

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 Al₂O, Al₄O₄C, and Al₄C₃ was proven by experiments on mixtures of Al₂O₃ and activated carbon in an Ar atmosphere submitted to heat pulses by an induction furnace. Thermochemical equilibrium calculations indicate that the Al₂O₃-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 Al₄C₃ is decreased, and the yield of aluminum is improved. Significant further enhancement in the carbothermic reduction of Al₂O₃ is predicted by using CH₄ as the reducing agent, again in the presence of limited amounts of oxygen. In this case, an important by-product is syngas, with a H₂/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 CO₂ emission avoidance of about 91%, vis-à-vis the conventional production of Al by electrolysis and of methanol by steam reforming of CH₄. When using carbon (such as coke or petcoke) as reducing agent, fuel savings of 66% and CO₂ 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.

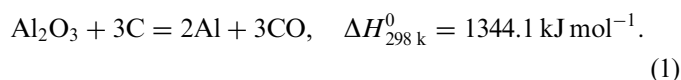
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Keywords: Alumina; Aluminum; Aluminum carbide; Aluminum oxycarbides; Aluminum suboxide; Carbon; Carbon dioxide; Carbothermic reduction; Coke; Fischer–Tropsch; Fluorocarbons; Fuel saving; Graphite carbon-C(gr); Induction furnace; Methane; Methanol;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

1. Introduction

Aluminum is currently produced industrially via the Hall–Héroult process by dissolving Al₂O₃ in fused NaF–AlF₃ (cryolite) followed by direct current electrolysis, in which CO₂ is discharged at a sacrificial carbon anode and Al is deposited at the bottom of the cell. The production of each kg of Al

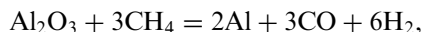
requires the consumption of 0.4–0.5 kg of the carbon anode [1]. The main drawbacks of the electrolytic production are its very high energy consumption (0.186 GJ/kg Al), the release of perfluorocarbons, and the high specific CO₂-equiv emissions (7.42 kgCO₂-equiv/kg Al) [2]. The greenhouse gas emission by the electrolytic Al production contributes 2.5% to the world anthropogenic CO₂-equiv emissions [3]. Much effort has been spent to achieve the carbothermic reduction of Al₂O₃ to metallic Al. Using carbon or CH₄ as reducing agents, the overall reactions can be represented by



Abbreviations: C(gr), Graphite carbon; CO₂-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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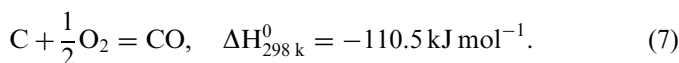
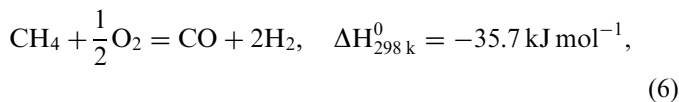
$$\Delta H_{298\text{K}}^0 = 1568.7 \text{ kJ mol}^{-1}. \quad (2)$$

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 $\text{Al}_4\text{O}_4\text{C}$. 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),



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,



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 $\text{Al}_4\text{O}_4\text{C}$, 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.

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