

SOLID STATE CARBOTHERMAL REDUCTION OF ALUMINA

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Abstract

The Hall-Héroult process, the only commercial technology for aluminum production requires high energy and is a major origin of perfluorocarbons and green house gases. A promising alternative process, carbothermal reduction of alumina to metallic aluminum has advantages of lower capital cost, less energy consumption, and lower emission of green house gases. Carbothermal reduction processes under development are based on formation of aluminum carbide-alumina melts at high temperatures. Solid state carbothermal reduction of alumina is possible at reduced CO partial pressure. This paper presents results of experimental study of carbothermal reduction of alumina into aluminum carbide in Ar, He and H₂ atmospheres at 1500-1700°C. The reduction rate of alumina increases with increasing temperature, and is significantly faster in He and H₂ than in Ar. Increasing gas flow rate and decreasing pressure favors the reduction.

Introduction

Aluminum is the most abundant metallic element, representing 8% of the earth's crust, and the third most abundant element after oxygen and silicon [1]. Metallic aluminum is the second most widely used metal next to steel. The Hall-Héroult process is essentially the only method for the commercial production of aluminum, which requires high energy consumption (~13 kWh/kg of aluminum for the best cells [2]), releases perfluorocarbons, and emits a large amount of greenhouse gases. High capital cost of electrolytic cells for producing aluminum is another drawback for this method.

Carbothermal reduction of alumina is the most promising alternative process to replace the current Hall-Héroult process for the production of aluminum, with high potential for greater productivity, lower capital investment, less consumption of electric power, and less emission of greenhouse gases. The major aluminum producers have researched this method over the last few decades. In one of the earliest works published in 1963 [3], alumina was reduced in an electric arc furnace at 2400-2500°C with formation of a mixture of aluminum and aluminum carbide (Al₄C₃) with low content of alumina. Further development of carbothermal aluminum production evolved in the direction of a two-stage process. Cochran and Fitzgerald [4] invented a stack-type reactor, which was separated into two zones. A liquid alumina-aluminum carbide mixture was produced in the upper reaction zone, and was transferred to the lower reaction zone, in which alumina reacted with Al₄C₃ with formation of liquid aluminum and carbon monoxide. The two-zone method was also used by Persson [5] and Dougan and Southam [6]. Dmitriev and Karasev [7] proposed to use an induction shaft furnace for carbothermal reduction of alumina to produce Al₄C₃, which was

dissociated by electrolysis into aluminum and carbon in the lower zone of the same furnace. In Lacamera's invention [8], alumina was carbothermally reduced into molten mixture of aluminum and Al₄C₃ (10-30 wt%) in an electric arc furnace at 2000 to 2100°C, and then aluminum scrap was added to cool the melt to 900 to 1000°C to separate reduced aluminum. Unreacted Al₄C₃ was recycled to the high temperature electric arc furnace where it reacted with alumina to produce aluminum.

Since 2000, Alcoa and Elkem companies in collaboration with Carnegie Mellon University have carried out investigations on carbothermal production of aluminum using two-zone reduction vessel [9-15]. Aluminum was carbothermally reduced in the first reaction compartment to form a 50% Al₂O₃-50% Al₄C₃ melt at approximately 2000°C. Further reaction between them took place in the second compartment at approximately 2200°C to form aluminum, which was tapped, degassed and cast.

Although extensive investigations have been made, no any alternative process has been successful in replacement of the Hall-Héroult process. The major difficulties in development of a competitive carbothermal process include very high temperatures needed for reduction/smelting reactions, the formation of aluminum carbides, and many engineering problems in materials handling, including recovering of volatiles and delivery of energy to attain over 2000°C. A lack of knowledge of reaction mechanisms and kinetics of alumina reduction is one the main barriers to overcome these problems.

This work studies solid state reduction of alumina to Al₄C₃ under different conditions (gas atmosphere and temperature) with the aim to establish the fundamentals of solid state carbothermal reduction of alumina.

Experimental

The raw materials used in the study were alumina powder of 99.7% purity and <10 μm in size, and synthetic graphite with a powder size <20 μm. Both chemicals were supplied by Sigma-Aldrich, Australia. The reduction mixture was prepared by mixing raw materials with C/Al₂O₃ molar ratio of 6. A wet mixing method was used to obtain a uniform mixture. After drying, the powder was pressed statically into cylindrical pellets of 8 mm in diameter and about 10 mm in height.

The gases used in the study were argon, helium and hydrogen of 99.999% purity, all supplied by BOC Gases, Sydney, Australia. The flow rate of the gases was controlled by mass-flow controllers (model 5850E, Brooks Instrument, Hatfield, PA). Compositions of effluent gases were monitored by a CO/CO₂/CH₄ IR analyzer (Advanced Optima AO2020, ABB, Germany).

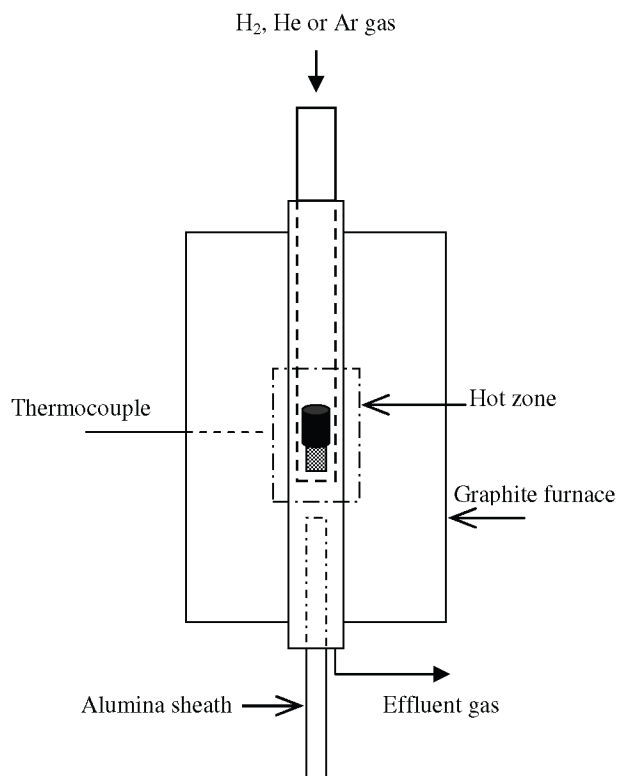


Figure 1. Schematic reaction system.

The reduction experiments were carried out in a graphite furnace (Model 1000-3560-FP20, Thermal Technology Inc., USA). Figure 1 shows the schematic of the reaction system. A graphite tube of 10 mm i.d. and 19 mm o.d. was used as a sample holder and reactor, which was inserted into the external graphite tube of 24 mm i.d. to confine the gas from a furnace chamber. Both graphite tubes were coated with a thermo-settable resin, and heated up slowly, to form a layer of vitreous carbon so that the graphite tubes became gas impermeable. An alumina tube was inserted from the bottom which worked as an aluminum vapor condenser/deposit collector. The reduction temperature was controlled by a type B thermocouple inserted from the side of the furnace. After the sample was loaded into the reactor, the furnace with established temperature profile was first vacuumed to <0.4 torr residual pressure, and then was heated to ~400°C to further remove the gases and water adsorbed inside the graphite furnace. After the vacuum reached <0.4 torr, the furnace was refilled with Ar gas, and the reactor was purged by the gas used in the experiments until all the readings from the gas analyzer approached zero. Then the furnace was heated at 60°C/min to the experimental temperature, and the readings from the gas analyzer started to be recorded. After reduction completed, the sample was cooled within the furnace with continuously flowing gas until the temperature was less than 100 °C. Samples and deposits were collected and stored in desiccators to avoid reacting of Al_4C_3 with moisture.

Phase composition of the reduced samples was analyzed with the powder X-Ray diffraction (XRD) (Philips X'pert Multipurpose X-

Ray Diffraction System (MPD)). The oxygen content of the samples was measured by LECO (Model TC-436DR). The extent of reduction was defined as percentage of oxygen removed from alumina.

Results

Effect of Temperature and Gas Atmosphere

Carbothermal reduction of alumina was studied in hydrogen, helium and argon, in a temperature range of 1500 to 1700°C. All experiments were carried out for 5 hours under 1 atm, with a gas flow rate of 1 NL/min. The extent of alumina reduction versus temperature is shown in Figure 2. Both temperature and gas atmosphere have strong effects on the reduction. The reduction was the slowest in argon. At 1500°C, the extent of reduction was only 5%, and Al_4C_3 could not be detected by XRD analysis. The extent of reduction increased to 54 and 76% when the temperature was increased to 1550 and 1600°C, respectively. At 1700°C, the extent of reduction was 97%. In hydrogen, the reduction achieved 42% at 1500°C, and increased to 88 and 97% with increasing temperature to 1550 and 1600°C, respectively. The reduction was the fastest in helium. The extent of reduction increased from 68 to 97% with increasing temperature from 1500 to 1550°C.

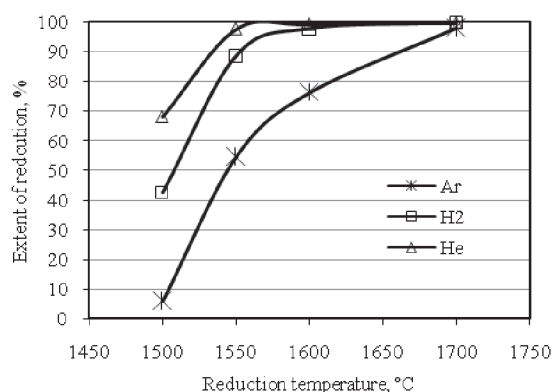
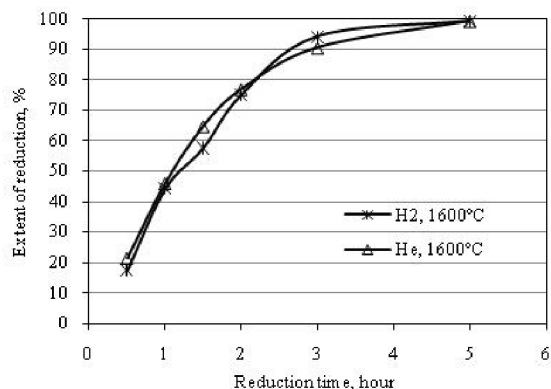


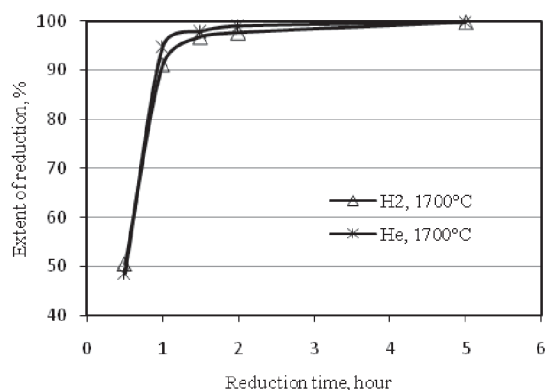
Figure 2. Conversion of alumina in the carbothermal reduction at different temperatures and gas atmospheres (reduction time 5 hours).

Effect of Reduction Time

The effect of reduction time on the extent of reduction of alumina was investigated under gas flow rate of 1NL/min with 1 atm pressure. The experiments were carried out in He and H₂ atmospheres and at 1600 and 1700 °C, respectively. The extent of reduction versus time is presented in Figure 3. At these relatively high temperatures, progress of reduction in hydrogen and helium were similar. At 1600°C (Figure 3(a)) the reduction reached about 20% within the first 30 min and 45% within one hour. After 3 hours of reduction, more than 90% of reduction had achieved. The reduction was close to completion after 5 hours of reduction. At 1700°C (Figure 3(b)), up to 50 % of reduction had achieved within the first 30 min. This was increased to 90-95% after one hour reduction. The reduction was close to completion in 2 hours.



(a) Reduction at 1600°C



(b) Reduction at 1700°C

Figure 3. Carbothermal reduction of alumina in He and H₂ atmospheres (a) at 1600°C, and (b) at 1700°C

Figure 4 presents the XRD patterns of the samples reduced for different time at 1600°C in H₂. The XRD patterns of the samples reduced in helium under otherwise the same conditions were very similar to those in hydrogen. After half an hour reduction, small peaks of Al₄C₃ were detectable. Along with progress of the reduction, the relative intensities of Al₂O₃ peaks decreased, and the relative intensities of Al₄C₃ peaks increased. After 5 hours reaction, Al₂O₃ peaks disappeared.

Figure 5 presents the XRD patterns of the samples reduced in hydrogen at different reduction time at 1700°C, 1 atm pressure, and 1NL/min flowrate. The Al₂O₃ peaks had become very weak after one hour reduction, and were practically undetectable after 1.5 hours. However, the Al₄C₃ peaks did not sustain and, when the reduction time was extended to 5 hours, most of the Al₄C₃ disappeared, leaving mainly graphite in the sample. This means that Al₄C₃ formed by carbothermal reduction is not stable at these reduction conditions. In comparison, the XRD pattern of the sample reduced in He at 1700°C for 5 hours (Figure 6) shows significant amount of Al₄C₃, even though alumina conversion to aluminum carbide was basically completed in 2 hours as in hydrogen. These results indicate that aluminum carbide is more stable in helium than in hydrogen atmosphere.

Effect of Pressure

The effect of pressure on the carbothermal reduction was investigated in hydrogen and helium by changing the gas pressure from 1.0 to 1.4 atm at 1600°C and gas flow rate 1.0 NL/min. The reduction period was 2 hours. The experimental results are presented in Table I. In both atmospheres, the extent of reduction decreased with increasing pressure. In hydrogen, the extent of reduction decreased by 16% and in helium by 19% when the gas pressure was increased from 1.0 to 1.4 atm.

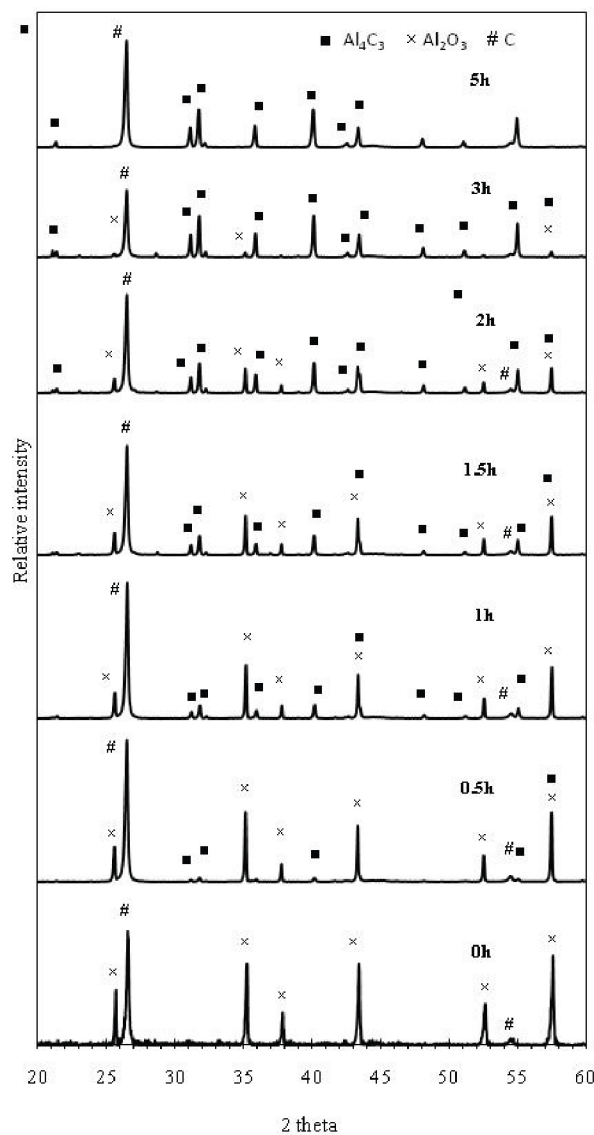


Figure 4. XRD patterns of samples reduced in hydrogen at 1600°C for different time. The pressure was 1 atm and gas flow rate was 1.0 NL/min.

Table I. Effect of pressure on the reduction of alumina

Atmosphere	1.0 atm	1.2 atm	1.4 atm
H ₂	75%	64%	59%
He	77%	60%	58%

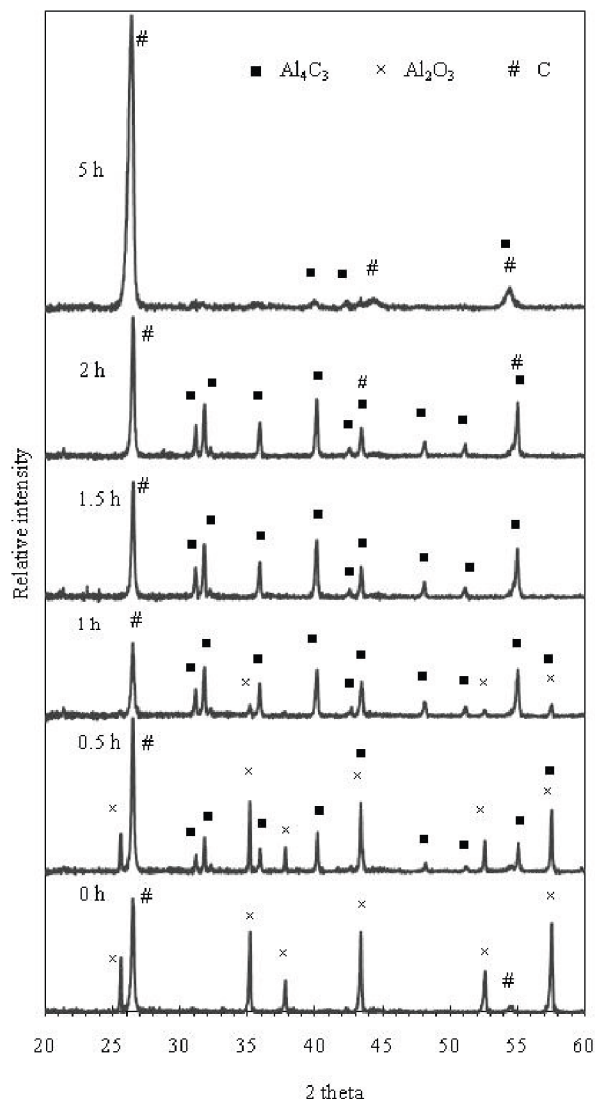


Figure 5. XRD patterns of samples reduced in hydrogen at 1700°C for different time. The pressure was 1 atm and gas flow rate was 1.0 NL/min.

Effect of Flow Rate

The effect of gas flow rate on the reduction of alumina was investigated in Ar, He and H₂ at 1600°C, 1atm pressure, 2 hours reduction time. The flow rate varied from 1 NL/min to 0.5 NL/min. Table II shows the extent of reduction of different experiments. It can be seen that decreasing the flow rate decreased the extent of reduction of alumina consistently.

Table II. Effect of flow rate on the reduction of alumina

Flow rate	H ₂	He	Ar
1.0 NL/min	75%	77%	58%
0.5 NL/min	64%	63%	47%

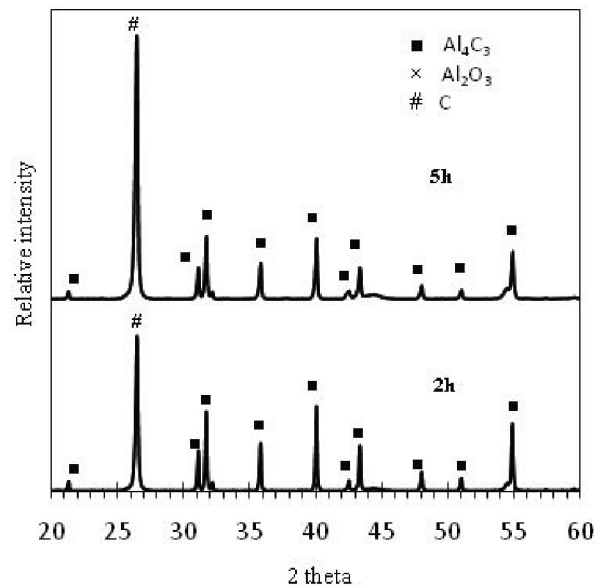
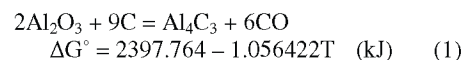


Figure 6. XRD patterns of samples reduced in helium at 1700°C for 2 and 5 hours. The pressure was 1 atm and gas flow rate was 1.0 NL/min.

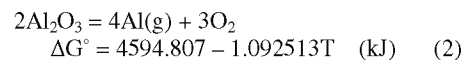
Discussion

The overall reaction of conversion of alumina to aluminum carbide Al₄C₃ is:



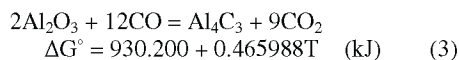
The equilibrium partial pressure of CO for this reaction is shown in Figure 7; it increases with increasing temperature. At 1400°C, the equilibrium CO partial pressure is only 0.05 kPa. It increases to 1.13 kPa at 1600°C and approaches 100 kPa at 1900°C. Therefore, reduction of alumina at temperatures below 1900°C is thermodynamically possible only at reduced CO partial pressure. Increasing temperature favors the reduction of alumina both kinetically and thermodynamically. Increasing gas flow rate and decreasing pressure of the gas, decrease CO content in the gas phase, and facilitates carbothermal reduction of alumina.

Lefort *et al.* [17] considered thermal decomposition of alumina:



The oxygen equilibrium partial pressure in this reaction is extremely low, 10⁻²⁰–10⁻¹³ kPa, what makes this reaction infeasible.

It is broadly accepted that carbothermal reduction of solid oxides proceeds through the gas phase, when an oxide is reduced by CO which is regenerated by the Boudouard reaction [17-20]. The reduction of alumina by CO can be presented by the following reaction:



Apart from this reaction, alumina can be reduced by carbon to aluminum or Al_2O vapor following Reactions (4) and (5):

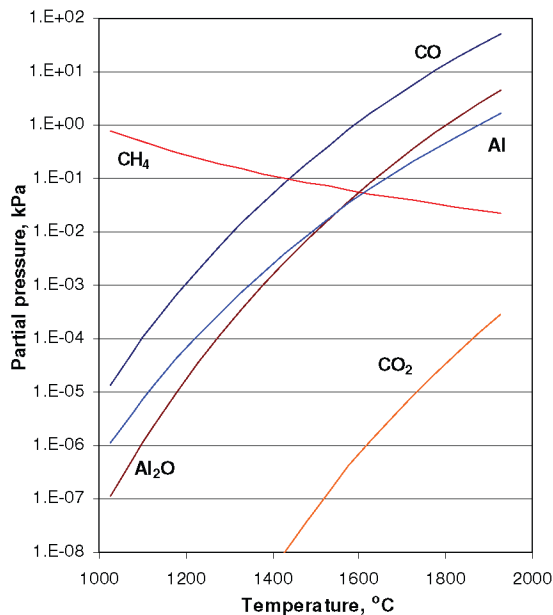
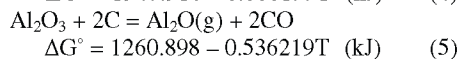
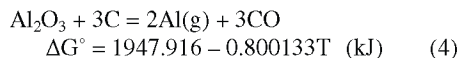
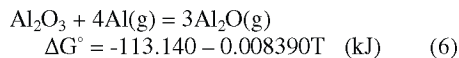
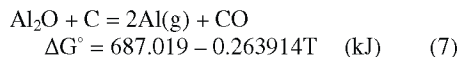


Figure 7. Equilibrium partial pressure of intermediate gas species in carbothermal reduction of alumina. The partial pressure of hydrogen is assumed to be 100 kPa in the formation of methane.

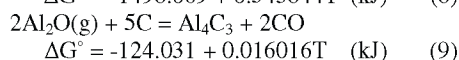
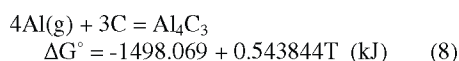
Reduction of alumina in these reactions can also proceed by CO. Al in the gas phase may further react with Al_2O_3 to form Al_2O vapor:



Al_2O deposited on the graphite, may be converted to Al vapor:



Finally, Al and Al_2O react with graphite to form aluminum carbide:



Equilibrium partial pressures of CO, CO_2 , Al and Al_2O for these

reactions are presented in Figure 7.

The equilibrium partial pressure of CO_2 is by 4-7 orders lower than those of Al and Al_2O . It can be suggested that gaseous Al and Al_2O play a major role in the alumina reduction to aluminum carbide.

Reduction of alumina to gaseous Al and Al_2O (Reactions (4)-(6)) was observed in experiments at high temperatures: the alumina plug at the bottom of the reactor was strongly corroded, and almost disappeared in some cases; the evaporated volatiles were deposited on the low temperature section of the reactor tube. The deposit was identified by XRD to be mainly $\text{Al}_4\text{O}_4\text{C}$, which was formed by reaction of Al and Al_2O vapor with CO.

The following mechanism can be suggested for reduction of alumina. The reduction starts with Reactions (4) and (5); alumina is further reduced to Al_2O vapor by gaseous aluminum (Reaction (6)), while Al_2O is reduced to Al vapor by Reaction (7). Then Al_4C_3 is formed by Reactions (8) and (9).

Reduction of alumina in helium and hydrogen was much faster than in argon. The difference of reaction rates in these gases reflects the effect of diffusion on the reduction rate, what supports the suggested reduction mechanism. Internal mass transfer in the gas phase plays a major role in the reduction kinetics in the reaction cycle: Al vapor reacts with Al_2O_3 to form gaseous Al_2O ; the latter diffuses to graphite and reacts with carbon regenerating Al vapor; then the Al vapor diffuses to Al_2O_3 phase. The partial pressures of Al and Al_2O are relatively low. The driving force for diffusion of Al vapor from graphite to alumina and of Al_2O from alumina to graphite (the difference in Al and Al_2O partial pressures at the alumina-gas and graphite-gas interfaces) is also low. This makes the overall reaction rate sensitive to the diffusivity of gas species, which is much higher in hydrogen and helium than in argon.

It has been well established that carbothermal reduction of titania is much faster in hydrogen than in helium and argon [18,19]. The enhancing effect of hydrogen on the carbothermal reduction was attributed to formation of methane which plays a role of carbon carrier. However, the rate of carbothermal reduction of alumina in hydrogen is close to or even lower than that in the helium atmosphere. This shows that the role of methane in reduction of alumina is very limited.

As shown in Figures 5 and 6, Al_4C_3 in H_2 atmosphere is less stable than in helium. Correspondingly, more deposit was collected in reduction experiments in hydrogen than in helium and argon.

Conclusions

Carbothermal reduction of alumina was studied in hydrogen, helium and argon. Alumina was reduced to aluminum carbide Al_4C_3 . The reduction rate increased with increasing temperature.

Carbothermal reduction of alumina involves formation of Al and Al_2O vapor, which play a major role in the reduction mechanism. Carbothermal reduction of alumina is faster in helium than in hydrogen, and much faster than in argon, what is attributed to higher diffusivity of gas species in helium compared with in

argon.

In helium gas at 1 atm, carbothermal reduction was close to completion at 1550°C in 5 hours and at 1700°C in 2 hours. Increasing gas flow rate or decreasing gas pressure increases the reduction rate. Al_4C_3 formed by carbothermal reduction is more stable in helium than in hydrogen.

Acknowledgements

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