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Chlorination-disproportionation of Al_4O_4C and Al_4C_3 in vacuum

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ABSTRACT

The chlorination-disproportionation of Al_4O_4C and Al_4C_3 in vacuum was investigated by thermodynamic analysis and experiments using the side products of the AlCl disproportionation process of alumina, consisting of Al_4O_4C, Al_4C_3, Al_2O_3 and C, as raw materials. It was demonstrated that the chlorinations of Al_4O_4C and Al_4C_3 with $AlCl_3$ in vacuum are thermodynamically favorable, and their kinetics feasibilities were supported by the experiments at 1643 K–1843 K. The metallic aluminum obtained in the experiments contained a certain carbon formed from the disproportionation of CO.

1. Introduction

The traditional Hall-Héroult process is the major industrial process for the production of aluminum today, characterized by high energy-consumption and high cost. While the process is growing mature, alternative processes are constantly being explored. The carbothermal reduction process is promising due to its potential to cut cost [1,2]; however it remains the formidable technical challenges. The direct carbothermal process requires high temperatures above 2273 K [3–5], in which a large of byproducts (aluminum carbide, aluminum oxycarbide, *etc*) and unreacted raw materials would melt and mix with molten aluminum, resulting in difficulties to separate aluminum from the molten mixture [3–7].

The AlCl disproportionation process in vacuum, developed from the direct carbothermal reduction process and based on the carbothermal reduction-chlorination-disproportionation of alumina, could overcome the above problems with the required temperatures lower and the aluminum products apart from the residues [8,9]. The process includes two steps: Firstly, the gaseous AlCl is generated from the carbothermal reduction-chlorination of alumina at higher temperatures; and then it disproportionates to metallic aluminum and gaseous $AlCl_3$ at lower temperatures, as shown in Eqs (1) and (2).

$$Al_2O_3(s) + 3C(s) + AlCl_3(g) = 3AlCl(g) + 3CO(g) \tag{1}$$

$$3AlCl(g) = 2Al(s) + AlCl_3(g) \tag{2}$$

The extraction rate of aluminum depends on the first step, in which the carbothermal reduction of alumina generates Al_2O, Al and CO gases, and a portion of the Al_2O and Al are chlorinated by $AlCl_3$ to form AlCl, represented by the overall reaction as Eq. (1), and the rest of the Al_2O and Al react with CO to form side products consisting of Al_4C_3, Al_4O_4C, Al_2O_3 and C in the colder region, resulting in a decrease in the extraction rate of aluminum [10,11].

It is required to ascertain whether the aluminum in the side products could be recovered, especially in Al_4C_3 and Al_4O_4C. Although the previous research proposed that aluminum could be produced by the chlorination of Al_4C_3 or Al_4O_4C and disproportionation of AlCl [12], this work still focused on this issue, with improved thermodynamic calculation and experiments.

2. Thermodynamic analysis on the chlorinations of Al_4O_4C and Al_4C_3

It has turned out that the disproportionation of AlCl can occur at a low enough temperature [10,11], and therefore thermodynamic

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analysis should be concentrated on the chlorinations of Al_4O_4C and Al_4C_3 to form AlCl. Yu et al. [12] proposed that Al_4O_4C and Al_4C_3 could be chlorinated to AlCl above 1394.43 K and 1231.42 K respectively under 50 Pa according to thermodynamic calculations, without specifying the partial pressures of each gas. The Gibbs free energy changes of the chlorination of Al_4C_3 and Al_4O_4C should be a function of the partial pressures of each gas as well as temperature.

The chlorination of Al_4O_4C can be represented by the overall reaction as Eq. (3).

$$Al_4O_4C(s) + AlCl_3(g) = 3AlCl(g) + CO(g) + Al_2O_3(s) \tag{3}$$

The standard Gibbs free energy change (ΔG^{θ}) of reaction (3) was calculated using Chemical Reaction and Equilibrium of Software (HSC) (the data of Al_4O_4C, $AlCl_3$ and AlCl from Ref. [13], the data of Al_2O_3 and CO from Ref. [14] and Ref. [15] respectively), and then plotted vs temperature (T) in Fig. 1. As can be seen, ΔG^{θ} decreases with temperature, but it is positive at all temperatures from 300 K to 1900 K, demonstrating that the chlorination of Al_4O_4C could not occur below 1900 K under standard atmosphere pressure. A very nice linear relation can be found between ΔG^{θ} and T, which should be due to the fact that the temperature dependence of the change in heat capacity is small. The regression equation was shown as Eq. (4).

$$\Delta G^{\theta}(J) = 939148.4 - 473.7T \tag{4}$$

In the nonstandard atmosphere, the Gibbs free energy change (ΔG) is a function of temperature (T) and equilibrium constant (K_p), $\Delta G(J) = \Delta G^{\theta} + RT\ln K_p$, where R is the ideal gas constant, thus the Gibbs free energy change can be also expressed as $\Delta G(J) = \Delta G^{\theta} + 19.146T\lg K_p$ [16].

For reaction (3), $K_p = (p_{AlCl}/p^{\theta})^3(p_{CO}/p^{\theta})/(p_{AlCl_3}/p^{\theta})$, where p_{AlCl}, p_{CO}, and p_{AlCl_3} are the partial pressures of AlCl, CO and $AlCl_3$ respectively, and p^{θ} is the standard atmospheric pressure. Then the Gibbs free energy change can be expressed as a function of temperature and the partial pressures of AlCl, CO and $AlCl_3$, as shown in Eq. (5).

$$\Delta G\left(J\right) = \Delta G^{\theta} + 19.146T\lg p_{AlCl}^{3}p_{CO}\Big/p_{AlCl_3}\left(p^{\theta}\right)^{3} \tag{5}$$

In the AlCl disproportionation process, the gaseous $AlCl_3$ is provided continually through a special unit, and hence the $AlCl_3$ partial pressure may be assumed to be constant. In the experiments the sublimation temperature of $AlCl_3$ was maintained at 358 K–363 K, and the vapor pressures of $AlCl_3$ at 358 K and 363 K are 28 Pa and 49 Pa respectively, calculated from the relation between the vapor pressure and temperature [17]. Consequently the $AlCl_3$ partial pressure was set to 30 Pa.

The total pressure of the reaction system equals to the sum of the $AlCl_3$, AlCl and CO partial pressures, $p_{tot} = p_{AlCl} + p_{AlCl_3} + p_{CO}$, where p_{AlCl}=$3p_{CO}$ according to Eq. (3), and$p_{AlCl_3} = 30$ Pa, and then Eq. (6) was deduced from Eqs. (4) and (5).

$$\Delta G\left(J\right) = 939148.4 - 807.9T + 19.146T\lg(p_{tot} - 30)^{4} \tag{6}$$

From Eq. (6), ΔG of reaction (3) at the $AlCl_3$ partial pressure of 30 Pa was plotted vs temperature in Fig. 2. As can be seen, the required temperature for the chlorination of Al_4O_4C decreases apparently at reduced pressures, and the equilibrium temperatures are 1326 K, 1409 K and 1474 K at the total pressures of 50 Pa, 100 Pa and 200 Pa, respectively.

The chlorination of Al_4C_3 can be represented by the overall reaction as Eq. (7)

$$Al_4C_3(s) + 2AlCl_3(g) = 6AlCl(g) + 3C(s) \tag{7}$$

ΔG^{θ} of reaction (7) was calculated using HSC (the data of Al_4C_3, $AlCl_3$ and AlCl from Ref. [13], the data of C from Ref. [18]), and plotted vs temperature in Fig. 3. As can be seen, ΔG^{θ} decreases with temperature at 300 K–1900 K, and it is negative below 1702 K. The linear regression equation was shown as Eq. (8).

$$\Delta G^{\theta}(J) = 1041473 - 611.826T \tag{8}$$

For reaction (7), $K_p = (p_{AlCl}/p^{\theta})^6/(p_{AlCl_3}/p^{\theta})^2$, where p_{AlCl} and p_{AlCl_3} are the partial pressures of AlCl and $AlCl_3$ respectively, and p^{θ} is the standard atmospheric pressure. Then ΔG of reaction (7) is expressed as a function of temperature and the partial pressures of $AlCl_3$ and AlCl, as shown in Eq. (9).

$$\Delta G\left(J\right) = \Delta G^{\theta} + 19.146T\lg p_{AlCl}^{6}\Big/p_{AlCl_3}^{2}\left(p^{\theta}\right)^{4} \tag{9}$$

The total pressure of the reaction system equals to the sum of the $AlCl_3$ and AlCl partial pressures, $p_{tot} = p_{AlCl} + p_{AlCl_3}$, and setting

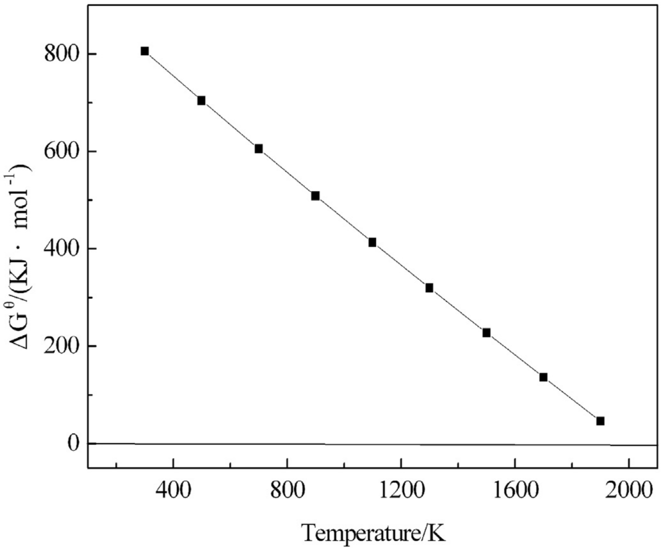

Fig. 1. ΔG^{θ} of reaction (3) vs temperature.

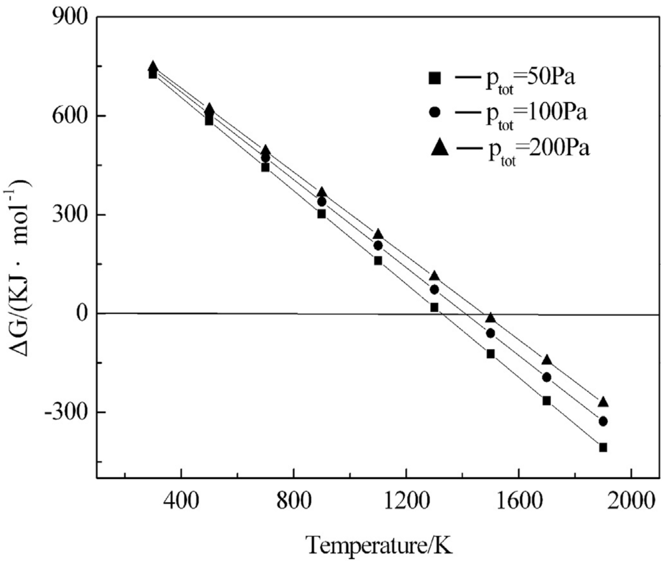

Fig. 2. ΔG of reaction (3) at $AlCl_3$ partial pressure of 30 Pa vs temperature.