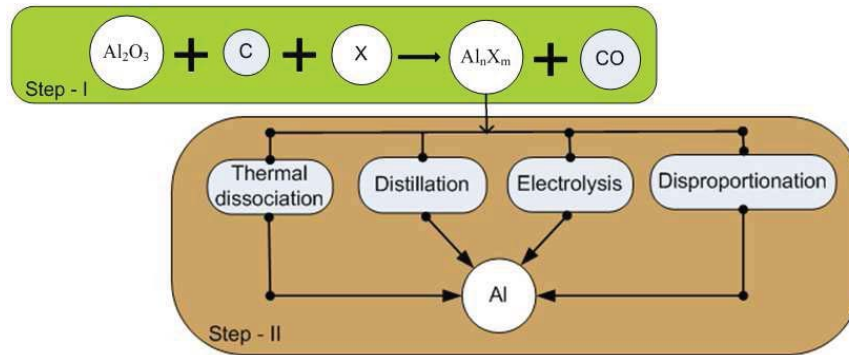
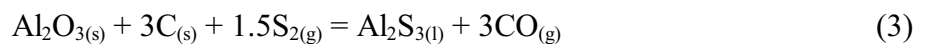


Fig 2: Schematic of indirect carbothermal reduction process of aluminium from alumina

This paper will look at more details on the sulphide route. An optimisation of the step-1 is presented for better conversion. The different thermodynamic analyses for the step-2 are also presented.

PREVIOUS STUDIES ON AL PRODUCTION THROUGH SULPHIDE ROUTE

In this route alumina potentially can be converted to aluminium sulphide, Al₂S₃, by using any possible sulphur source in the presence of carbon reductant. There had been some research in the carbosulphidation route of aluminium production. A sulphide process was patented by Loutfy *et al.* (Loutfy, Keller et al., 1981) in 1981 using pure carbon and sulphur operating above the Al₂S₃ melting temperature. Aluminium ore was reacted with carbon and sulphur containing gas at 1300-1500 K to obtain molten aluminium sulphide (Al₂S₃) (step-1).



Loutfy *et al.* (Loutfy, Keller et al., 1981) suggested a disproportionation of aluminium monosulphide (AlS) to extract aluminium metal. The Al₂S₃ produced in the Reaction (3) was further heated to 1327-1627°C in the presence of aluminium to produce aluminium monosulfide (AlS) and sulphur. Then AlS was cooled to a temperature below its disproportionation temperature 927-1097°C to form molten aluminium sulphide (Al₂S₃) and metal aluminium according to the following reactions (step-2):



Loutfy *et al.* (Loutfy, Keller et al., 1981) did not mention anything about the pressure in which the process is carried out. Thermodynamic assessment by Dewan et al. (Dewan, Rhamdhani et al., 2011) indicated that the reactions (4) and (5) do not occur at ambient pressure.

In 1984 Minh *et al.* (Minh, Loutfy et al., 1984) patented an aluminium extraction process from Al₂S₃ by electrolysis at 700-800°C utilizing an electrolytic bath containing alkali metal chloride and/or alkaline earth metal chlorides (MgCl₂-NaCl-KCl and MgCl₂-NaCl-KCl-AlCl₃). Using these electrolytes about 70-85% current efficiency was obtained. In 2004, Van Der Plas (Van Der Plas, 2004) patented a similar process for aluminium production by electrolysis of Al₂S₃

using a molten chloride salt (MgCl₂-NaCl-KCl) bath. A recycling process for sulphur gas was proposed to increase the Al₂S₃ production yield from Al₂O₃ in the sulphidation stage.

Xiao *et al.* (Xiao, Van Der Plas et al., 2004; Xiao, van der Plas et al., 2007) studied the thermochemical behaviour of Al₂S₃ in molten salt and the sulphidation kinetics of Al₂O₃ reaction with CS₂ gas. An optimum temperature for sulphidation of γ -Al₂O₃ was found to be about 850°C. Temperature and cryolite addition to the electrolytic bath had positive effect on the current density. The particle size of γ -Al₂O₃ had no effect on the reaction kinetics.

Sportel and Verstraten (Sportel & Verstraten, 1999; Sportel & Verstraten, 2003) from Corus patented a process where Al₂S₃ is produced from alumina using CS₂ as a sulphur source. Subsequently, the aluminium metal can be extracted by electrolysis producing sulphur gas at the anode which can be recycled to the production of CS₂.

Another main reaction for aluminium sulphide in the sulphidation process:



This process is preferably performed in the range 750-1100°C and 5-35 bar. Typically a temperature of 850°C and 30 bar is applied in case solid Al₂S₃ is required (Sportel & Verstraten, 2003). Al₂S₃ can be electrolytically decomposed in such as molten cryolite at about 727-927°C to produce sulphur gas and molten aluminium (Loutfy, Keller et al., 1981).

The production of CS₂ is a proven technology and possibilities of electrowinning Al from Al₂S₃ is addressed by Lans *et al.* (Lans, Bohte et al., 2003; Xiao, Soons et al., 2003; Xiao, Van Der Plas et al., 2004). By this process, the current efficiency of 60% was obtained compared to the average values of 90-95% in the modern Hall-Heroult process for aluminium production (Xiao, van der Plas et al., 2007).

Equilibrium Calculations of Al-C-S Reaction Systems – step 1

The equilibrium calculations were carried out using FactSage 6.1 thermodynamic package (Bale, Bélisle et al., 2009). The details of this thermochemical package, such as the database and various calculation modules, can be found elsewhere (Bale, Bélisle et al., 2009). FactSage is an integrated databases computing system for chemical thermodynamic. This package has optimized database for solutions, such as alloys, liquid and solid oxides and slags. For pure components, the data are from JANAF Thermochemical Tables and thermodynamic properties data (Barin, 1993). The solution model for liquid slag phase is using a modified quasi-chemical model (Eriksson, Wu et al.).

The equilibrium calculations for Al-C-S reaction system were carried at temperatures 1000°C to 1800°C at 1 atm pressure. To study the influences of pressure, more equilibrium calculations were carried out at various pressures (50 - 1000 Pa). For initial equilibrium calculations, stoichiometric amounts of carbon and sulphur to reduce 1 mol of Al₂O₃ were used, following an assumed complete reaction Equation (7):

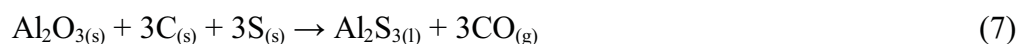


Figure 3 is showing equilibrium compositions at 1100-1800°C with sulphur producing significant amounts of gases with majority of CO at higher temperatures. Al₂S₃ is the main intermediate aluminium compound when sulphur is reacted with Al and C at 1100-1800°C. At 1 atmospheric pressure, sulphur can not reduce all Al₂O₃ to an aluminium compound even at

1800°C. Formation of Al_2S_3 is very low at 1100-1300°C (0.1012 mol Al_2S_3 / mol Al_2O_3) at 1 atm pressure and increases with increasing temperature to 1800°C (0.647 mol Al_2S_3 / mol Al_2O_3). Formation of CO is lower at 1100°C (0.035 mol/mol Al_2O_3) and significantly increases with increasing temperature (1.94 mol/mol Al_2O_3 at 1800°C). Along with CO and other gases significant amount of CS_2 gas is also formed at 1100°C (0.84 mol/ mol Al_2O_3). This content decreases to 0.015 mol/ mol Al_2O_3 when temperature is at 1800°C.

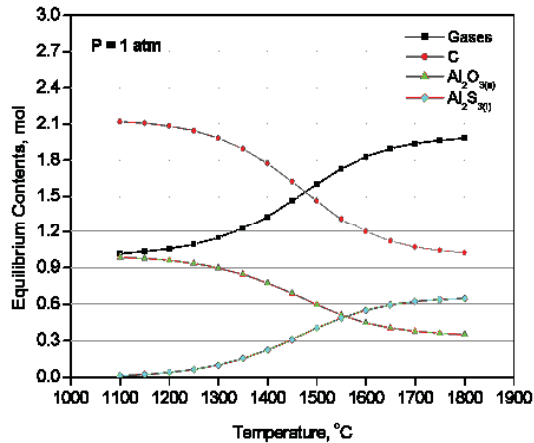


Fig 3: Predicted equilibrium phases formed when sulphur reacted with alumina and graphite mixture at 1100-1800°C (Al_2O_3 : C : S = 1 : 3 : 2)

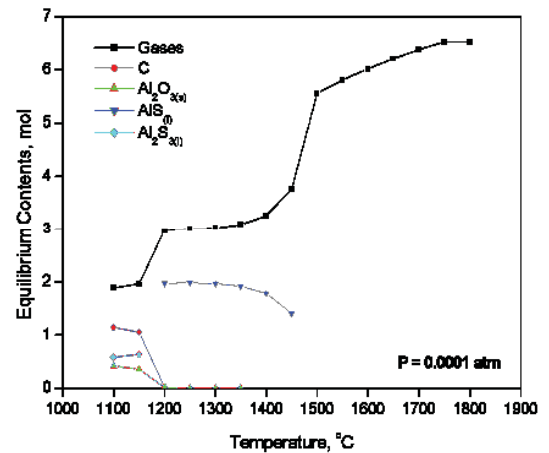


Fig 4: Predicted equilibrium phases formed when sulphur is added to alumina and graphite mixture at 1100-1800°C and 10^{-4} atm pressure

Effect of Total Pressure

A pressure change has a significant effect on the formation of aluminium sulphide compounds. The predicted equilibrium phases obtained from the Al_2O_3 -C-S system at 1100-1800°C are presented in Figure 4. AIS becomes the main sulphur containing liquid phase when pressure is reduced to 10^{-4} atm. Formation of liquid Al_2S_3 phase diminishes at 1150°C and liquid AIS is obtained above 1200°C. Maximum amount of AIS liquid phase is obtained at 1250°C (1.9795 mol/mol Al_2O_3) and then it decreased with increasing temperature to 1450°C (1.4056 mol/mol Al_2O_3). Above 1450°C no aluminum sulphide compounds were obtained and all products are obtained in various gaseous form.

Effect of Al_2S_3 to S ratio

Molar ratio (Al_2O_3 : S) changes can significantly improve the conversion yield of alumina to aluminium sulphide. Figure 5 is showing the equilibrium phases obtained when molar ratio of sulphur to alumina (Al_2O_3 : S) is increased from 1:2 to 1:3. Addition of extra sulphur into the Al_2O_3 -C-S system improves the formation rate of Al_2S_3 . Around 0.97080 mol Al_2S_3 /mol Al_2O_3 can be achieved at 1800°C when ration is increased to 1:3. In ambient pressure, with a molar ratio Al_2O_3 : S = 1:2 about 65% of alumina can be converted to Al_2S_3 at 1800°C. It can be seen from Figure 6 that similar amount of conversion can be achieved at 1550°C and 97% can be achieved at 1800°C when molar ratio is increased to 1:3. Further increment of the ratio to 1:4 increases the conversion yield up to 1500°C (about 77%) then it becomes similar as 1:3 at 1600°C (about 82-84%). Formation of gaseous products in Al_2O_3 -C-S system is very low at 1300°C and increases with increasing temperature to 1800°C. CS_2 is the main gas phase obtained in gaseous products (about 82 mol% of the gaseous products) at 1100°C and decreases with increasing temperature. At higher temperature formation of CS_2 goes down to

about 0.008% and CO becomes the major component, about 98% when temperature is increased to 1800°C. At reduced pressure, CO becomes the main gas phase in the gaseous products obtained from the reactions. About 93% of the gaseous products can be CO at 1100°C when pressure is kept at 10⁻⁴ atm.

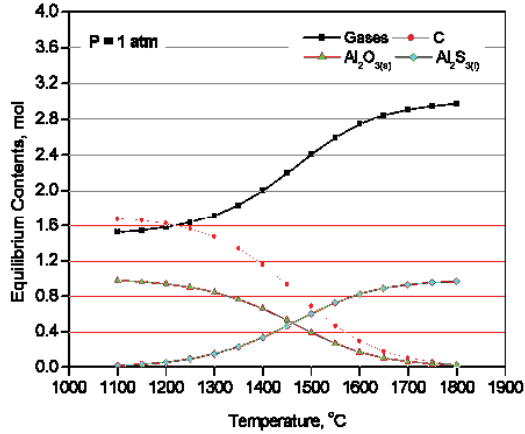


Fig 5: Predicted equilibrium phases formed when sulphur reacted with alumina and graphite mixture at 1100-1800°C (Al₂O₃ : C : S = 1 : 3 : 3)

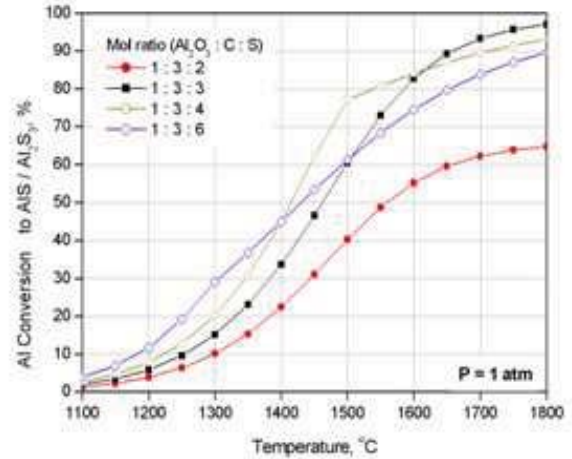


Fig 6: Predicted Al₂O₃ conversion when mole ratio of Al₂O₃ : C : S is increased from 1 : 3 : 2 to 1 : 3 : 6 at 1 atm pressure

From the thermodynamic analyses, summary of the reaction system, equilibrium calculation for carbothermic conversion of alumina to aluminium sulphide and their advantage/disadvantages are presented in Table 1 (for Al₂O₃ : C : S = 1 : 3 : 2 and 1 atm pressure).

Tab 1: An example of equilibrium calculation results of production of aluminium sulphide from alumina/aluminium ores

Process	Sulphide	Advantages:
General Reaction System	$Al_2O_{3(s)} + 3C_{(s)} + 2S_{(s)} = 2AlS_{(l)} + 3CO_{(g)}$	<ul style="list-style-type: none"> • Can be operated at low temperature (<1500°C) to form solid Al₂S₃ (which easy to handle and available in a reproducible form). (depending pressure) • High yield of alumina conversion. • Availability of technologies to handle sulphur gases. • Can be merged with sulphur plants in petrochemical industries.
Temperature, °C	1200 – 1800	
ΔH, kJ	7.71×10^2	
Yield, %	10% (1300° C, 1 atm) 65% (1800° C, 1 atm) The yield can increased significantly by lowering the total pressure.	
Other Contents in equilibrium,	Al ₂ O ₃	
	C	1.0233
		Disadvantages: <ul style="list-style-type: none"> • Al₂S₃ has a very high affinity to oxygen that comes into contact and converts aluminium sulphide back into alumina. • Produce odour
		Other Consideration:

mol	Total Gases	1.982	<ul style="list-style-type: none"> Produces significant CO gases, which can be used as fuel.
	CO	1.944	
	CS ₂	1.65 x 10 ⁻²	

Thermodynamic Analysis For Al Extraction – step 2

Thermal Dissociation of Al₂S₃ and AlS

Further thermodynamic analysis was carried out for the step – 2 of the process, i.e. extraction of Al from aluminium sulphide.

Predicted equilibrium phases obtained through thermal dissociation of Al₂S₃ at 1 atm pressure is presented in Figure 7. Al₂S₃ is a stable phase and starts to dissociate to various aluminium sulphide compounds and gaseous aluminium and sulphur above 2400°C. About 0.04 mol of Al_(g)/mol Al₂S₃ is obtained at 2600°C, which is very low conversion rate. This temperature is very high and not feasible in regular industrial practice. When the pressure is lowered to 0.1 atm, Al₂S₃ starts to dissociate to various aluminium sulphide compounds and gaseous aluminium and sulphur above 2100°C, as shown in the Figure 8. About 0.04 mol of Al_(g)/mol Al₂S₃ can be obtained at 2200°C, which gradually increases to 0.31 mol when temperature is increased to 3000°C.

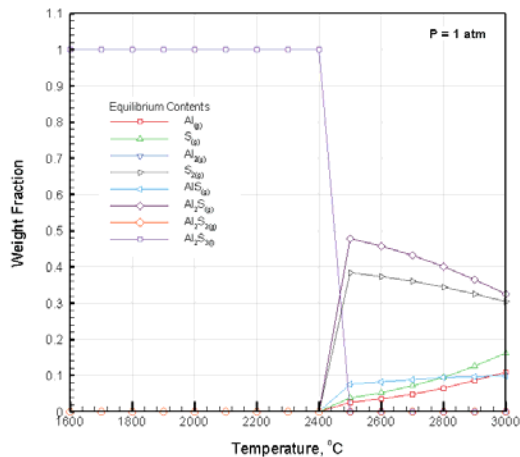


Fig 7: The phases formed in equilibrium during thermal dissociation of aluminium sulphide at 1600-3000°C and 1 atm pressure.

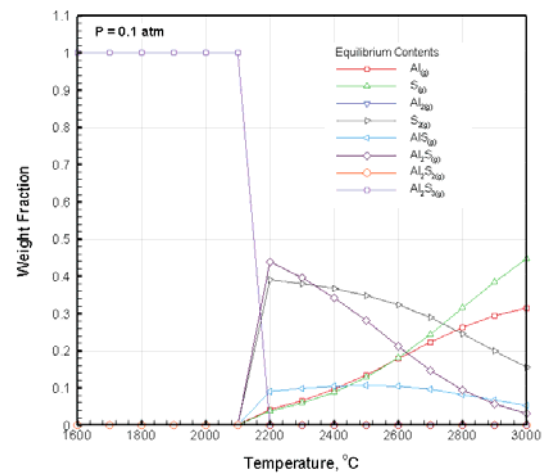


Fig 8: The phases formed in equilibrium during thermal dissociation of aluminium sulphide at 1600-3000°C and 0.1 atm pressure.

Predicted equilibrium phases obtained through thermal dissociation of Al₂S₃ at 10⁻⁴ atm pressure is presented in Figure 9. Al₂S₃ begins to dissociate to various aluminium sulphide compounds and gaseous aluminium and sulphur above 1560°C. Gaseous sulphur (S₂) is the main dissociated component obtained at lower temperature range. About 0.14 mol of Al_(g)/mol Al₂S₃ is obtained at 1570°C. This content gradually increases to 0.34 mol when temperature is increased to 2000°C. Formation of S_(g) is low at lower temperatures range. About 0.09 mol/ mol Al₂S₃ is obtained at 1700°C and then it sharply increases with increasing

temperatures. About 0.39 mol of $S_{(g)}$ is obtained at 2000°C. Formation of both $AlS_{(g)}$ and $Al_2S_{(g)}$ are higher at lower temperatures and then it gradually decreases with increasing temperature.

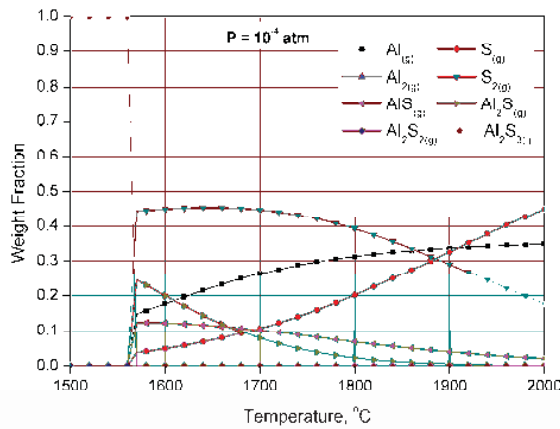


Fig 9: The predicted equilibrium phases obtained during thermal dissociation of Al_2S_3 at 1500-2000°C at 10^{-4} atm

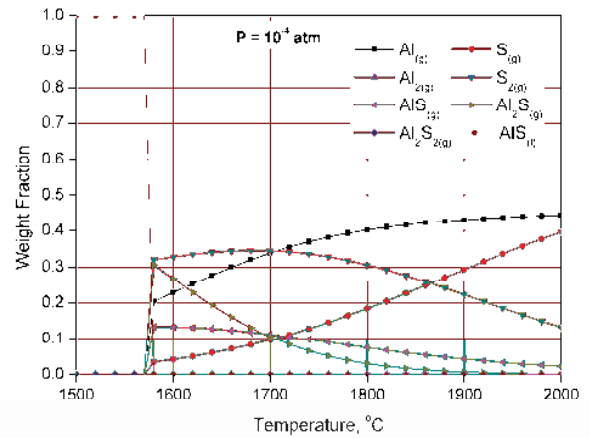


Fig 10: The predicted equilibrium phases obtained during thermal dissociation of AlS at 1500-2000°C at 10^{-4} atm

Similarly equilibrium phases obtained during thermal dissociation of AlS at 10^{-4} atm pressure is presented in Figure 10. Except $S_2(g)$, formation of all other gaseous and liquid phases remain same. At 1580°C, about 0.32 mol $S_{2(g)}$ /mol AlS is obtained which slightly increases to 0.34 mol when temperature is increased to 1690°C. Above 1690°C the formation of $S_2(g)$ gradually decreases. About 0.14 mol $S_{2(g)}$ /mol AlS is obtained when temperature is at 2000°C. Figure 11 shows aluminium yield from thermal dissociation of Al_2S_3 at various pressures in a temperature range of 1600-3000°C. Decreasing pressure significantly improves the production of gaseous aluminium and sulphur. By decreasing pressure from 1 atm to 0.001 atm, aluminium yield can be increased from 0 to 61% at 1900°C.

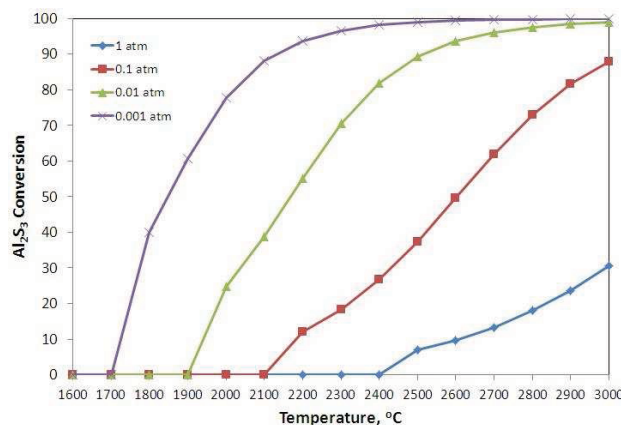


Fig 11: Predicted Al_2S_3 conversion from thermal dissociation at various pressures in temperature range 1600°C to 3000°C.

Disproportionation of AlS

Figure 12 shows the results of equilibrium calculations for disproportionation of AlS in a temperature range of 800-3000°C and 1 atm pressure. $AlS_{(liq)}$ starts to form above 1100°C and

completely dissociated to various aluminium sulphide compounds and aluminium gas above 2200°C. This suggests that the Reaction (5) cannot occur at ambient pressure.

Further thermodynamic analysis was carried out to analyse the effect of pressure at 1500°C. This temperature was chosen because the equilibrium conversion is acceptable and the temperature can be achieved in industrial practice. The results are shown in Figure 13 and suggested that aluminium can be extracted from aluminium sulphide by disproportionation if the pressure is kept below $10^{-4.5}$ atm. Only about 37.5 wt% gaseous aluminium metal can be obtained when the pressure is about 10^{-5} atm. At 1500°C AIS is a stable phase in equilibrium when pressure is higher than $10^{-4.4}$ atm.

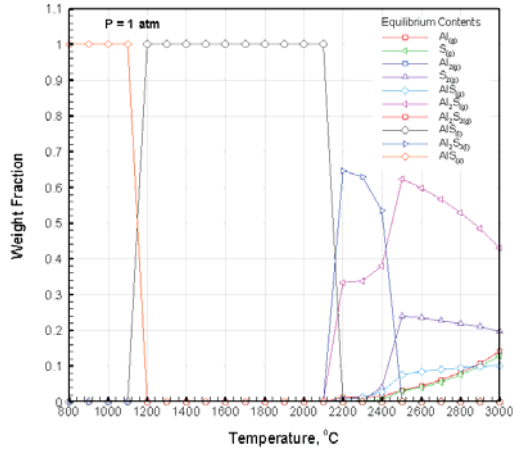


Fig 12: Solid and gaseous phases formed in equilibrium during disproportionation of AIS at 800-3000°C and 1 atm pressure

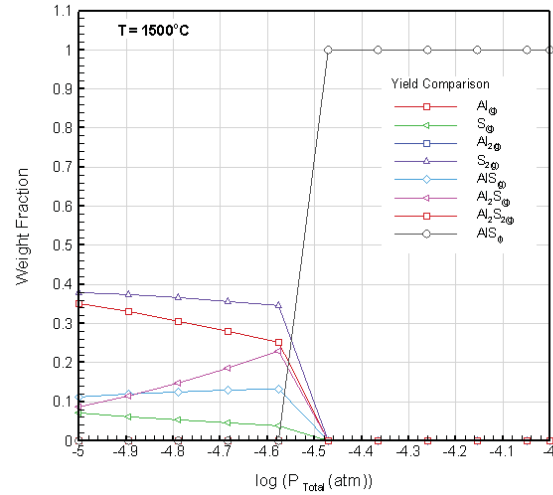
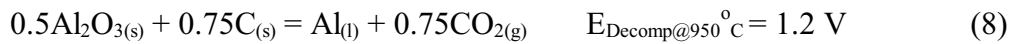


Fig 13: Aluminium production yield from disproportionation of AIS at 1500°C.

Electrolysis

The extraction of metals by the electrolysis of their sulphides in molten salts is very attractive from the viewpoint of energy utilization. By improving the cell design and electrolyte composition, the theoretical energy consumption needed for 1 kg of aluminium of 8.41 kWh could be approached, which is considerably lower than the value of 14 kWh/kg aluminium in the Hall-Heroult process (Xiao, van der Plas et al., 2007). Among aluminium compounds practical for the production of aluminium, Al_2S_3 has the lowest theoretical decomposition potential, compared to those of Al_2O_3 (Hall-Heroult process) and $AlCl_3$ (Alcoa process) (Minh, Loutfy et al., 1982).

The decomposition voltage for various aluminium compounds, such as Al_2O_3 , $AlCl_3$, Al_2S_3 and AlN in temperature range 700°C to 1100°C is presented in Figure 13. The associated reactions are shown below:



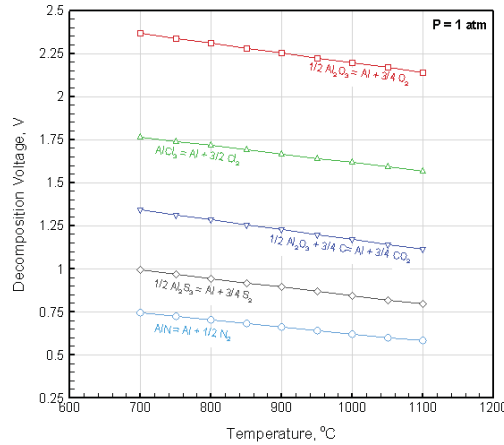


Fig 13: Decomposition voltage of various Al-compounds at temperature range of 700-1100°C.

In equilibrium conditions, theoretically higher voltage is required to decompose AlCl_3 compared to Al_2S_3 and AlN at 700°C. Electrolysis of Al_2S_3 in cryolite and chloride electrolytes have been suggested previously (Van Der Plas, 2004; Van Der Plas & Xiao, 2006; Xiao, van der Plas et al., 2007). One of the major problems associated with Al_2S_3 electrolysis process is lower solubility of Al_2S_3 in the molten bath.

Table 2 summarises the comparison among the processes for aluminium extraction from aluminium sulphide. The required voltage (0.98 V, Fig 13) for electrolysis of Al_2S_3 is much lower compared to the Hall-Heroult process (1.82 V) (Sportel & Verstraten, 2003) and can be performed at 700-800°C. Aluminium sulphide has a higher solubility in chloride bath for electrolysis. This electrolytic process can save energy up to 25% from the requirements for the aluminium chloride process (Minh, Loutfy et al., 1984). High yield can be achieved and 1 kg metallic aluminium can be produced from 2.8 kg of aluminium sulphide (Minh, Loutfy et al., 1984).

Tab 2: Aluminium extraction from aluminium sulphide

Process	Electrolysis	Advantages:
Overall Reaction	$2\text{Al}_2\text{S}_3 = 4\text{Al} + 3\text{S}_2$	<ul style="list-style-type: none"> • Required voltage (0.98 V), much lower compared to the Hall-Heroult process (1.82 V) (Sportel & Verstraten, 2003). • Electrolysis can be performed at 700-800°C. • Aluminium sulphide has a higher solubility in chloride bath for electrolysis. • Sulphide electrolytic process can save energy up to 25% compared to aluminium chloride process (Minh, Loutfy et al., 1984). • Availability of technologies to handle sulphur gases.
Temp, °C	800	
E°_{decom}, V	0.95	
Major reactions: $\text{Al}_2\text{S}_3 + 2\text{Fe} = \text{Fe}_2\text{S}_3 + 2\text{Al}$ $\Delta H_{1200} = 196.808 \text{ kJ}$ $6\text{S} + 2\text{AlCl}_3 = 2\text{Al} + 3\text{S}_2\text{Cl}_2$ $\Delta H_{750} = 1088.0067 \text{ kJ}$ $2\text{Al}_2\text{S}_3 = 4\text{Al} + 3\text{S}_2$ Cathode $2\text{Al}^{3+} + 6\text{e}^- = 2\text{Al}$ Anode $2\text{AlS}_3^{3-} - 6\text{e}^- = \text{Al}_2\text{S}_3 + 1.5\text{S}_2(\text{gas})$		
		Disadvantages: <ul style="list-style-type: none"> • Chloride salt bath, difficult to handle. • Produced elemental sulphur needs to be

Overall $\text{Al}_2\text{S}_3 = 2\text{Al} + 1.5\text{S}_2$ (gas)		recycled. <ul style="list-style-type: none"> Alumina present in the electrolysis cell may dissolve and saturate the electrolyte.
Process	Disproportionation and Thermal Decomposition	Disadvantages: <ul style="list-style-type: none"> Requires high temperature (temperature maybe reduced by applying low pressure) Much of the chemistry and equilibria involved in this process is unknown. Complex equilibria at high temperatures Sulphur gas produced needs to be recycled to increase the product yield. Difficulties in separating $\text{Al}_{(g)}$ from other by products.
Overall Reaction	$2\text{Al}_2\text{S}_3 = 4\text{Al} + 3\text{S}_2$	
Temp, °C	2434 at 1 atm <1700 at vacuum	
Major reactions $\text{Al}_2\text{S}_3 = 2\text{AlS} + \text{S}$ $3\text{AlS} = \text{Al}_2\text{S}_3 + \text{Al}$		

CONCLUDING REMARKS

The thermodynamics of two-stage aluminium production, i.e. reduction of alumina to intermediate compounds followed by dissociation to aluminium (through electrolysis, thermal dissociation, and disproportionation) have been investigated for carbusulphidation route. Effect of temperature, pressure and mole ratio has been studied for Al_2O_3 -C-S system. Results showed, Al_2S_3 is the main intermediate aluminium compound when sulphur and carbon are reacted with Al_2O_3 at 1100-1800°C and AlS becomes the main sulphur containing liquid phase when pressure is reduced. Molar ratio (Al_2O_3 : S) changes has effect on the conversion yield of alumina to aluminium sulphide. With a molar ratio Al_2O_3 : S = 1:2 about 65% of aluminum can be converted to Al_2S_3 at 1800°C. With increasing ratio to 1:3, about 97% of aluminum can be converted at 1800°C. Further thermodynamic analysis was also carried out to investigate the subsequent process (2nd stage of process) to extract aluminium from the intermediate compounds (thermal dissociation, disproportionation, and electrolysis). From thermodynamic perspective; thermal dissociation, electrolysis and disproportionation can be used for the sulphide route. It has been shown that the equilibria of disproportionation and thermal decomposition of sulphides are quite complex. Further thermodynamic analysis is required to find the optimum conditions. It should be noted that the analysis presented in this report is based on results of equilibrium calculations which give the theoretical limits of the associated processes. Nevertheless, this provides a basis for the development of new route for aluminium production. Further improvement and optimisation of the new route may include consideration of non-equilibrium processes.

REFERENCES

www.world-aluminium.org. (2012), from <http://www.world-aluminium.org/About+Aluminium/Story+of>.

Bale, C. W., E. Bélisle, P. Chartrand, S. A. Deckerov, G. Eriksson, K. Hack, I. H. Jung, Y. B. Kang, J. Melançon, A. D. Pelton, C. Robelin and S. Petersen (2009). "FactSage Thermochemical Software and Databases -- Recent Developments." CALPHAD: Computer Coupling of Phase Diagrams and Thermochemistry 33(2): 295-311.

Barin, I. (1993). Thermochemical Data of Pure Substances. Weinheim Germany, VCH Verlagsgesellschaft mbH.

Brooks, G., M. Cooksey, G. Wellwood and C. Goods (2007). "Challenges in Light Metals Production." Mineral Processing and Extractive Metallurgy 116(1): 25-33.

Dewan, M. A., M. A. Rhamdhani, G. A. Brooks, B. J. Monaghan and L. Prentice (2011). "Alternative Al Production Methods: Part II - Thermodynamic Analyses of Indirect Carbothermal Routes." Submitted to Metallurgical and Materials Transactions B.

Eriksson, G., P. Wu and A. D. Pelton "Critical Evaluation and Optimization of the Thermodynamic Properties and Phase Diagrams of the MgO---Al₂O₃, MnO---Al₂O₃, FeO---Al₂O₃, Na₂O---Al₂O₃, and K₂O---Al₂O₃ systems." CALPHAD: Computer Coupling of Phase Diagrams and Thermochemistry 17(2): 189-205.

Gardner, H. J., K. Grojtoheim and B. J. Welch (1981). ICSOBA Symposium, Tihany, Hungary.

Halmann, M., A. Frei and A. Steinfeld (2007). "Carbothermal Reduction of Alumina: Thermochemical Equilibrium Calculations and Experimental Investigation." Energy 32(Compendex): 2420-2427.

Kvande, H. (1999). Inert Electrodes in Aluminum Electrolysis Cells. Light Metals 1999. C. E. Eckert. Warrendale, PA, TMS: 369-376.

Lans, S., J. Bohte, Y. Xiao, A. Van Sandwijk and M. A. Reuter (2003). The Possibilities of electrowinning of Al from Al₂S₃. The International Symposium on Light Metals 2003, Vancouver, Canada.

Loutfy, R. O., R. Keller and N. P. Yao (1981). Method of Winning Aluminum Metal from Aluminous Ore. U. S. Patent: 4,265,716, The United States of America as represented by the United States Department of Energy.

Minh, N. Q., R. O. Loutfy and N. P. Yao (1982). "The Electrochemical Behavior of Al₂S₃ in Molten MgCl₂ + NaCl + KCl Eutectic." Journal of Electroanalytical Chemistry 131: 229-242.

Minh, N. Q., R. O. Loutfy and N. P. Yao (1984). Production of Aluminum Metal by Electrolysis of Aluminum Sulfide. U. S. Patent: 4,4645,234, The United States of America as represented by the United States Department of Energy, Washington, D.C.

Motzfeldt, K., H. Kvande, A. Schei and K. Grjotheim (1989). Carbothermal Production of Aluminum. Dusseldorf, Germany, Aluminium-Verlag.

Murray, J. P. (1999). "Aluminum Production using High-Temperature Solar Process Heat." Solar Energy 66(2): 133-142.

Namboothiri, S., M. P. Taylor, J. J. J. Chen, M. M. Hyland and M. Cooksey (2007). "Aluminium Production Options with a Focus on the Use of a Hydrogen Anode: A Review." Asia-Pacific Journal of Chemical Engineering 2(Compendex): 442-447.

OECD (1976). Industrial Adaptation in the Primary Aluminium Industry. Paris, OECD Publications Center.

Rhamdhani, M. A., M. A. Dewan, G. A. Brooks, B. J. Monaghan and L. Prentice (2011). "Alternative Al Production Methods: Part I - A Review of Indirect Carbothermal Routes." Submitted to Metallurgical and Materials Transactions B.

Russell, A. S., L. L. Knapp and E. Haupin (1979). Production of Aluminum. U. S. Patent: 3,725,222, Aluminum Company of America.

Sohn, H. Y. and D. D. Harbuck (1986). "Alumina from Coal Wastes Through the Formation of Aluminum Nitride by Carbothermal Reduction under Nitrogen." Industrial & Engineering Chemistry Product Research and Development 25(2): 367-372.

Sportel, H. and C. W. F. Verstraten (1999). Method and Apparatus for the Production of Aluminum from Alumina Ore by Aluminum Sulfide Process. World Patent: Patent Application WO 00/37691, Corus Aluminium Walzprodukte GmbH.

Sportel, H. and C. W. F. Verstraten (2003). Method and Apparatus for the Production of Aluminium. U. S. Patent: 6,565,733. C. A. W. GmbH.

Steinfeld, A. and G. Thompson (1994). "Solar Combined Thermochemical Processes for CO₂ Mitigation in the Iron, Cement, and Syngas Industries." Energy 19(10): 1077-1081.

Thonstad, J., P. Fellner, G. M. Haarberg, J. Hives, H. Kvande and A. Sterten (2001). Aluminium Electrolysis: fundamentals of the Hall-Heroult process. Dusseldorf, Aluminium Verlag.: 340-346.

Van Der Plas, D. W. (2004). Process for the Electrolysis of Aluminumsulfide. World Intellectual Property Organization: WO 2004/08800, Corus Technology BV, CA Ijmuiden (NL).

Van Der Plas, D. W. and Y. Xiao (2006). Method and Apparatus for the Production of Aluminium. U. S. Patent: US2006/0226026, Corus Aluminium Walzprodukte GmbH, Koblenz (DE).

Withers, J. C. and G. V. Upperman (1982). Electrolytic Cell for the Production of Aluminum. U. S. Patent: 4,338,177, Metallurgical, Inc., Lakewood, Ohio. U. S. Patent: 4,338,177.

Xiao, Y., J. Soons, S. Lans, A. Van Sandwijk, M. A. Reuter and D. W. Van Der Plas (2003). Sulfidation of Al_2O_3 with CS_2 gas. The International Symposium on Light Metals 2003, Vancouver, Canada.

Xiao, Y., D. W. van der Plas, J. Bohte, S. C. Lans, A. van Sandwijk and M. A. Reuter (2007). "Electrowinning Al from Al_2S_3 in Molten Salt." Journal of The Electrochemical Society 154(6): D334-D338.

Xiao, Y., D. W. Van Der Plas, J. Soons, S. C. Lans, A. Van Sandwijk and M. A. Reuter (2004). "Sulfidation of Al_2O_3 with CS_2 gas for Compact Aluminium Production Process." Canadian Metallurgical Quarterly 43(2): 283-292.