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Carbothermal reduction of alumina: Thermochemical equilibrium calculations and experimental investigation

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Abstract

The production of aluminum by the electrolytic Hall–Héroult process suffers from high energy requirements, the release of perfluorocarbons, and vast greenhouse gas emissions. The alternative carbothermic reduction of alumina, while significantly less energy-intensive, is complicated by the formation of aluminum carbide and oxycarbides. In the present work, the formation of Al, as well as Al_2OC, Al_4O_4C, and Al_4C_3 was proven by experiments on mixtures of Al_2O_3 and activated carbon in an Ar atmosphere submitted to heat pulses by an induction furnace. Thermochemical equilibrium calculations indicate that the Al_2O_3-reduction using carbon as reducing agent is favored in the presence of limited amounts of oxygen. The temperature threshold for the onset of aluminum production is lowered, the formation of Al_4C_3 is decreased, and the yield of aluminum is improved. Significant further enhancement in the carbothermic reduction of Al_2O_3 is predicted by using CH_4 as the reducing agent, again in the presence of limited amounts of oxygen. In this case, an important by-product is syngas, with a H_2/CO molar ratio of about 2, suitable for methanol or Fischer–Tropsch syntheses. Under appropriate temperature and stoichiometry of reactants, the process can be designed to be thermo-neutral. Using alumina, methane, and oxygen as reagents, the co-production of aluminum with syngas, to be converted to methanol, predicts fuel savings of about 68% and CO_2 emission avoidance of about 91%, vis-à-vis the conventional production of Al by electrolysis and of methanol by steam reforming of CH_4. When using carbon (such as coke or petcoke) as reducing agent, fuel savings of 66% and CO_2 emission avoidance of 15% are predicted. Preliminary evaluation for the proposed process indicates favorable economics, and the required high temperatures process heat is readily attainable using concentrated solar energy.

Keywords: Alumina; Aluminum; Aluminum carbide; Aluminum oxycarbides; Aluminum suboxide; Carbon; Carbon dioxide; Carbothermic reduction; Coke; Fischer–Tropsch; Fluorocarbons; Fuel saving; Graphite carbon-C(gr); Induction furnace; Methane; Methanol; Petcoke; Syngas; Thermochemical equilibrium; Thermo-neutral

1. Introduction

Aluminum is currently produced industrially via the Hall–Héroult process by dissolving Al_2O_3 in fused NaF–AlF_3 (cryolite) followed by direct current electrolysis, in which CO_2 is discharged at a sacrificial carbon anode and Al is deposited at the bottom of the cell. The production of each kg of Al requires the consumption of 0.4–0.5 kg of the carbon anode [1]. The main drawbacks of the electrolytic production are its very high energy consumption (0.186 GJ/kg Al), the release of perfluorocarbons, and the high specific $CO_{2\text{-equiv}}$ emissions (7.42 kg$CO_{2\text{-equiv}}$/kg Al) [2]. The greenhouse gas emission by the electrolytic Al production contributes 2.5% to the world anthropogenic $CO_{2\text{-equiv}}$ emissions [3]. Much effort has been spent to achieve the carbothermic reduction of Al_2O_3 to metallic Al. Using carbon or CH_4 as reducing agents, the overall reactions can be represented by

$$Al_2O_3 + 3C = 2Al + 3CO, \quad \Delta H^0_{298\,\mathrm{k}} = 1344.1\,\mathrm{kJ\,mol^{-1}}. \tag{1}$$

Abbreviations: C(gr), Graphite carbon; CO_2-equiv, Carbon dioxide equivalent; MSR, Methane steam reforming; Petcoke, Petroleum coke; PDF, Powder diffraction file; Ton, Metric ton; WGS, Water–gas shift; XRD, X-ray diffraction

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$$Al_2O_3 + 3CH_4 = 2Al + 3CO + 6H_2,\quad \Delta H^0_{298\,k} = 1568.7\,kJ\,mol^{-1}. \tag{2}$$

Reactions (1) and (2) are thermodynamically favorable at above 2320 and 1770 K, respectively [4]. However, both reactions are complicated by the formation of aluminum carbide, Al_4C_3, and of the oxycarbides Al_2OC, and Al_4O_4C. At the ALCOA Corporation, a stack-type reactor was developed in which a charge of Al_2O_3 and C was inserted in a high-temperature upper reaction zone to form a liquid mixture of Al_2O_3 and Al_4C_3 that was then transferred to a lower reaction zone for the extraction of liquid Al. The total energy demand of 0.121 GJ/kg Al by this process for both electric energy and carbon consumption was thus significantly lower than that by the Hall–Héroult process. Replacement of the electrochemical process by carbothermic reduction of Al_2O_3 would decrease the total greenhouse gas emissions by at least 30% [5]. In spite of considerable effort, the carbothermic reduction of alumina to aluminum remains a formidable technical challenge, due to the high temperatures required, and to the formation of aluminum carbide and oxycarbide byproducts [2].

A differential thermal analysis method had been applied to study the aluminum–oxygen–carbon system at reduced pressures at 1700–2200 °C [6]. The results indicated that the direct reduction according to Eq. (1) did not occur. Instead, Al was proposed to be formed by the following steps occurring at progressively higher temperatures in the order listed, resulting in the overall reaction (1),

$$2Al_2O_3 + 3C = Al_4O_4C + 2CO, \tag{3}$$

$$Al_4O_4C + 6C = Al_4C_3 + 4CO, \tag{4}$$

$$Al_4O_4C + Al_4C_3 = 8Al + 4CO. \tag{5}$$

The present work examines the thermodynamic constraints for achieving the carbothermic reduction of Al_2O_3 to Al by combining it with the exothermic partial oxidation of either methane to H_2 and CO, or of carbon to CO,

$$CH_4 + \frac{1}{2}O_2 = CO + 2H_2,\quad \Delta H^0_{298\,k} = -35.7\,kJ\,mol^{-1}, \tag{6}$$

$$C + \frac{1}{2}O_2 = CO,\quad \Delta H^0_{298\,k} = -110.5\,kJ\,mol^{-1}. \tag{7}$$

The conditions were determined for avoiding or minimizing the formation of Al_4C_3 and of the partial reduction byproducts, such as Al_2O and AlO. The approach taken is analogous to that used for the carbothermic reduction of iron and zinc ores to the corresponding metals, and for the calcination of limestone, combined with the reforming/partial oxidation of CH_4 [7–10]. These thermodynamic constraints seem not to have been reported previously. In addition, experiments were performed to find conditions suitable for the application of concentrated solar energy to the production of aluminum.

2. Experimental tests

In the present work, the carbothermic reduction of Al_2O_3 mixed with activated carbon was examined initially by thermogravimetry coupled with gas chromatography of gaseous products, and by heating the above mixtures in an induction furnace.

2.1. By thermogravimetry:

A mixture of Al_2O_3 (Alfa Aesar) and active carbon (Fluka 5105, ca. 85%) (molar ratio 1:3) in a graphite crucible was placed into the sample holder of a high-temperature thermogravimeter (Netzsch STA 409) under a constant Ar flow of 200 ml/min. Evolved gases were sampled every 3 min for gas chromatography (MTI Micro GC P200, equipped with a MS 5A column and a TC detector). The temperature was raised at a rate of 40 °C/min until 1550 °C, and then kept at this temperature for 10 h. The observed weight loss was 54.0% of that required from Eq. (1), and the amount of CO determined by gas chromatography was 15% of the theoretical. The residue in the crucible was identified by XRD to consist mainly of Al_4C_3. No Al was detected on the walls of the reactor. This analysis was performed using a Philips X'Pert MPD/DY636 instrument, and identification of peaks was carried out with the Philips Analytical Software for XRD. In a similar experiment, the reactants were kept for 17 h at 1766 °C, resulting in a weight loss of 71.4%, again without formation of Al.

2.2. By induction furnace heating:

The mixture of Al_2O_3 and active carbon (135 mg; molar ratio 2:9) was placed in a glassy carbon crucible (SIGRADUR G; inner diameter 9 mm, wall thickness 3 mm) supported on an Alox holder in a vertical quartz tube (inner diameter 31 mm) under an Ar flow of 5 lit/min, surrounded by the induction furnace (BBC Co., Model IG 261 W-18). The sample was exposed to heat pulses of 30 s at a power level of 18 kW. The deposit formed on the cold section of the quartz wall was determined by XRD to contain Al_2OC, Al, and Al_4C_3 (see Fig. 1). The XRD spectrum of the residue in the crucible (Fig. 2) was attributed to Al_4O_4C, Al_2OC, and AlN. The formation of the Al-oxycarbides is in agreement with previous reports [6]. The AlN production indicates some air leakage into the reaction chamber. The confirmation of the production of elementary Al on the quartz wall is based on the observed intensity ratio of 80.0/37.0 = 2.16 for the two major peaks at 2Theta 49.027° and 57.179°. This is closely similar to the reported ratio of 100.0/47.0 = 2.13 for the two largest peaks for pure Al (PDF-No. 00-004-0787) at 2Theta 48.919° and 57.147°. The temperature in the crucible was determined indirectly by using the melting points of selected materials.

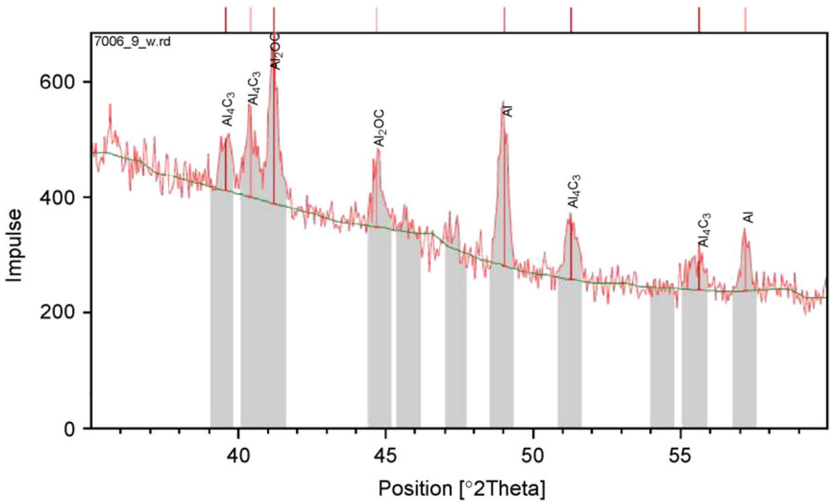

Fig. 1. XRD spectrum of the wall deposit after induction furnace heating of an Al_2O_3–active carbon mixture.

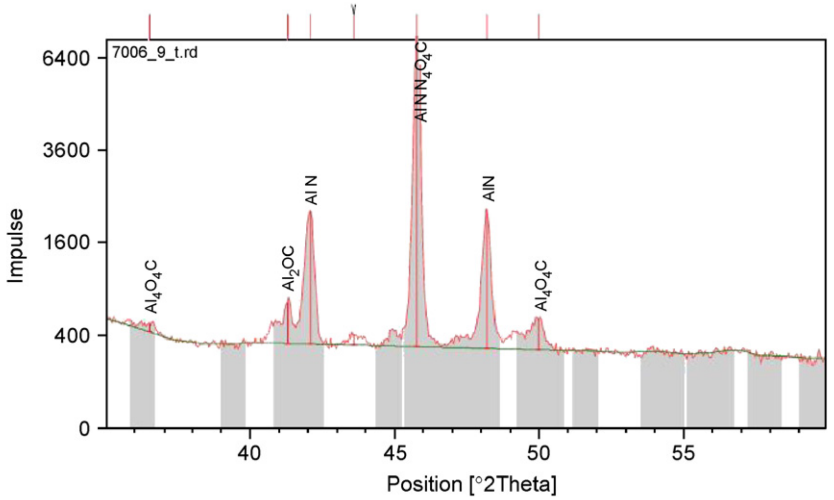

Fig. 2. XRD spectrum of the crucible residue after induction furnace heating of an Al_2O_3–active carbon mixture.

It was within the range of 2248 K (m.p. $CaTiO_3$) and 2319 K (m.p. Al_2O_3).

3. Thermodynamic analysis

Thermochemical equilibrium calculations were performed using the CET85 and FactSage program codes [11,12], assuming closed systems. Results were expressed as mole fractions against temperature, all at 1 bar pressure. Products with mole fractions of less than 10^{-5} were not considered. Reaction enthalphies were calculated using the data of the NIST chemistry web-book [13]. Substantial reduction of Al_2O_3 to Al was found to occur only above the melting point of Al, 933.5 K, and to be almost complete only close to the boiling point, 2767 K. Four different cases were examined with respect to CO_2 emission avoidance, fuel saving, and economics—all for a proposed annual plant supplied with 0.102×10^6 ton Al_2O_3—with initial reactants described by: (a) $Al_2O_3 + 4CH_4 + 0.4O_2$; (b) $Al_2O_3 + 4C + 0.6O_2$; (c) $Al_2O_3 + 28.9C + 13O_2$; (d) $Al_2O_3 + 4C$.

3.1. *Reaction of alumina with carbon*

The carbothermic reduction of Al_2O_3 is simulated with an initial reaction mixture of $Al_2O_3 + 4C$. The equilibrium composition in the temperature range 1800–2800 K is presented in Fig. 3. CO is not shown. Al is formed at above 2300 K, Al_4C_3 is used up at above 2600 K, and C(gr) is still present even at 2800 K. At 2700 K, the reaction can be described by,

$$Al_2O_3 + 4C = 1.71Al(g) + 0.13Al_2O(g) + 0.01Al_2(g) + 2.87CO(g) + 1.13C(gr). \quad (8)$$

The excess of unused carbon appears as the product C(gr). The yield of Al according to Eq. (8) is 85.4%.

3.2. *Reaction of alumina with carbon and oxygen*

The carbothermic reduction of Al_2O_3 is examined using a small excess of carbon (such as coke, petcoke, or

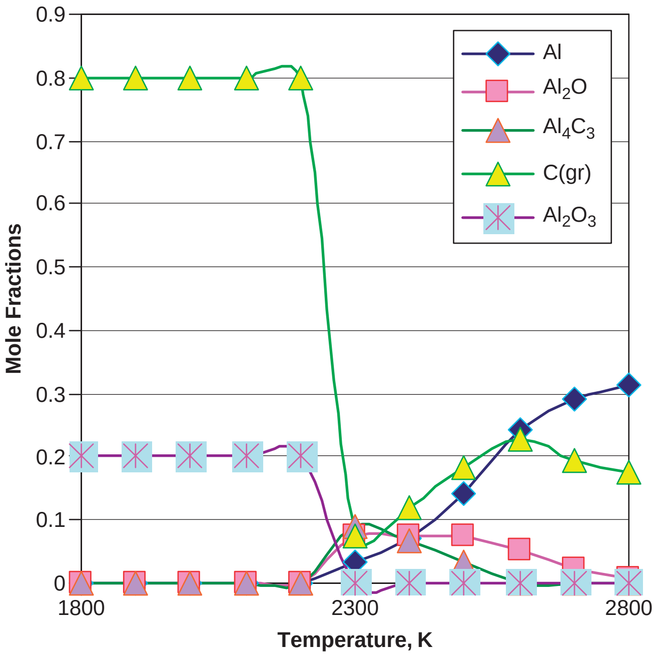

Fig. 3. Equilibrium composition as a function of temperature for the system Al_2O_3+4C at 1 bar total pressure.

charcoal) in the presence of a limited amount of O_2. The temperature dependence of the equilibrium composition in the range 1800–2800 K is presented in Fig. 4. The main gaseous product, CO, is not shown. Al_2O_3 is reduced at above 2300 K, while Al and Al_2O are formed at above 2200 K. Al_4C_3 is unstable at above 2600 K, and is used up at 2700 K. At 2700 K, the calculated yield of conversion of Al_2O_3 to Al is 79.1%, and the net reaction is represented by,

$$Al_2O_3 + 4C + 0.6O_2 = 1.58Al(g) + 0.20Al_2O(g) + 0.01Al_2(g) + 4CO(g). \tag{9}$$

The reaction is endothermic by 1.66 GJ/kmol Al_2O_3. As shown in detail in Appendix A (Table A1) and assuming that the process heat is provided by combustion of coke, the proposed annual co-production of 0.0427×10^6 ton Al and 0.038×10^6 ton CH_3OH-after partial water–gas shift of CO to H_2-requires a total input of 3.24×10^6 GJ (or 0.099×10^6 ton coke), and releases 0.304×10^6 ton CO_2. The conventional separate production of the same amounts of Al and CH_3OH requires 7.942×10^6 GJ [15] and 1.691×10^6 GJ [16], respectively, or a total of 9.63×10^6 GJ. Thus, the fuel saving by the co-production relative to the conventional separate processes is 66.4%. In addition, the CO_2 emissions from the corresponding Al and CH_3OH productions are 0.3168×10^6 and 0.0397×10^6 ton CO_2, respectively, or a total of 0.357×10^6 ton CO_2. Thus, the CO_2 emission avoidance by the co-production relative to the conventional separate processes amounts to 14.8%.

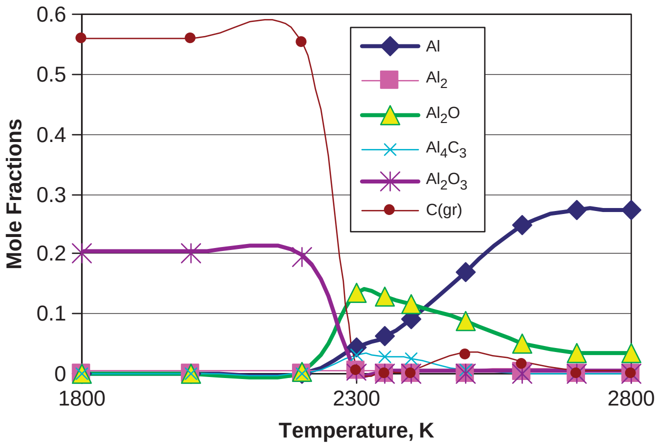

Fig. 4. Equilibrium composition as a function of temperature for the system $Al_2O_3+4C+0.6O_2$ at 1 bar total pressure.

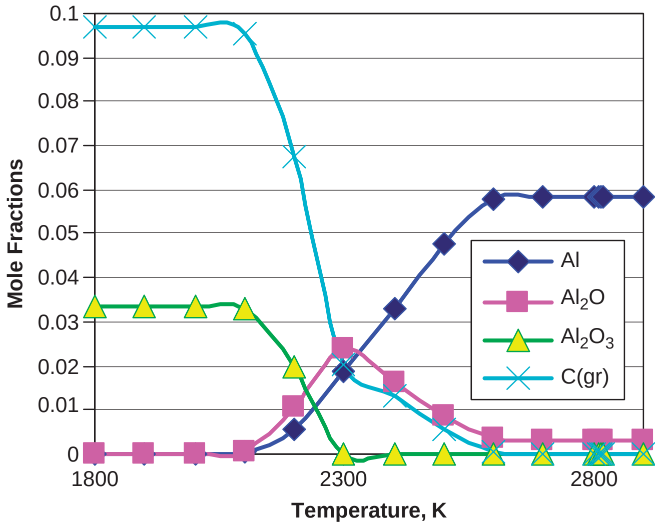

Fig. 5. Equilibrium composition as a function of temperature for the system $Al_2O_3+28.9C+13O_2$ at 1 bar total pressure.

3.3. *Reaction of alumina with excess of carbon and oxygen*

Using a considerable excess of carbon and oxygen relative to Al_2O_3, it is possible to arrive at conditions at which the reaction becomes thermo-neutral, i.e. the enthalpy change between products at a given reaction temperature and the reactants at ambient temperature equals zero. Such conditions were found using an initial mixture at 300 K and 1 bar, with molar ratio $Al_2O_3 : C : O_2 = 1 : 28.9 : 13$. The equilibrium composition of the system is shown by Fig. 5 for the 1800–2900 K range. The main gaseous product, CO, is not shown. Al is formed at 2100 K, while Al_2O_3 and C(gr) are used up at 2300 K and 2600 K, respectively. At 2800 K, the reaction becomes slightly exothermal. At 2815 K, the net reaction is represented by

$$Al_2O_3 + 28.9C + 13O_2 = 1.80Al(g) + 0.10Al_2O(g) + 0.002Al_2(g) + 28.9CO(g). \tag{10}$$

Under these conditions, the yield of Al from Al_2O_3 would be 90.0%, and the product mixture would be free of Al_4C_3 and C(gr).

As described in Appendix A (Table A2), the proposed annual co-production of 0.0486×10^6 ton of Al and of 0.277×10^6 ton methanol requires an input of 11.4×10^6 GJ (0.347×10^6 ton) of coke, and results in the emission of 0.848×10^6 ton CO_2. The conventional separate production of the above amounts of Al and methanol requires 9.04×10^6 GJ and 11.0×10^6 GJ, respectively, or a total of 20.03×10^6 GJ. Thus, the fuel saving by the co-production relative to the conventional separate processes amounts to 43.1%. The CO_2 emission by the conventional production of such amounts of Al and methanol is 0.3606×10^6 and 0.290×10^6 ton CO_2, respectively, or a total of 0.651×10^6 ton CO_2. Thus, the excess CO_2 emission by the co-production relative to the conventional separate processes amounts to 23.2%.

3.4. *Reaction of alumina with methane and oxygen*

The carbothermic reduction of Al_2O_3 is examined using a small excess of CH_4 (CH_4/Al_2O_3 molar ratio 4) and a very limited amount of oxygen ($O_2/CH_4 = 0.1$). The CH_4 concentration in the proposed initial gas mixture is thus 91%, much above the upper flammable limit of CH_4 in air, i.e. 15% [14]. The equilibrium composition as a function of temperature in the range of 1800–2900 K is presented in Fig. 6. Al_2O_3 is completely reduced, i.e. its mole fraction is less than 10^{-5} at above 2200 K, while Al and AlH are formed at 2000 K. Al_4C_3 is stable in the 2100–2400 K range. Carbon, as C(gr), is used up above 2500 K. The gaseous aluminum suboxide Al_2O starts to appear at 2000 K, is maximal at 2200 K, and disappears almost completely above 2900 K. Monoatomic hydrogen, H, starts to appear above 1800 K. At 2700 K, the net reaction is represented by

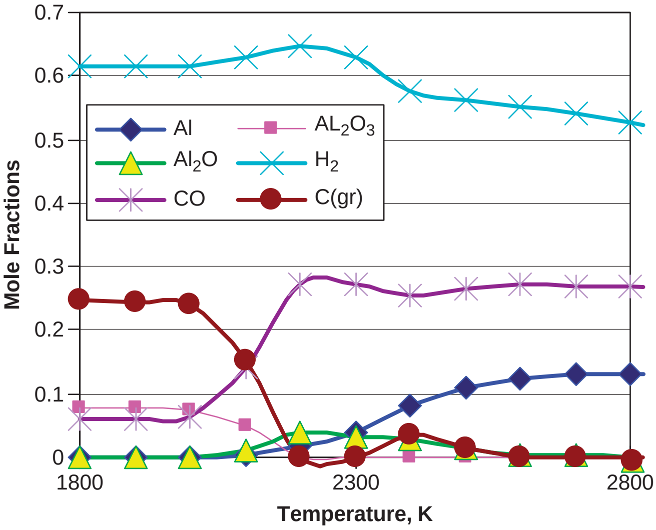

Fig. 6. Equilibrium composition as a function of temperature for the system $Al_2O_3 + 4CH_4 + 0.4O_2$ at 1 bar total pressure.

$$Al_2O_3 + 4CH_4 + 0.4O_2 = 1.81Al(g) + 0.12AlH(g) + 0.03Al_2O(g) + 7.54H_2(g) + 0.58H(g) + 3.77CO(g). \tag{11}$$

At this temperature, the monoatomic gaseous Al is accompanied by smaller amounts of the monovalent species AlH and Al_2O, while C(gr) is used up. H_2 is partially dissociated to monoatomic H. The calculated yield of conversion of Al_2O_3 to Al is 90.4%. The $(H_2+0.5H)/CO$ molar ratio equals 2.08. Such a syngas mixture, when cooled down to about 700–800 K, would be suitable for methanol or Fischer–Tropsch syntheses. The reaction of Eq. (5) is moderately endothermic, requiring a process heat of 0.9 GJ/kmol Al_2O_3. No CO_2 would be released by this reaction. CO_2 emissions derived from the combustion of fossil fuels could be eliminated if concentrated solar energy is used as the source of high-temperature process heat.

As shown in Appendix A (Table A3), the estimated annual co-production of 0.0488×10^6 ton Al and 0.109×10^6 ton CH_3OH requires a total fuel input (including process heat) of 4.475×10^6 GJ, and releases 0.0451×10^6 ton CO_2. The conventional separate production of Al by the electrolytic Hall-Héroult process requires 186 GJ/ton Al, and causes the release of 7.42 ton $CO_{2\text{-equiv}}$ per ton Al [6]. In addition, the separate production of methanol by steam-reforming of CH_4 (MSR) requires 44.5 GJ of NG/ton methanol [15], and releases 1.044 ton $CO_{2\text{-equiv}}$ per ton of methanol [16]. Thus, the conventional separate production of the above amounts of Al via electrolysis and of methanol via MSR would require 9.077×10^6 GJ and 4.851×10^6 GJ, respectively, or a total of 13.93×10^6 GJ. The fuel saving by the proposed co-production relative to the conventional separate processes is 67.9%. Further, the separate production of such amounts of Al and CH_3OH releases 0.362×10^6 ton CO_2 and 0.114×10^6 ton CO_2, respectively, or a total of 0.476×10^6 ton CO_2. Thus, the CO_2 emission avoidance by the proposed co-production relative to the conventional separate processes amounts to 90.5%. The annual production of 0.0488×10^6 ton Al and of 0.109×10^6 ton methanol would cover 0.16% and 0.3% of the annual world production of Al [17] and methanol [18], respectively.

4. Discussion

In laboratory scale experiments, using inductance furnace heating, the carbothermic reduction of Al_2O_3 by activated carbon was demonstrated to produce Al, together

Table 1
Comparison of equilibrium compositions of reaction products at 2500 K and 1 bar from initial mixtures of 1 mol Al_2O_3 with either 4C, $4C+0.5O_2$, or $4CH_4+0.5O_2$

Initial reactants (mol)	Al (mol)	Al_2O (mol)	H_2 (mol)	CO (mol)	C(gr) (mol)	Al_4C_3 (mol)	% Al yield
Al_2O_3+4C	0.661	0.342	–	2.658	0.857	0.162	33.0
$Al_2O_3+4C+0.5O_2$	0.881	0.456	–	3.544	0.309	0.049	44.0
$Al_2O_3+4CH_4+0.5O_2$	1.487	0.185	7.714	3.815	0*	0*	74.3

*Less than 10^{-5}moles.

with Al_2OC, Al_4C_3, and Al_4O_4C. Thermochemical equilibrium calculations were used to suggest further improved conditions for such reactions. Table 1 compares the predicted production of Al in three reaction systems at 2500 K. The carbothermic reduction of Al_2O_3 by carbon, both in the absence and presence of oxygen, would involve the formation of substantial amounts of Al_4C_3. By contrast, the reduction of Al_2O_3 by CH_4 in the presence of oxygen not only would markedly increase the yield of Al, but also would co-produce a useful H_2–CO mixture and inhibit the production of Al_4C_3 or C(gr). The favorable effect of the addition of limited amounts of oxygen are due to the exothermic partial oxidation of carbon or CH_4, which compensates partially or fully for the endothermic carbothermic reduction of Al_2O_3. The co-production of syngas and metals such as Al, Fe, and Zn could provide considerable fuel savings along with a substantial mitigation of CO_2 emissions [19,20]. The application of concentrated solar energy as the source of process heat could further eliminate greenhouse gas emissions derived from the combustion of fossil fuels. High temperature thermochemical processes carried out in solar furnaces included the carbothermal reductions of Fe_3O_4, MgO, and ZnO with C(gr) and CH_4 to produce Fe, Mg, and Zn, respectively, the carbothermal reductions of Al_2O_3, CaO, SiO_2, and TiO_2 with C(g) in an inert atmosphere to produce Al_3C_4, CaC_2, SiC, and TiC, respectively, and the carbothermal reductions of Al_2O_3, SiO_2, TiO_2, and ZrO_2 with C(g) in a N_2 atmosphere to produce AlN, Si_3N_4, TiN, and ZrN, respectively [21–29]. The tentative economic evaluations described in the Appendix A suggest favorable competitiveness, which is mainly due to the fuel saving attained by the co-production of aluminum and syngas. Further work is warranted, particularly on the kinetics of these reactions and on the recovery of metallic aluminum from the gas phase.

Appendix A

The tentative economic evaluations are shown in Tables A1–A3.

Table A1
Economic evaluation for aluminum and methanol production from an initial mixture of alumina, coke (represented by carbon), and oxygen, initially at 300 K and 1 bar, calculated to be transformed at 2815 K and 1 bar according to $Al_2O_3+4C+0.6O_2=1.58Al+0.20Al_2O+0.01Al_2+4CO$. After 2/3 WGS of CO to H_2, the resulting syngas would be converted to methanol. Ton = metric ton

Design parameters	
Design Al_2O_3 feed (ton/yr)	0.102×10^6
Annual coke feed (ton/yr)	0.048×10^6
Annual coke feed (GJ/yr)[a]	1.57×10^6
Annual process heat (GJ/yr)	1.67×10^6
Total fuel feed (GJ/yr)	3.24×10^6
Annual O_2 feed (ton/yr)	0.0192×10^6
Annual Al production (ton/yr)	0.0427×10^6
Annual methanol production (ton/yr)[b]	0.038×10^6
Total annual CO_2 release (ton/yr)[c]	0.304×10^6
Capital costs (million US$)	
Equipment and facility[d]	50.0
Interest during construction (10% of facility investment)	5.0
Start-up expenses and working capital (10%)	5.0
Total	60.0
Annual costs (million US$)	
Capital cost (15% of total)	9.0
Operation and maintenance (2% of total)	1.2
Coke cost (US$130/ton)[e]	6.2
Al_2O_3 cost (US$33.6/ton)[f]	34.3
O_2 cost (US$40/ton)[g]	16.6
Total	67.3
Annual sales (million US$)	
Aluminum (US$2800/ton)[h]	119.6
Methanol (US$336/ton)[i]	12.8
Total	132.4

[a] Taking as the HHV of coke the value for graphite, 0.3935 GJ/kmol.
[b] Assume 90% overall yield in WGS of 2/3 of CO to syngas, and its conversion to methanol.
[c] Incl. CO_2 from the combustion of process heat fuel, assumed to be coke.
[d] Estimated total cost, including the high–temperature reactor, heat exchanger, WGS reactor, and methanol synthesis reactor.
[e] November 2005; see www.eia.doe.gov/cneaf
[f] April 2007; alumina price usually linked 11–13% to the LME aluminum price. See www.globalalumina.com
[g] L. Basye, S. Swaminathan, "Hydrogen Production Costs", 1997; Report DOE/GO/101-778.
[h] April 2007, London Metal Exchange; see www.lme.com
[i] April 2007; see www.methanex.com

Table A2
Economic evaluation for aluminum and methanol production from an initial mixture of alumina, coke (represented by carbon), and oxygen, initially at 300 K and 1 bar, calculated to be transformed in a thermo-neutral reaction at 2815 K and 1 bar according to $Al_2O_3 + 28.9C + 13O_2 = 1.80Al + 0.10Al_2O + 28.9CO$. After 2/3 WGS of CO to H_2, the resulting syngas would be converted to methanol. Ton = metric ton

Design parameters	
Design Al_2O_3 feed (ton/yr)	0.102×10^6
Annual coke feed (ton/yr)	0.347×10^6
Annual coke feed (GJ/yr)[a]	11.4×10^6
Annual coke feed (mmbtu/yr)	10.9×10^6
Annual O_2 feed (ton/yr)	0.416×10^6
Annual Al production (ton/yr)	0.0486×10^6
Annual methanol production (ton/yr)[b]	0.277×10^6
Annual CO_2 release (ton/yr)	0.848×10^6
Capital costs (million US$)	
Equipment and facility[c]	50.0
Interest during construction (10% of facility investment)	5.0
Start-up expenses and working capital (10%)	5.0
Total	60.0
Annual costs (million US$)	
Capital cost (15% of total)	9.0
Operation and maintenance (2% of total)	1.2
Coke cost (US$130/ton)[d]	45.1
Al_2O_3 cost (US$336/ton)[e]	34.3
O_2 cost (US$40/ton)[f]	16.6
Total	106.2
Annual sales (million US$)	
Aluminum (US$2,800/ton)[g]	136.1
Methanol (US$336/ton)[h]	93.1
Total	229.2

[a] Taking as the HHV of coke the value for graphite, 0.3935 GJ/kmol.
[b] Assume 90% overall yield in WGS of 2/3 of CO to syngas, and its conversion to methanol.
[c] Estimated total cost, including the high-temperature reactor, heat exchanger, WGS reactor, and methanol synthesis reactor.
[d] November 2005; see http://www.eia.doe.gov/cneaf
[e] April 2007; alumina price usually linked 11–13% to the LME aluminum price. See www.globalalumina.com
[f] L. Basye, S. Swaminathan, "Hydrogen Production Costs", 1997; Report DOE/GO/101-778.
[g] April 2007, London Metal Exchange; see www.lme.com
[h] April 2007; see www.methanex.com

Table A3
Economic evaluation for aluminum and methanol production from an initial mixture of alumina, NG (natural gas), and oxygen, initially at 300 K and 1 bar, calculated to be transformed in a thermo-neutral reaction at 2700 K and 1 bar according to $Al_2O_3 + 4CH_4 + 0.4O_2 = 1.81Al + 0.12AlH + 0.03Al_2O + 7.54H_2 + 3.77CO$. The resulting syngas would be converted to methanol. Ton = metric ton

Design parameters	
Design Al_2O_3 feed (ton/yr)	0.102×10^6
Annual NG reaction feed (GJ/yr)[a]	3.563×10^6
Annual process heat (GJ/yr)	0.912×10^6
Total fuel feed (GJ/yr)	4.475×10^6
Total fuel feed (mmbtu/yr)	4.242×10^6
Annual O_2 feed (ton/yr)	0.0128×10^6
Annual Al production (ton/yr)	0.0488×10^6
Annual methanol production (ton/yr)[b]	0.109×10^6
Annual CO_2 release (ton/yr) from proc. heat[c]	0.0451×10^6
Capital costs (million US$)	
Equipment and facility[d]	50.0
Interest during construction (10% of facility investment)	5.0
Start-up expenses and working capital (10%)	5.0
Total	60.0
Annual costs (million US$)	
Capital cost (15% of total)	9.0
Operation and maintenance (2% of total)	1.2
NG cost (US$7.415/mmbtu)[e]	31.5
Al_2O_3 cost (US$336/ton)[f]	34.3
O_2 cost (US$40/ton)[g]	0.5
Total	76.5
Annual sales (million US$)	
Aluminum (US$2800/ton)[h]	136.6
Methanol (US$336/ton)[i]	36.6
Total	173.2

[a] Taking as the HHV of NG 0.8908 GJ/kmol.
[b] Assume 90% yield in methanol synthesis.
[c] Only from the process fuel, assumed to be NG.
[d] Estimated total cost, including the high temperature reactor, heat exchanger, and methanol synthesis reactor.
[e] April 2007; see: New York Mercantile Exchange, www.nymex.com
[f] April 2007; alumina price usually linked 11–13% to the LME aluminum price. See www.globalalumina.com
[g] L. Basye, S. Swaminathan, "Hydrogen Production Costs", 1997; Report DOE/GO/101-778.
[h] April 2007, London Metal Exchange; see www.lme.com
[i] April 2007. See Methanex Corporation, www.methanex.com

References

[1] Frank WB, et al. Aluminum. In: Ullman's encyclopedia of industrial chemistry, vol. A1. VCH Publishers; 1985. p. 459.

[2] (a) Choate WT, Green JAS. US energy requirements for aluminum production: historical perspective, theoretical limits and new opportunities, January 2003. See: ⟨www.secat.net/docs/resources⟩;
(b) Choate W, Green J. Technoeconomic assessment of the carbothermic reduction process for aluminum production. Light Met 2006;445–450.

[3] Steinfeld A, Thompson G. Solar combined thermochemical processes for CO_2 mitigation in the iron, cement, and syngas industries. Energy 1994;19(10):1077–81.

[4] Steinfeld A. High-temperature solar thermochemistry for CO_2 mitigation in the extractive metallurgical industry. Energy 1997;22: 311–6.

[5] (a) Cochran CN, Fitzgerald NM. Energy efficient production of aluminum by carbothermic reduction of alumina (Aluminum Co. of America, Japan). US (1981). CODEN: USXXAM US 4299619 A 19811110. Patent Application: US 80-125644 19800228;
(b) Myklebust H, Runde P. Greenhouse gas emissions from aluminum carbothermic technology compared to Hall–Heroult technology. Light Met 2005:519–22.

[6] Cox JH, Pidgeon LM. The aluminum–oxygen–carbon system. Can J Chem 1963;41:671–83.

[7] Halmann M, Frei A, Steinfeld A. Thermo-neutral production of metals and hydrogen or methanol by the combined reduction of the oxides of zinc or iron with partial oxidation of hydrocarbons. Energy 2002;27(12):1069–84.

[8] Halmann M, Steinfeld A. Thermo-neutral co-production of calcium oxide and syngas by combined decomposition of calcium carbonate and partial oxidation—CO_2 reforming of methane. Energy Fuels 2003;17(3):774–8.

[9] Halmann M, Steinfeld A. Combined thermo-neutral processes for CO_2 emission avoidance and fuel saving in the metallurgical and lime industries. Stud Surf Sci Cataly 2004;153:481–6.

[10] Halmann M, Steinfeld A. Production of lime, hydrogen, and methanol by the thermo-neutral combined calcination of limestone with partial oxidation of natural gas or coal. Energy 2006;31:1533–41.

[11] Gordon S, McBride JB. NASA SP-273, NASA Lewis Research, Cleveland, OH, 1976. A PC version prepared by T. Kappauf, M. Pipho, and E. Whitby for E. A. Fletcher at the University of Minnesota was used in the present study.

[12] Thermochemical Software & Database Package FactSage, Centre for Research in Computational Thermochemistry, Ecole Polytechnique de Montreal, Canada, 〈www.crct.polymtl.ca〉.

[13] National Institute of Standards and Technology, Standard reference data program, chemistry webbook, 〈http://webbook.nist.gov/chemistry〉.

[14] Handbook of chemistry and physics. 85th ed. CRC Press: Boca Raton, Florida; 2004–2005, pp. 16–17.

[15] Hiller H, et al. Gas Production. In Ullmann's encyclopedia of industrial chemistry, vol. A12. VCH Publ. 1989. p. 289.

[16] Werder M, Steinfeld A. Life cycle assessment of the conventional and solar thermal production of zinc and synthesis gas. Energy 2000;25: 395–409.

[17] London Metal Exchange on December 2005. See: 〈www.lme.com〉.

[18] See: 〈http://www.methanol.org〉.

[19] Halmann M, Steinberg M. Greenhouse gas carbon dioxide mitigation: science and technology. Boca Raton, Florida: Lewis Publishers; 1999. p. 261.

[20] Murray J. Investigation of opportunities for high-temperature solar energy in the aluminum industry. Subcontract Report, NREL/SR-550-39819, May 2006. See 〈http://www.osti.gov/bridge〉.

[21] Steinfeld A, Fletcher EA. Theoretical and experimental investigation of the carbothermic reduction of Fe_2O_3, using solar energy. Energy 1991;16:1011–9.

[22] Steinfeld A, Kuhn P, Karni J. High temperature solar thermochemistry: production of iron and synthesis gas by Fe_3O_4-reduction with methane. Energy 1993;18:239–49.

[23] Steinfeld A, Frei A, Kuhn P. Thermoanalysis of the combined Fe_3O_4-reduction and CH_4-reforming processes. Metall Mater TransB 1995;26:509–15.

[24] Steinfeld A, Brack M, Meier A, Weidenkaff A, Wuillemin D. A solar chemical reactor for the co-production of zinc and synthesis gas. Energy 1998;23:803–14.

[25] Kräupl S, Steinfeld A. Operational performance of a 5 kW solar chemical reactor for the co-production of zinc and syngas. ASME J Solar Energy Eng 2003;125:124–6.

[26] Osinga T, Olalde G, Steinfeld A. Solar carbothermal reduction of ZnO: shrinking packed-bed reactor modelling and experimental validation. Ind Eng Chem Res 2004;43:7981–8.

[27] Duncan DA, Dirksen HA. Calcium carbide production in a solar furnace. SERI/TR-98326-1, Golden, CO, 1980.

[28] Murray JP, Steinfeld A, Fletcher E. Metals, nitrides, and carbides via solar carbothermal reduction of metal oxides. Energy 1995;20: 695–704.

[29] Murray JP. Solar production of aluminum by direct reduction of ore to Al–Si alloy: preliminary results for two processes. J Solar Energy Eng 2001;123:125–32.