PRODUCTION OF ALUMINUM SULFIDE THROUGH CARBOSULFIDATION UTILISING H₂S

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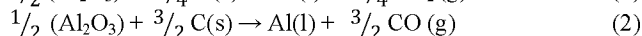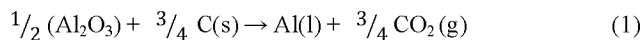[3]CSIRO Process Science and Engineering, VIC 3169, Australia

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Abstract

Indirect carbothermal reduction of alumina for the production of aluminum utilizes different reducing agents to convert alumina into intermediate aluminum compounds. In the present study, the carbosulfidation route for aluminum production utilizing $H_2S(g)$ as the reductant and sulfur source has been investigated, in particular the formation of Al_2S_3 in the first step of the process. The results of the thermodynamic analysis predicted that conversion of $Al_2O_3(s)$ to $Al_2S_3(l)$ significantly increases above 1400°C at 1 atmosphere pressure. Experimental investigations were carried out at temperatures of 1100 to 1500°C using dilute $H_2S(g)$ gas in argon. The reaction products were analyzed using scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), X-ray diffraction (XRD), inductively-coupled plasma absorption emission spectroscopy (ICP-AES) and chemical filtration. The X-ray diffraction results confirmed the presence of $Al_2S_3(s)$. Percentage of conversion from Al_2O_3 to Al_2S_3 was found to be over 80% at 1500°C.

Introduction

Aluminum is the most widely used nonferrous metal in the world and is the third most abundant element in the earth's crust and constitutes 7.3% by mass [1]. Australia is the second largest producer of alumina in the world, which is the primary source of aluminum production [1]. Alumina (Al_2O_3) is produced from bauxite ore by Bayer process, which is then processed in Hall-Heroult cell to produce aluminum. Hall-Heroult cell is an electrolysis cell containing Al_2O_3 dissolved in NaF-AlF_3 (cryolite). The electrochemical reactions can be represented by the following reactions [2]

$$\tfrac{1}{2}(Al_2O_3) + \tfrac{3}{4} C(s) \rightarrow Al(l) + \tfrac{3}{4} CO_2(g) \tag{1}$$

$$\tfrac{1}{2}(Al_2O_3) + \tfrac{3}{2} C(s) \rightarrow Al(l) + \tfrac{3}{2} CO(g) \tag{2}$$

The cost of the Bayer process represents about 27% of the cost of aluminum production [3], while the Hall-Heroult process uses about three quarters of the total energy. Most of this energy is electrical energy.

The electrolysis of alumina requires high capital costs, large amounts of energy (12.9-15 DC kWh/kg Al [4], 0.186 GJ/kg Al [5]) and is associated with a substantial environmental burden [6]. Apart from substantial CO_2 and SO_2 emissions from the production of electrical energy, the Hall-Heroult process generates greenhouse gas emissions such as CF_4 and C_2F_6 from carbon electrode and liquid cryolite (Na_3AlF_6) reactions during "anode effects". When the alumina ore content of the electrolytic bath falls below critical levels required for electrolysis, rapid voltage increases occur, termed "anode effects". Anode effects cause carbon from the anode and fluorine from the dissociated molten cryolite bath to combine, producing CF_4 and C_2F_6.

The obvious drawbacks of the Hall-Heroult process have led to numerous research efforts to find alternative routes for primary aluminum production throughout the 20th and early 21st centuries. The most important alternatives that have been envisaged include modified Hall-Heroult process utilising inert anodes [7], the use of $AlCl_3$ as an intermediate step in the production of Al [8] and the carbothermic reduction of alumina [9]. Alcoa vigorously pursued the electrolysis of aluminum chloride in the 1960s and 1970s and halted the operation in 1980s, reportedly owing to difficulties with production and handling aluminum chloride [10]. In case of direct carbothermal reduction of alumina/aluminous ores, a mixture of aluminum carbide and metallic aluminum is formed when alumina/aluminous ores are reduced by solid carbon at higher temperatures [11]. Equilibrium analyses show that the driving forces for both aluminum carbide and aluminum metal formation by carbothermic reduction of alumina are similar, therefore it is difficult to get high yield of pure aluminum. The main problems with this route were high operating temperature and aluminum vapor back reactions with carbon monoxide [12] to form aluminum oxides and carbides that reduce the aluminum yield.

Problems associated with the direct carbothermal reduction process could potentially be avoided by forming intermediate aluminum compounds before reduction to metal. This is referred to as the indirect carbothermal reduction method. The process includes at least two stages where alumina (or aluminum ores) is reduced to an intermediate compound by carbothermal reduction in the first stage followed by subsequent reduction of the compound to aluminum at later stages.

In a previous study, Rhamdhani et al. [13] provided a comprehensive review of the various multistage indirect carbothermal processes. The comparison of these processes, in terms of the thermodynamics, were also presented [14]. It was shown that from thermodynamic perspective, high conversion was possible when alumina is reduced to Al-chloride, Al-sulfide or Al-nitride. It was also shown that thermal dissociation and disproportionation may be suitable for extraction of Al from Al-chloride and Al-sulfide in the final step. Electrolysis could also be used for processing of Al-sulfide [15].

In the carbosulfidation route, alumina potentially can be converted to aluminum sulfide Al_2S_3 (solid or liquid) by using any possible sulfur source in the presence of carbon reductant. Huda et al. [16] carried out a thermodynamic assessment of the sulfide route, including the effect of temperature, pressure and chemistry for the Al_2O_3-C-S system. The results show that $Al_2S_3(l)$ should be the main intermediate aluminum compound when sulfur and carbon are reacted with $Al_2O_3(s)$ at 1100 to 1800°C and $AlS(l)$ becomes

the main sulfur containing liquid phase when the reaction is carried out at reduced pressure. The molar ratio of Al_2O_3 and S is predicted to have an effect on the conversion yield of alumina to aluminum sulfide. At a molar ratio of Al_2O_3: S = 1:2 about 65% of aluminum can be converted to $Al_2S_3(l)$ at 1800°C, whereas, increasing the ratio to 1:3 increases the conversion to 97% at 1800 °C.

The authors investigated the feasibility of this proposed H_2S route for industrial scale production. It appeared that utilizing H_2S as the reductant and sulfur source could be an attractive route from the economic perspective because of the availability of raw materials, cheap H_2S price, heat recovery, high yield and less overall energy requirement of the process.

Previous Studies on Carbosulfidation Route
A sulfide process was patented by Loutfy *et al.* [17] in 1981 using pure carbon and sulfur operating above the Al_2S_3 melting temperature. Alumina ore was reacted with carbon and sulfur containing gas between 1027 to 1227°C to obtain molten aluminum sulfide (Al_2S_3).

$$Al_2O_3(s) + 3C(s) + 1.5 \ S_2(g) = Al_2S_3(l) + 3CO(g) \qquad (3)$$
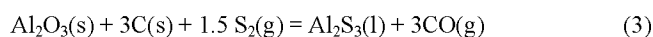
Loutfy *et al.* [17] suggested that disproportionation of aluminum monosulfide (AlS) could be used to extract aluminum metal. The Al_2S_3 produced in the Reaction (3) was further heated between 1327 to 1627°C in the presence of aluminum to produce aluminum monosulfide (AlS) and sulfur. Then AlS was cooled to form molten aluminum sulfide (Al_2S_3) and metal aluminum according to the following reactions:

$$Al_2S_3(l) = 2AlS(l) + S(s) \qquad (4)$$
$$3AlS(l) = Al_2S_3(l) + Al(l) \qquad (5)$$

Loutfy *et al.* [17] did not discuss the effect of pressure on the process. A thermodynamic assessment by Dewan *et al.* [14] indicated that the reactions (4) and (5) do not occur at atmospheric pressure.

Electrolysis of Al_2S_3 (Extraction of Al from Al_2S_3)
The extraction of metals by the electrolysis of their sulfides in molten salts is very attractive from the viewpoint of energy utilization. Previous study by Xiao *et al.* [15] showed that by improving the cell design and electrolyte composition, the theoretical energy consumption needed for 1 kg of aluminum of 8.41 kWh could be achieved, which is considerably lower than the value of 14 kWh/kg aluminum in the Hall-Heroult process [15]. Among aluminum compounds practical for the production of aluminum, Al_2S_3 has the lowest theoretical decomposition potential, compared to those of Al_2O_3 (Hall-Heroult process) and $AlCl_3$ (Alcoa process) [18]. Electrolysis of Al_2S_3 in cryolite and chloride electrolytes have been suggested previously [15, 19, 20]. The required voltage (0.98 V) for electrolysis of Al_2S_3 is much lower compared to the Hall-Heroult process (1.82 V) [21] and can be performed at 700 to 800°C. This electrolytic process can save energy up to 25% from the requirements for the aluminum chloride process [22].

In 1984 Minh *et al.* [22] patented an aluminum extraction process from Al_2S_3 by electrolysis at 700 to 800°C utilizing an electrolytic bath containing alkali metal chloride and/or alkaline earth metal chlorides ($MgCl_2$-NaCl-KCl and $MgCl_2$-NaCl-KCl-$AlCl_3$). Using

these electrolytes about 70 to 85% current efficiency was obtained. In 2004, Van Der Plas [19] patented a similar process for aluminum production by electrolysis of Al_2S_3 using a molten chloride salt ($MgCl_2$-NaCl-KCl) bath.

The present study was carried out with an aim to evaluate alternative sulfur sources for the carbosulfidation process. $H_2S(g)$ was found to be an attractive alternative solution as a sulfur source, in particular when the carbosulfidation process is integrated within petrochemical processes. The approach taken in this study includes thermodynamic analysis of the Al_2O_3-C-H_2S system followed by experimental studies. Results from the thermodynamic assessment and experimental investigation will be discussed in the following sections.

Equilibrium Calculations of Al_2O_3-C-H_2S Reaction Systems

The equilibrium calculations were carried out using FactSage 6.1 thermodynamic package. The details of this thermochemical package, such as the database and various calculation modules, can be found elsewhere [23]. 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 [24] and thermodynamic properties data [25]. The solution model for the liquid slag phase is a modified quasi-chemical model [26].

The equilibrium calculations for Al_2O_3-C-H_2S system were carried at temperatures 1000°C to 2000°C at different pressures. For all equilibrium calculations, 3 moles of C and 3 moles of H_2S were considered for 1 mole of Al_2O_3. Figure 1 shows equilibrium calculation of $Al_2O_3+3C+3H_2S$ for temperature range of 1000 to 2000°C at two different pressures (1 atm and 0.001 atm). The predicted condensed (liquid and solid) phases at pressure of 1 and 0.001 atm are shown in the Figures 1(a-b) and 1(c-d), respectively. Figures 1(b) and 1(d) show that significant amounts of gases are produced with majority of $H_2(g)$ and CO(g) at higher temperatures. Al_2S_3 is predicted to be the main intermediate aluminum compound when H_2S is reacted with Al_2O_3 and C at 1000 to 2000°C at 1 atmospheric pressure. Formation of Al_2S_3 is predicted to be very low at 1100 to 1300°C at 1 atm pressure (0.1012 mol Al_2S_3/ mol Al_2O_3) and predicted to increase with increasing temperature to 1800°C. Formation of CO is predicted to be lower at 1100°C (0.035 mol/mol Al_2O_3) and significantly increases with increasing temperature (2.6 mol/mol Al_2O_3 at 1800°C). Along with CO and other gases significant amount of $H_2(g)$ gas is also predicted to form at 1100°C (1.37 mol/ mol Al_2O_3). This content of $H_2(g)$ was predicted to increase to 2.62 mol/mol Al_2O_3 when temperature is at 1800°C.

Pressure is predicted to have a significant effect on the formation of Al_2S_3. Formation of AlS is predicted to increase with decreasing pressure. At 1500°C and 0.001 atm pressure, formation of AlS is 0.23 mol/ mol Al_2O_3, which reduces to almost zero at 1600°C. Formation of liquid Al_2S_3 phase is predicted to diminish at 1650°C at 0.001 atm. Above 1650°C and 0.001 atm pressure, all predicted products are in various gaseous form, no aluminum sulfide compounds in condensed form were predicted. Not much change in the formation of gaseous components was predicted by the equilibrium calculations due to changing pressure.
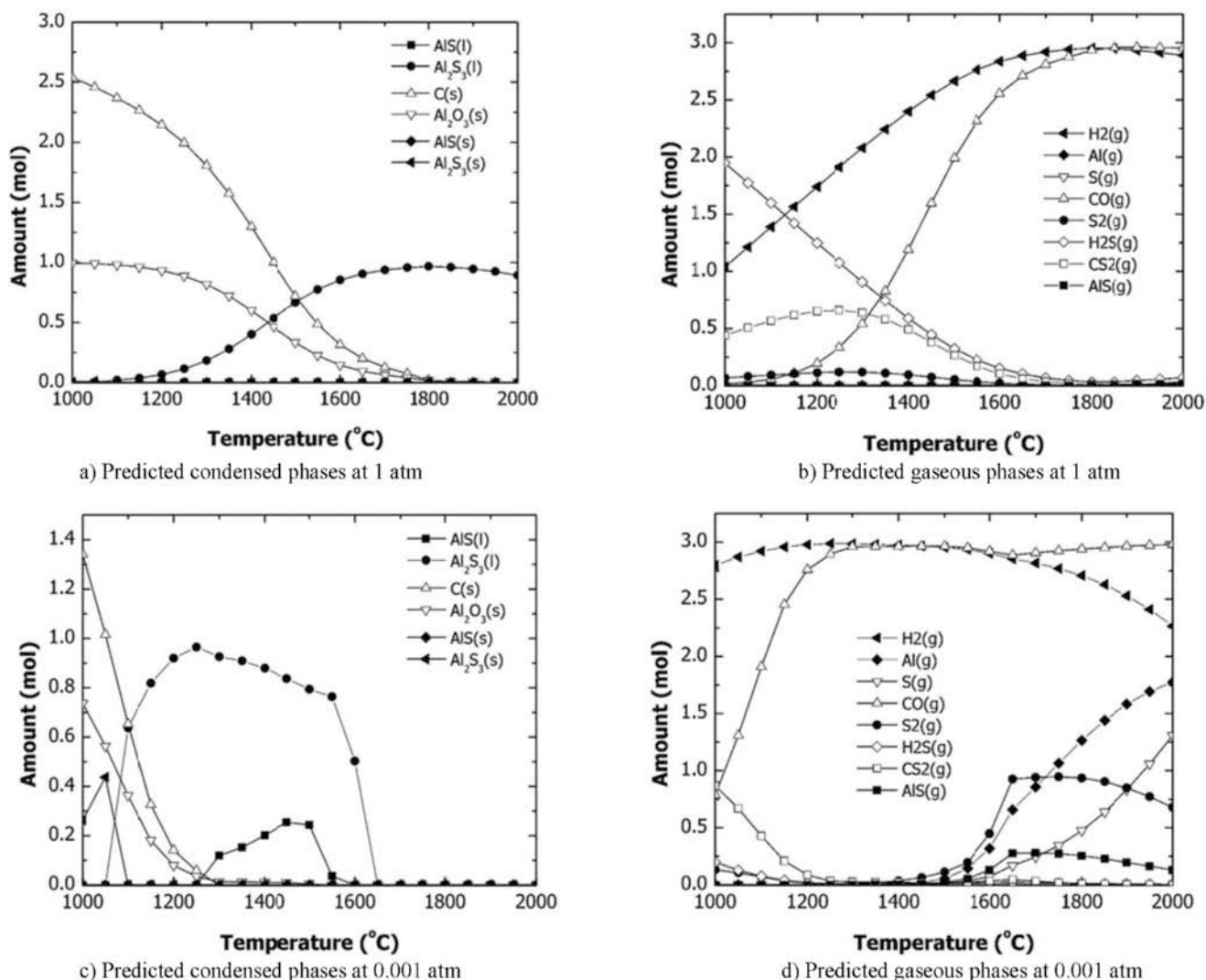
a) Predicted condensed phases at 1 atm

b) Predicted gaseous phases at 1 atm

c) Predicted condensed phases at 0.001 atm

d) Predicted gaseous phases at 0.001 atm

Figure 1: Predicted equilibrium phases in the $Al_2O_3+3C+3H_2S$ system at T = 1000°C to 2000°C: a) condensed phases at 1 atm, b) gaseous phases at 1 atm, c) condensed phases at 0.001 atm, and d) gaseous phases at 0.001 atm.

Experimental Investigation on Al_2O_3-C-H_2S Reaction Systems

Experimental Procedure

Experimental investigation on carbosulfidation of $Al_2O_3(s)$ by using C(s) and dilute $H_2S(g)$ (5% H_2S – 95% Ar) at different temperatures (1100 to 1600 °C) and reaction duration were carried out using a horizontal tube resistance-furnace (Nabertherm RHTV 200-600). Mixtures of $Al_2O_3(s)$ and C(s) powders (1 to 6 molar ratio) were pressed at 84 MPa pressure to form pellets with diameter of 11mm. Excess carbon was added to ensure that enough carbon is present at the reaction temperature. Three pellets were placed in an alumina boat and inserted into the furnace. The furnace was then sealed and put under vacuum before purging with the dilute H_2S (5% H_2S – 95% Ar). A schematic diagram of the experimental setup is shown in Figure 2. The gas was injected directly on top the sample by using a gas injection tube (made of high purity alumina) throughout the experimental cycle. The pellets were heated up under H_2S-Ar atmosphere and were held at the target temperatures (1100°C to 1600°C) for different time intervals (3 to 12 hours) before being cooled down to room temperature.
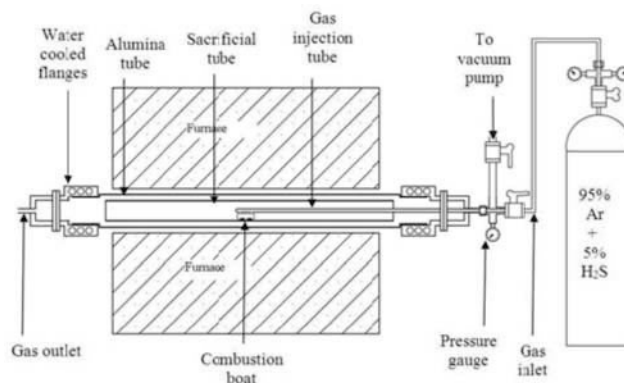

Figure 2: A schematic diagram of the experimental set up using a horizontal tube furnace

The samples, after the experiments were analyzed using XRD (X-ray diffraction), SEM (scanning electron microscopy), EDS

(energy dispersive X-ray spectroscopy), ICP-AES (inductively coupled plasma) and chemical filtration. XRD analyses of the samples were carried out using BRUKER D8 Advanced X-ray Diffractometer with a graphite monochromator using Cu K_α radiation (Theta range 2.5° to 45°, step size 0.02°, $\lambda = 1.5406$). The samples were ground by using mortar and pestle before putting into the sample holder of the XRD machine (approximate weight for each sample is 1 g).

The microstructures of the samples and the qualitative elemental composition were examined using SEM and EDS techniques in a variable pressure SEM (FE SEM Carl ZEISS SUPRA 40VP) with an accelerating voltage of 20 keV. ICP – AES analyses were carried out to quantify the elements in the sample after the experiments. The aluminum content was determined by borate fusion followed by nitric acid dissolution. The resultant solution was analyzed using Varian 730ES Inductively Coupled Plasma. The carbon and sulfur were analyzed using LECO CS200 combustion analyzer.

X-ray Diffraction Analysis
The first set of experiments was carried out for 3 hours at temperatures of 1100 to 1400°C at 1 atm total pressure. The X-ray diffractograms of these samples are shown in Figure 3. The results confirmed the formation of Al_2S_3 in the temperature range studied as indicated by the presence of peaks labeled 2 in the difractograms. However, at this 3 hours reaction time it appears that only a small amount of Al_2S_3 is formed. It can be seen from Figure 3 that there are major traces of unreacted corundum Al_2O_3 (peaks labeled 1) and graphite (peaks labeled 3).
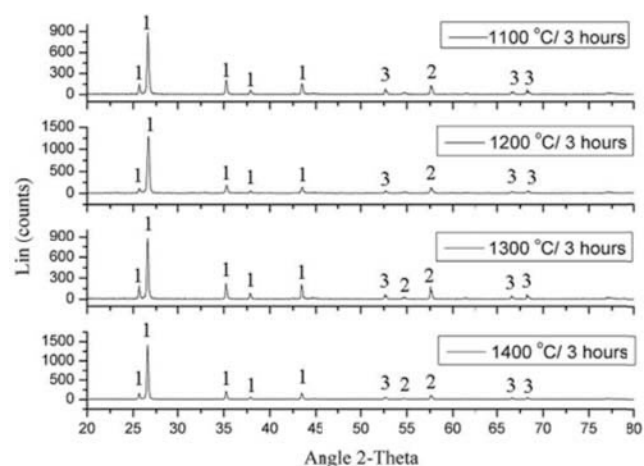

Figure 3: X-Ray diffraction pattern of the samples after 3 hours experiments at temperatures of 1100 to 1400°C. (1 = corundum (Al_2O_3), 2 = aluminum sulfide (Al_2S_3) and 3 = Graphite (C))

Further experiments at longer reaction time were carried out at 1300 to 1500°C. Figure 4 shows the comparison of XRD pattern of the samples after experiments at 1400°C for three different times (3, 6 and 9 hours). Al_2O_3 and Al_2S_3 peaks are marked by "1" and "2", respectively. As shown in Figure 4, significant aluminum sulfide (Al_2S_3) was detected after 6 and 9 hours of reaction. This is indicated by the higher and sharper Al_2S_3 peaks at 6 and 9 hours compared to those from at 3 hours. Al_2O_3 peaks are still present, indicated that some Al_2O_3 remains and unreacted

in the samples. However, it can also be seen clearly that there is a gradual decrease of the intensity with increasing reaction time. Figure 5 shows the results of XRD from samples obtained from the experiments carried out at 1500°C at different reaction time. Similar to the results from samples at 1400°C, significant Al_2S_3 was observed after 6 hours of reaction. At 9 hours of reaction, the Al_2S_3 peaks are sharper. The results in Figures 4 and 5 confirm the formation of Al_2S_3 at 1400°C and 1500°C, and that the amount increases with increasing of reaction temperature.
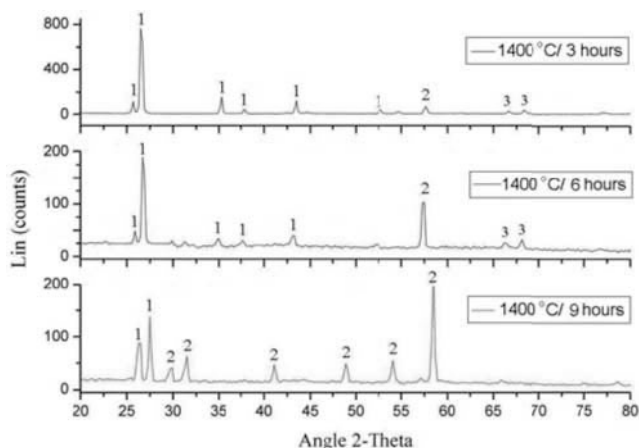

Figure 4: X-ray diffraction pattern of the samples after 3, 6, and 9 hours experiments at 1400 °C. (1 = corundum (Al_2O_3), 2 = aluminum sulfide (Al_2S_3) and 3 = Graphite (C))
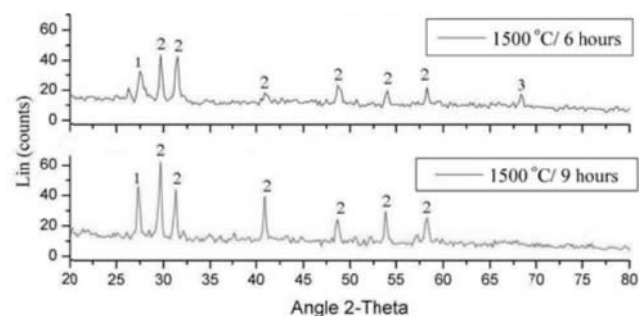

Figure 5: X-ray diffraction pattern of the samples after 6 and 9 hours experiments at 1500 °C. (1 = corundum (Al_2O_3), 2 = aluminum sulfide (Al_2S_3) and 3 = Graphite (C))

SEM and EDS Analysis
Secondary electron images of the typical microstructure of the sample after the experiments are shown in Figure 6. It can be seen from Figure 6(a) that the surface of the sample consists of packed re-crystallised grains. Figure 6(b) shows the surface at higher magnification. The boundaries between the grains appear to be fused and the edges are smooth and rounded. Some small globular particles are also present on the surface of the grains. These shapes of the particles and surface morphology are characteristics of a surface that undergo a melting and recrystallisation during the process. It should be noted that Al_2S_3 is a liquid above 1100°C at 1 atm.

EDS analyses were carried out on the surface of the samples to evaluate the presence of different elements. Figure 6(c) shows the

EDS spectrum of the surface indicating the presence of Al, S, O, and C. This result, along with the X-Ray diffractogram, suggests that S from H_2S reacted with the surface forming Al_2S_3, and that some unreacted Al_2O_3 is present below this surface.
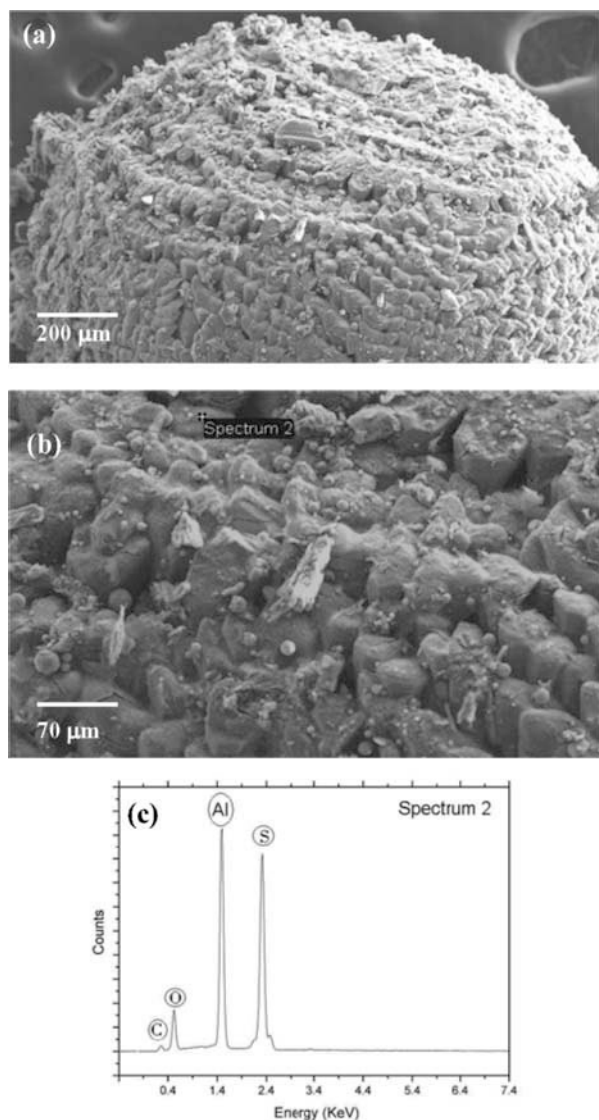

Figure 6: (a) A secondary electron (SE) image of a surface of sample after experiment at T = 1500°C, Time = 6 hours; (b) a higher magnification SE image of the surface; (c) an EDS spectrum of the surface shown in (b) indicating the presence of Al, S, C, O.

ICP-AES and LECO Analyses

The results from ICP – AES and LECO are shown in Table I. As shown in Table I, the concentration of S was measured to be 4.6 wt% in the sample reacted for 6 hours at 1300°C. High concentration of S was observed in the samples reacted at 1400°C and 1500°C. At 1400°C, the concentration of S increased from 41.1 wt% (at 6 hours) to 45.8 wt% (at 9 hours). Similarly at 1500°C, the concentration of S increased significantly from 17.8 wt% (at 3 hours) to 45.9 wt% (at 9 hours).

Determination of η (Conversion)

The percentage of conversion from Al_2O_3 to Al_2S_3 was determined by chemical dissolution and filtration. As pure Al_2S_3 completely dissolves in hydrochloric acid (HCl), a portion of the experimental samples were dissolved in HCl (36% w/w aqueous solution) and the solution was then filtered out. The amount of mass that dissolves in HCl represents the formed Al_2S_3 while the residues are the unreacted Al_2O_3 and C.

Table I: Results of ICP-AES and LECO analyses of samples reacted at 1300°C, 1400°C and 1500°C

Temperature (°C)	Duration (hours)	wt% Al	wt% S	wt% C	wt% O
1300	6	38.5	4.6	25	31.8
1400	6	38.8	41.1	6.1	13.9
	9	37.3	45.8	6.5	10.3
1500	3	31.7	17.8	24.4	25.9
	9	40.3	45.9	0.8	12.9

Table II: The conversion of Al_2O_3 to Al_2S_3 from selected samples at 1400°C and 1500°C

Temperature (°C)	Duration (hours)	Weight of Sample (g)	% of Conversion (η)
1400	6	0.2012	75.4%
	9	0.2051	77%
1500	6	0.2186	78.9%
	9	0.2060	81.6%

Approximately 0.2g of ground samples from each experiment was put into 20 ml HCl (36% w/w aqueous solution) in an Erlenmeyer flask. The solution was then stirred vigorously for few minutes and left for approximately 3 hours to allow all Al_2S_3 to be dissolved. The solution, along with the residue was then filtered using filter paper. The filter papers with the residues were then dried and weighed. The dried filter paper with the residue was then weighed to determine the weight loss of the sample due to dissolution. From these dissolution and filtration processes, the percent of conversion (η) of Al_2O_3 to Al_2S_3 was calculated using following equation:

$$\eta = \frac{amount\ of\ Al_2S_3\ formed}{amount\ of\ initial\ Al_2O_3} \times 100\%$$

$$\eta = \frac{amount\ of\ sample\ dissolved}{amount\ of\ initial\ Al_2O_3} \times 100\%$$

The details of calculated conversion from selected experiments are shown in Table II. The highest conversion was found for experiment at 1500°C and 9 hours duration. The conversion showed an increasing trend with respect to time and temperature. Thermodynamic analysis also predicted (Figure 1(a)) that formation of $Al_2S_3(s)$ increases significantly (from 0.40 mol / mol Al_2O_3 to 0.66 mol / mol Al_2O_3) from 1400 to 1500°C.

In summary, the results, from XRD, SEM, EDS, ICP and conversion calculation, indicate that it is possible to form high amount of Al_2S_3 from Al_2O_3 using C and H_2S gas in the range of conditions studied. The results also suggest that the conversion to

Al_2S_3 increases with increasing temperature and duration of experiments.

One of the attractive reasons why the indirect carbothermal route through high temperature processing is that at high temperature reaction kinetics are fast which can translate to high throughput of materials and products. In the range of conditions studied using the reactor configuration shown in Figure 2, however, it appears that the kinetics are relatively slow. This probably reflects the formation of a liquid surface layer of Al_2S_3 covering the Al_2O_3 that limits interfacial area for reaction and provides a diffusion barrier. At this early stage, it is hard to know the ideal reactor design, but the authors visualize a packed bed arrangement that allows the liquid product to drain away. The use of dilute H_2S (5%H_2S in Ar) could also be another reason that contribute to the relatively slow kinetics.

From the experimental results and thermodynamic analysis, at this stage, it can be said that kinetics control the carbosulfidation process. Further investigation is required to identify the reaction kinetics and rate controlling variables. Investigations on kinetic study including the effect of gas flow rate, temperature, time duration, pelletising pressure are in progress.

Conclusion

The thermodynamic analysis of the carbosulfidation reaction followed by experimental investigation was carried out as to evaluate the first step of the indirect carbothermal reduction for aluminum production utilizing $H_2S(g)$. The process consists of two stages – i.e. reduction of alumina to intermediate compounds Al_2S_3 followed by dissociation to aluminum (through electrolysis, thermal dissociation, and disproportionation). The effect of temperature and pressure has been studied for Al_2O_3-C-H_2S system. The results showed, $Al_2S_3(l)$ is the main intermediate aluminum compound when $Al_2O_3(s)$ is reacted with C(s) and $H_2S(g)$ at 1100 to 2000°C and AlS(l) becomes the main sulfur containing liquid phase when pressure is reduced. X-ray diffraction analysis of the experimental sample confirmed the formation of Al_2S_3. Chemical dissolution and filtration analysis showed percentage of conversion from Al_2O_3 to Al_2S_3 is 81.6% for experiment at 1500°C for 9 hours duration. The study provides a basis for the development of new route for aluminum production utilizing $H_2S(g)$, which can provide an attractive route when merged with petrochemical industries. For design and development of industrial scale production, further investigation is necessary including detailed kinetic study to determine rate limiting steps.

Acknowledgement

References

1. *www.world-aluminium.org*. 2012; Available from: http://www.world-aluminium.org/About+Aluminium/Story+of.

2. J. C. Withers and G. V. Upperman, in *U. S. Patent: 4,338,177*1982, Metallurgical, Inc., Lakewood, Ohio.

3. J. P. Murray, Solar Energy, 66(2): (1999). 133-142.

4. S. Namboothiri, M. P. Taylor, J. J. J. Chen, M. M. Hyland, and M. Cooksey, Asia-Pacific Journal of Chemical Engineering, 2(Compendex): (2007). 442-447.

5. M. Halmann, A. Frei, and A. Steinfeld, Energy, 32(Compendex): (2007). 2420-2427.

6. Y. Xiao, D. W. Van Der Plas, J. Soons, S. C. Lans, A. Van Sandwijk, and M. A. Reuter, Canadian Metallurgical Quarterly, 43(2): (2004). 283-292.

7. H. Kvande, in *Light Metals 1999*, C.E. Eckert, Editor 1999, TMS: Warrendale, PA. p. 369-376.

8. A. S. Russell, L. L. Knapp, and E. Haupin, in *U. S. Patent: 3,725222*1979, Aluminum Company of America.

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

10. J. Thonstad, P. Fellner, G. M. Haarberg, J. Hives, H. Kvande, and A. Sterten, 2001, Aluminium Verlag.: Dusseldorf. p. 340-346.

11. Moissan, Compt. rend., 119: (1894). 15.

12. P. T. Stroup, Transactions of the Metallurgical Society of Aime, 230(3): (1964). 356-&.

13. M. A. Rhamdhani, M. A. Dewan, G. A. Brooks, B. J. Monaghan, and L. Prentice, Submiited to Trans IMM C: (2011).

14. M. A. Dewan, M. A. Rhamdhani, G. A. Brooks, B. J. Monaghan, and L. Prentice, Submiited to Trans IMM C: (2011).

15. Y. Xiao, D. W. van der Plas, J. Bohte, S. C. Lans, A. van Sandwijk, and M. A. Reuter, Journal of The Electrochemical Society, 154(6): (2007). D334-D338.

16. N. Huda, M. A. Rhamdhani, M. A. Dewan, G. A. Brooks, B. J. Monaghan, and L. Prentice. in *Chemeca 2012*. Wellington, New Zealand. 2012.

17. R. O. Loutfy, R. Keller, and N. P. Yao, in *U. S. Patent: 4,265,716*1981, The United States of America as represented by the United States Department of Energy.

18. N. Q. Minh, R. O. Loutfy, and N. P. Yao, Journal of Electroanalytical Chemistry, 131: (1982). 229-242.

19. D. W. Van Der Plas, in *World Intellectual Property Organization: WO 2004/088002*004, Corus Technology BV, CA Ijmuiden (NL).

20. D. W. Van Der Plas and Y. Xiao, in *U. S. Patent: US2006/0226026*2006, Corus Aluminium Walzprodukte GmbH, Koblenz (DE).

21. H. Sportel and C. W. F. Verstraten, in *U. S. Patent: 6,565,733*, C.A.W. GmbH, Editor 2003.

22. N. Q. Minh, R. O. Loutfy, and N. P. Yao, in *U. S. Patent: 4,4645,234*1984, The United States of America as represented by the United States Departement of Energy, Washington, D.C.

23. C. W. Bale, E. Bélisle, P. Chartrand, S. A. Decterov, G. Eriksson, K. Hack, I. H. Jung, Y. B. Kang, J. Melançon, A. D. Pelton, et al., CALPHAD: Computer Coupling of Phase Diagrams and Thermochemistry, 33(2): (2009). 295-311.

24. *JANAF thermochemical tables*, ed. D.R. Stull and H. Prophet1971, Washington USA: U.S. National Bureau of Standards.

25. I. Barin, *Thermochemical Data of Pure Substances*1993, Weinheim Germany: VCH Verlagsgesellschaft mbH.

26. G. Eriksson, P. Wu, and A. D. Pelton, CALPHAD: Computer Coupling of Phase Diagrams and Thermochemistry, 17(2). 189-205.