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Research Paper

Thermodynamics analysis of carbothermal-chlorination reduction in aluminum production

Weijuan Yang *, Xiaowei Liu, Jianzhong Liu, Zhihua Wang, Junhu Zhou, Kefa Cen

State Key Laboratory of Clean Energy Utilization, Zhejiang University, Hangzhou 310027, China

HIGHLIGHTS

- Studying in thermodynamics the vacuum carbothermal-chlorination reduction for Al production.
- Studying the reaction efficiency and exergy efficiency with the temperature.
- The optimal reaction temperature region was obtained for carbothermal-chlorination reduction.
- Heat recovery was key to improve the energy consumption and exergy efficiency.
- Carbothermal-chlorination reduction performs better than electricity aluminum.

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ABSTRACT

Carbo-thermal reduction aluminum is regarded as the future aluminum production method for its low energy consumption. A thermodynamics analysis is performed, taking the Al–C two-step model as the objective. High temperature is beneficial to the reaction efficiency, but harmful to the exergy efficiency of the first reaction ($Al_2O_3 + 3C + AlCl_3 = 3AlCl + 3CO$, R1). The second reaction ($3AlCl = AlCl_3 + 2Al$, R2) presents an opposite pattern. An optimal reaction temperature window exists for the AlCl mediated carbon reduction method. The temperature of R1 is above 1520 K and that of R2 is 398–798 K in the optimal window. Heat recovery is significantly important in enhancing both exergy efficiency and energy consumption in actual processes. Energy consumption is reduced from 11,335 kW h/t(Al) to 8063 kW h/t(Al) when an ideal heat recovery is performed. Compared with electrolytic aluminum, carbothermol-chlorination reduction presents a significantly better performance in some condition. Energy consumption is 10,151 and 13,200 kW h/t(Al) in carbothermol-chlorination reduction and electrolytic aluminum, respectively. Moreover, 67% of the exergy efficiency of the carbothermol-chlorination reduction is greater by 1.7 times than that of the electrolytic aluminum.

1. Introduction

Aluminum is one of the most widely used metals all over the world [1]. This metal is applied widely in construction, manufacture, telecommunication, aeronautics, energy and other fields because of its characteristics of low density, corrosion resistance, high strength and energy density [2–5]. Aluminum industry plays an extremely important role in the human development processes and a total of 5×10^{11} t aluminum metal was produced in 2015 [6]. Therefore, a large-scale use of aluminum demanded a high-efficiency aluminum production industry. The modern aluminum production is mainly based on the Bayer and Hall–Héroult processes (Electrolytic aluminum, $2Al_2O_3 + 3C = 4Al + 3CO_2$, electrolysis, 1223.15–1263.15 K) invented about 100 years ago [7,8]. The appearance of the electrolytic aluminum (EA) reduced the difficulty in Al production and greatly improved the aluminum yield. However, high energy consumption and pollution still remain as the main faultiness of electrolytic aluminum, which causes difficulty in obtaining further development [7,9].

Researchers invented some new methods, such as using room temperature ionic liquids (RTILs) in aluminum production, to solve the energy consumption and pollution problems of the aluminum production industry [10]. The electrolytic reaction temperature is greatly reduced because the melting point of ionic liquids is usually below 373.15 K [11]. Thus this approach can save much heat energy than the traditional aluminum production method. Poulimenou et al. [8] examined the possibility of dissolving metallurgical alumina, hydrated alumina, and bauxites in $[Emim]HSO_4$. The results showed that hydrated alumina can be dissolved relatively

* Corresponding author.
E-mail address: yangwj@zju.edu.cn (W. Yang).

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Nomenclature

CCRA	carbothermal-chlorination reduction aluminum
CTR	carbo-thermal reduction
GHG	greenhouse gas
EA	electrolytic aluminum
E_x	exergy
E_x^0	standard chemical exergy
$E_{p,T}$	thermomechanical exergy of matter
E_H	exergy transfer accompanying heat
E_E	electricity exergy
ΔH	enthalpy change
ΔS	entropy change
ΔG	gibbs free energy change
i	exergy efficiency
η	reaction efficiency
x, y, z	stoichiometric number
AxByCz	compound formed by chemical elements A, B, and C
T	reacting temperature
Subtext	
1	reaction 1
2	reaction 2
E	electrolytic reaction

easily at 483 K. RTILs are still far away from industrial application because some important problems remain to be solved for electrodeposition, such as the deposition is easily affected by temperature and atmosphere [12]. Another promising aluminum production technology is the carbo-thermal reduction (CTR) derived from blast iron making. The method uses coal or carbon as a reducing agent to reduce oxide from alumina at high temperature. The reaction equation can be summarized into $Al_2O_3 + 3C = 2Al + 3CO$, which is thermodynamically favorable above 2320 K [13]. The advantages of the CTR are lower energy consumed and less GHG (greenhouse gas) emission than the electrolytic aluminum. However, the direct CTR has the two following shortcomings: (1) the reaction needs an extremely high temperature that only electric-arc furnaces or highly concentrated solar can obtain [14]; (2) some extra products, such as Al_4C_3 and Al_4O_4C [13], which are difficult to separate from solid aluminum, exist. These weaknesses limit the development and utilization of the CTR. Investigators have performed different studies on improving the reaction effects of the direct CTR. Yokokawa et al. [15] summarized the three complicated features of the alumina reduction: (1) severe volatilization of aluminum components; (2) carbide formation and high carbon solubility in liquid metals; and (3) complicated reaction path to metals. Different methods [16–18] have been determined to overcome these difficulties. Halmann et al. [13] investigated CH_4 as an reductant to reduce Al_2O_3, and they found that the presence of oxygen could raise the Al yield, produce useful by-products (H_2–CO mixture), and reduce the generation of Al_4C_3 or C(gr). A hot and reductive zone can be formed at the center of a blast furnace. Ujiie et al. [19] realized that the use of large cokes at a high oxygen blast rate can enhance its stability. Solar energy was designed to provide energy for the system [20,21]. Kruesi et al. [21] found that considerable energy was saved and concomitant CO_2 emissions was reduced when the concentrated solar energy was used as the source of high-temperature process heat. The solar reactor temperature can reach up to 2000 K. The solar-driven CTR is CO_2-neutral if the reducing agent is derived from a biomass source. The reaction pressure was studied in the experiments. Yu et al. [22] found the gaseous reduction product, (Al(g) or Al_2O(g), in the CTR of Al_2O_3 at 1623 K under a pressure of 5–30 Pa, which led to further reactions with CO to produce Al_4O_4C, Al_4C_3, and C. The experiment indicated that low pressure could debase the onset temperature.

A method using $AlCl_3$ as a transitional agent was investigated by the National Engineering Laboratory of Vacuum Metallurgy in Kunming [22,23]. $AlCl_3$ can react with alumina and carbon at given temperatures and can generate CO and AlCl. AlCl would decompose into Al and $AlCl_3$ at a lower temperature than the first step. The carbothermol-chlorination reduction of alumina (CCRA) avoids the direct contact of Al and C and decreases the reaction temperature at the same time. Further experiments on a vacuum furnace have been performed by Yuan, Feng, and Yu et al. [23–25], and they discovered Al_4O_4C and Al_4C_3, instead of Al_2O_3, participate in the chlorination reaction. This finding indicated that two step reactions or more occur in the AlCl generation. The reaction possibly occurs at a temperature of 1573.15 K under 5–50 Pa, and the average purity of the aluminum metal reaches 95.32%. The experiment results of the CCRA point out a feasible method of reducing the temperature of CTR.

Exergy analysis was one of normal methods to evaluate systems or devices from the view of available energy. Energy and exergy analysis has been applied to combined cogeneration system, compression ignition engine by researchers [26–29], otto engine and diesel cycle, and got significant results. It was effective to apply this method to aluminum production, and the job had been done by Efthymios et al. [7]. They found that the Bayer process was characterized by low exergy yield (31%) and the high energy and exergy cost of Hall–Héroult process is related primarily to the cost of electricity generation. It was pointed out that high temperature carbothermal reduction of alumina was a possible way to replace electrolytic process [7]. Exergy method was utilized to quantify the natural resource consumption of aluminum production, and to analyze the exergy change of the holding process in the aluminum holding furnace [30,31].

Summarily experiments on CCRA have been conducted and exergy analysis has been introduced to aluminum production process. However, the exergy analysis of aluminum production is mainly concentrated on traditional electrolytic aluminum process, and the CCRA development is unsatisfactory without a strong support from theoretical bodies of research. The thermodynamics analyses of the whole CCRA process were performed in this study, concerning reaction efficiencies, energy and exergy analysis, and comparison to electrolytic aluminum. This research studied on CCRA process to reveal the energy and exergy characteristics of the CCRA processes from the global perspective, which will provide some theoretical support and guide to the CCRA development.

2. Method

The two-step reactions are shown as Eqs. (R1) and (R2) as follows [25]:

$$Al_2O_3 + 3C + AlCl_3 = 3AlCl + 3CO \quad (p_1, T_1, \Delta H_1 > 0) \tag{R1}$$

$$3AlCl = AlCl_3 + 2Al \quad (p_2, T_2, \Delta H_2 < 0) \tag{R2}$$

A reaction model was built according to the two chemical equations (Eqs. (1) and (2)) to show the detailed aluminum production process. Carbon and alumina were heated and reacted with $AlCl_3$ in a reactor to produce aluminum chloride and carbon oxide. The products of R1 were transferred into the other reactor and were then converted into Al and $AlCl_3$ through disproportion. The CCRA