

Carbothermal reduction–chlorination–disproportionation of alumina in vacuum

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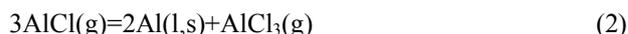
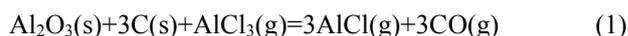
Abstract: The carbothermal reduction–chlorination–disproportionation of alumina in vacuum was investigated by XRD and thermodynamic analysis. The experiments on alumina and graphite at 1643–1843 K in vacuum were carried out. The results demonstrate that $\text{AlCl}_3(\text{g})$ reacts with $\text{Al}_2\text{O}(\text{g})$ or $\text{Al}(\text{g})$ generated from the carbothermal reduction of alumina to form $\text{AlCl}(\text{g})$, and the $\text{AlCl}(\text{g})$ disproportionates to aluminum and $\text{AlCl}_3(\text{g})$ at a lower temperature and the reaction rate of $\text{AlCl}(\text{g})$ reaches 90% at 980 K and 100 Pa. The aluminum can absorb CO to catalyze its disproportionation to C and CO_2 , and react backward with CO to form Al_4C_3 , Al_2O_3 , C and CO_2 , resulting in the aluminum product containing C, Al_4C_3 and Al_2O_3 . The impurities in the aluminum product decrease as the $\text{AlCl}(\text{g})$ disproportionation temperature decreases. AlCl_3 condenses at a temperature approximated to the room temperature.

Key words: carbothermal reduction; Al_2O_3 ; AlCl ; vacuum; disproportionation

1 Introduction

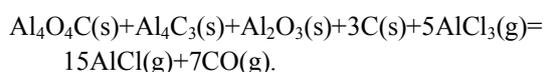
Despite the industrial supremacy of the Hall-Heroult electrolytic process, there have been sustained attempts to produce aluminum by the carbothermal reduction of alumina. The processes can be divided into two groups. In the first approach, alumina is directly reduced to aluminum using carbon as a reducing agent. The process has been studied extensively [1–3]. However, it remains to be a formidable technical challenge, due to the high temperature, and to the formation of aluminum carbide and oxycarbide [4]. In the second approach, aluminum is produced by carbothermal reduction with simultaneous chlorination of alumina. The present situation of the process was described in Ref. [5]. Recently, the researchers in Kunming University of Science and Technology, China have been carrying out research and developmental work on the latter approach to produce aluminum by carbothermal reduction–chlorination–disproportionation of alumina in vacuum, in which $\text{AlCl}(\text{g})$ is generated at high temperatures by the carbothermal reduction–chlorination of alumina and it will disproportionate into Al and AlCl_3 at low temperatures [6]. It can be

represented by the following overall reactions [6]:



Compared with the direct carbothermal reduction, the temperatures required for the process are considerably decreased, and the aluminum products don't need to be separated from residues because they are formed in the low temperature zone by the disproportionation of $\text{AlCl}(\text{g})$, apart from the carbothermal reduction–chlorination zone.

WANG et al [6] proved the practicality of the process through the experiments on the raw materials of bauxite and coal. YUAN et al [7–10] investigated the process by XRD, SEM and thermodynamic analysis, thereby proposing the following chlorination reactions:



The purpose of this work is to investigate the mechanism of the formation of Al through the carbothermal reduction–chlorination–disproportionation

of alumina at a temperature ranged from 1643 to 1843 K in vacuum.

2 Thermodynamic analysis

2.1 Carbothermal reduction–chlorination of alumina

The carbothermal reduction of alumina in Ar or vacuum was found to proceed through gas phase reactions, rather than direct solid–solid reactions [11–13]. Therefore, AlCl(g) should not be formed from the direct solid–solid–gas reactions of alumina, carbon and AlCl₃, and be formed from the chlorination reactions of the carbothermal reduction products with AlCl₃.

The carbothermal reduction of alumina in vacuum forms Al₂O, Al and CO. The overall reactions are [13]:



The initial reaction temperature for reaction (3) is lower than that for reaction (4) [14]. However, the Gibbs free energy change of reaction (3) decreases less sharply than that of reaction (4), so that the ΔG – T curves of reactions (3) and (4) intersect at temperature where ΔG of reaction (3) equals that of reaction (4) [14]. The intersection temperature decreases with decreasing the system pressure, as shown in Fig. 1. The main Al-containing products of the carbothermal reduction of alumina are Al at the left-upper side of the curve and Al₂O at the right-lower side of the curve [14].

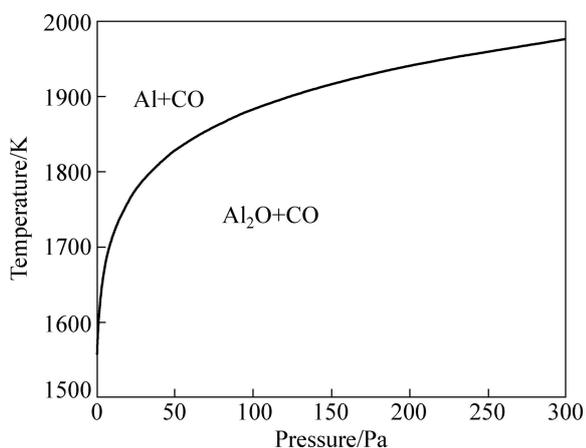
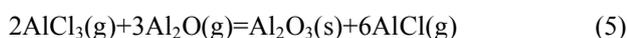


Fig. 1 Temperature at intersection of ΔG – T curves of reactions (3) and (4) vs system pressure [14]

The chlorination reaction of Al₂O(g) to AlCl(g) is postulated:



Based on the data of chemical reaction and equilibrium of software (HSC), the Gibbs free energy change (ΔG^\ominus) of reaction (5) was calculated and shown in Fig. 2. As can be seen, ΔG^\ominus values are all negative and

declined downwards in the range of 1200–1900 K. Furthermore, vacuum is beneficial for reaction (5) because it is a volume expansion reaction. Therefore, reaction (5) can occur under conditions studied.

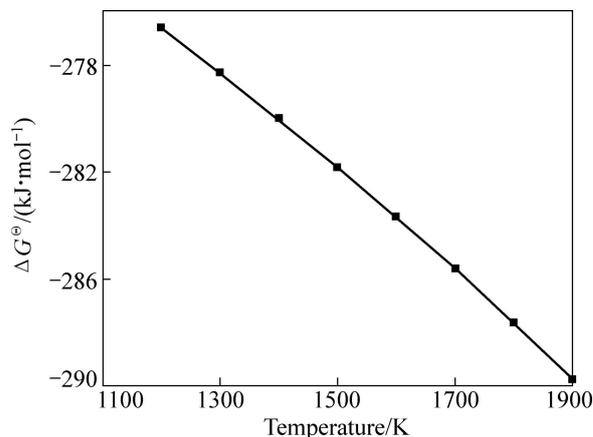


Fig. 2 ΔG^\ominus of reaction (5) vs temperature

The chlorination reaction of Al(g) to AlCl(g) is



Based on the data of HSC, the Gibbs free energy (ΔG^\ominus) of reaction (6) was calculated and shown in Fig. 3. As can be seen, ΔG^\ominus values are all negative and declined downwards in the range of 1200–1900 K. The system pressure has no influence on the Gibbs free energy change of reaction (6). Reaction (6) has ever been used to extract aluminum from Al alloy [15, 16].

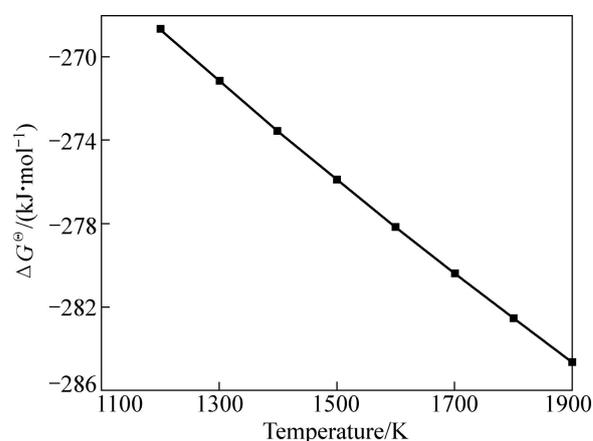


Fig. 3 ΔG^\ominus of reaction (6) vs temperature

2.2 Disproportionation of AlCl(g)

AlCl(g) disproportionates into Al and AlCl₃(g) according to Eq. (2) at low temperature. When the mole ratio of AlCl(g) to AlCl₃(g) was 0.5, the relationship of Gibbs free energy change (ΔG) of reaction (2) and temperature (T) was calculated based on the data of HSC using the method from Ref. [17], and shown in Fig. 4. As can be seen, ΔG value of reaction (2) decreases with

decreasing the temperature and increasing the system pressure in the range of 300–1900 K. Therefore, the larger the system pressure is, and the higher the temperature is, the more easily the $\text{AlCl}(\text{g})$ disproportionation is carried out.

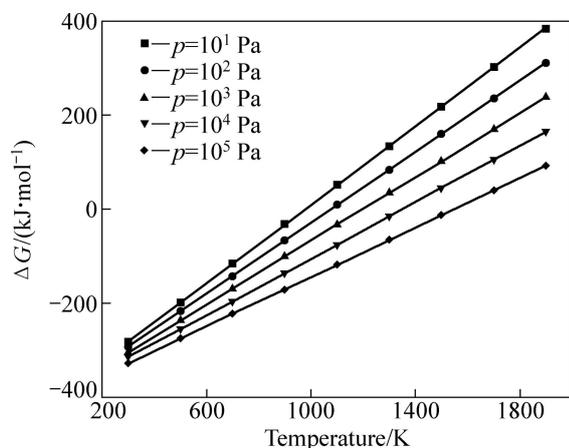


Fig. 4 ΔG of reaction (2) vs temperature at different pressures (the mole ratio of AlCl to AlCl_3 is 0.5)

3 Experimental

3.1 Apparatus

The experiments were carried out in the furnace designed by ourselves, as shown in Fig. 5 [18].

3.2 Experimental procedure

Alumina (analytical grade) and graphite (fixed carbon content of 99.85%) with molar ratio of 1:3 were thoroughly mixed and pressed in a closed die of 20 mm in diameter under 2 MPa to produce cylindrical pellets

with mass of about 5 g.

1) Carbothermal reduction of alumina (Experiments A)

The pellets were held in the graphite crucible placed in the vacuum furnace, and heated at a certain temperature for 30 min. The residues and condensates were then analyzed by X-ray diffraction technique using a D/max-3B diffractometer (Japan) with $\text{Cu K}\alpha$ radiation.

The experiments were conducted at 1643, 1693, 1743, 1793 and 1843 K, respectively. The highest pressure in the system reached 150 Pa. The present conditions were mainly in the range for producing Al_2O according to Fig. 1, and thereby alumina reacted with C to form Al_2O chiefly according to reaction (3).

2) Carbothermal reduction–chlorination–disproportionation of alumina (Experiment B)

The pellets were held in the graphite crucible placed in the vacuum furnace, and heated in the presence of AlCl_3 at a certain temperature for 30 min. The residues and condensates were then analyzed by X-ray diffraction technique using a D/max-3B diffractometer (Japan) with $\text{Cu K}\alpha$ radiation.

The experiments were conducted at 1643, 1693, 1743, 1793 and 1843 K, respectively. The highest pressure in the system reached 200 Pa.

4 Results and discussion

4.1 Phase composition of residues

The residues after heating the pellets in the absence of $\text{AlCl}_3(\text{g})$ (Experiments A) consisted of Al_2O_3 and C as the same as the raw materials, which was in agreement

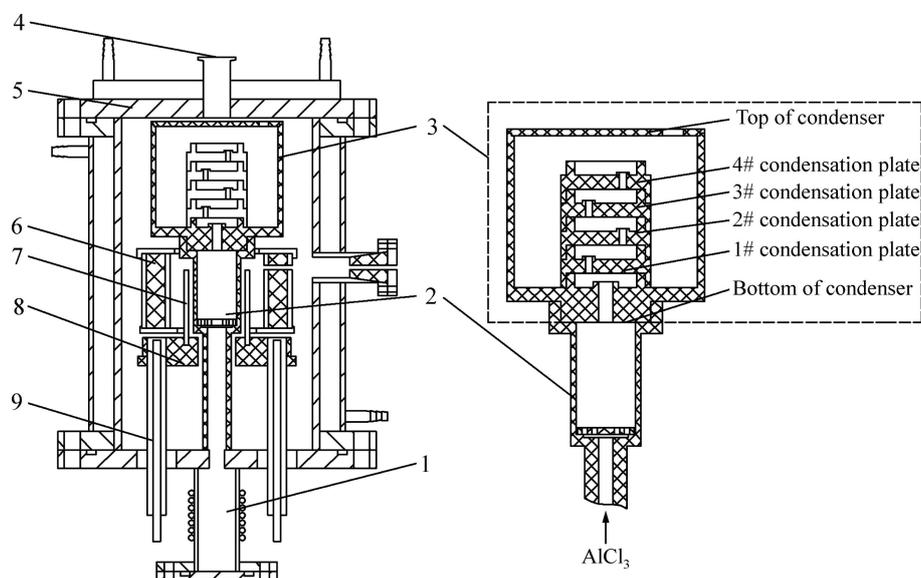


Fig. 5 Schematic diagram of vacuum furnace: 1— AlCl_3 evaporator; 2—Reaction crucible; 3—Graphite condenser; 4—Vacuum pump; 5—Water-cooled cover of furnace; 6—Thermal insulating layer; 7—Graphite exothermic body; 8—Exothermic body base; 9—Water-cooled electrode

with the earlier results that the products of the reactions of alumina and carbon in vacuum were all gases [13, 14].

The residues after heating the pellets in the presence of $\text{AlCl}_3(\text{g})$ (Experiments B) consisted of Al_2O_3 and C as well, which indicated that the reactions occurring were the same as those in the absence of $\text{AlCl}_3(\text{g})$. Therefore, $\text{AlCl}_3(\text{g})$ did not participate in the reaction of alumina and graphite, and AlCl should be formed by the reaction of $\text{AlCl}_3(\text{g})$ and the Al-containing gaseous products generated from the carbothermal reduction of alumina. The main Al-containing gaseous products should be Al_2O because the present conditions were mainly in the range for producing Al_2O according to Fig. 1.

4.2 Phase composition of condensates

Table 1 presents the phase composition of the condensates formed in the experiments.

Table 1 Composition of condensates

Condensation position	Experiments A	Experiments B
Upper part of reaction crucible	$\text{Al}_4\text{O}_4\text{C}$, Al_4C_3 , Al_2O_3 , C	$\text{Al}_4\text{O}_4\text{C}$, Al_4C_3 , Al_2O_3 , C
Bottom of condenser	Al_2O_3 , C	Al_2O_3 , C
1# condensation plate	–	Al, Al_4C_3 , C, Al_2O_3
2# condensation plate	–	Al, Al_4C_3 , C, Al_2O_3
3# condensation plate	–	Al
4# condensation plate	–	Al
Top of condenser	–	Al
Water cooled cover of furnace	–	AlCl_3

The XRD patterns of the condensates on the upper part of the reaction crucible formed by heating the pellets in the absence and the presence of $\text{AlCl}_3(\text{g})$ at 1743 K for 30 min are shown in Fig. 6. As can be seen, the condensates formed in the carbothermal reduction and in the carbothermal reduction–chlorination–disproportionation of alumina were identical in phase composition. The condensates could be the products of the back-reactions of Al_2O and CO formed by carbothermal reduction of alumina [13, 14]. However, the diffraction peak assigned to C in the XRD patterns of the condensate formed in the carbothermal reduction–chlorination–disproportionation was considerably weaker than that in the carbothermal reduction. The result supported the above conclusion that $\text{AlCl}_3(\text{g})$ did not participate in the reaction of alumina and graphite, and AlCl should be formed mainly by the reaction of $\text{AlCl}_3(\text{g})$ and $\text{Al}_2\text{O}(\text{g})$, and the reaction of $\text{Al}_2\text{O}(\text{g})$ and $\text{AlCl}_3(\text{g})$ occurred according to reaction (5) because Al_2O_3 formed by reaction (5) could react with carbon to result in a reduction in the amount of carbon.

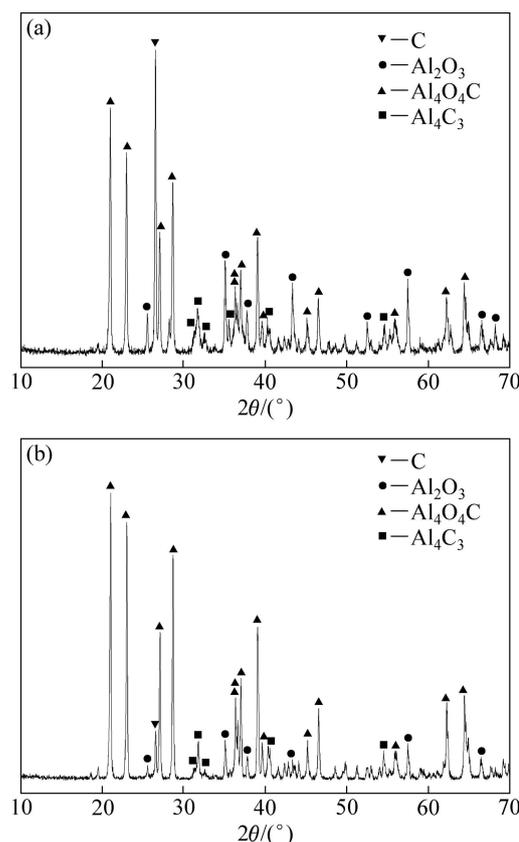


Fig. 6 XRD patterns of condensates on upper part of reaction crucible: (a) Carbothermal reduction; (b) Carbothermal reduction–chlorination–disproportionation

The XRD patterns of the condensates on the bottom of the condenser formed by heating the pellets in the absence and the presence of $\text{AlCl}_3(\text{g})$ at 1743 K for 30 min are shown in Fig. 7. As can be seen, both the condensates consisted of Al_2O_3 and C. The condensates should be formed mainly by the back-reactions of Al_2O and CO [13, 14]. However, the diffraction peaks assigned to Al_2O_3 in the patterns of the condensate formed in the carbothermal reduction–chlorination–disproportionation were considerably more intense than those in the carbothermal reduction, and the diffraction peaks assigned to $\delta\text{-Al}_2\text{O}_3$ were also observed besides those assigned to $\alpha\text{-Al}_2\text{O}_3$. It was further indicated that the chlorination reaction of $\text{Al}_2\text{O}(\text{g})$ occurred according to reaction (5), because reaction (5) could generate Al_2O_3 to result in a growth in the amount of Al_2O_3 , and the condenser bottom temperature was low enough to avoid reaction of Al_2O_3 with carbon.

For the carbothermal reduction, the gaseous products reacted backwards to condensate on the upper part of the reaction crucible and the bottom of the condenser. The gas from crucible into the condenser mainly consisted of CO, and consequently no condensate formed in the condenser. For carbothermal reduction–

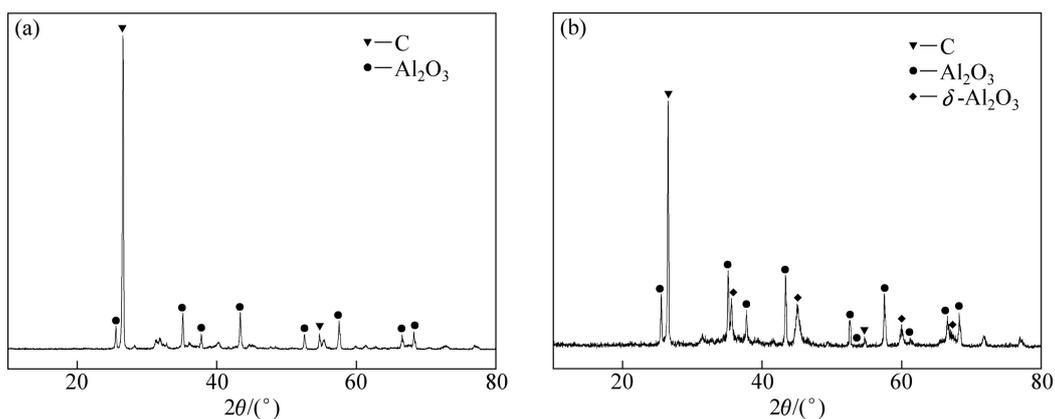


Fig. 7 XRD patterns of condensates on bottom of condenser: (a) Carbothermal reduction; (b) Carbothermal reduction–chlorination–disproportionation

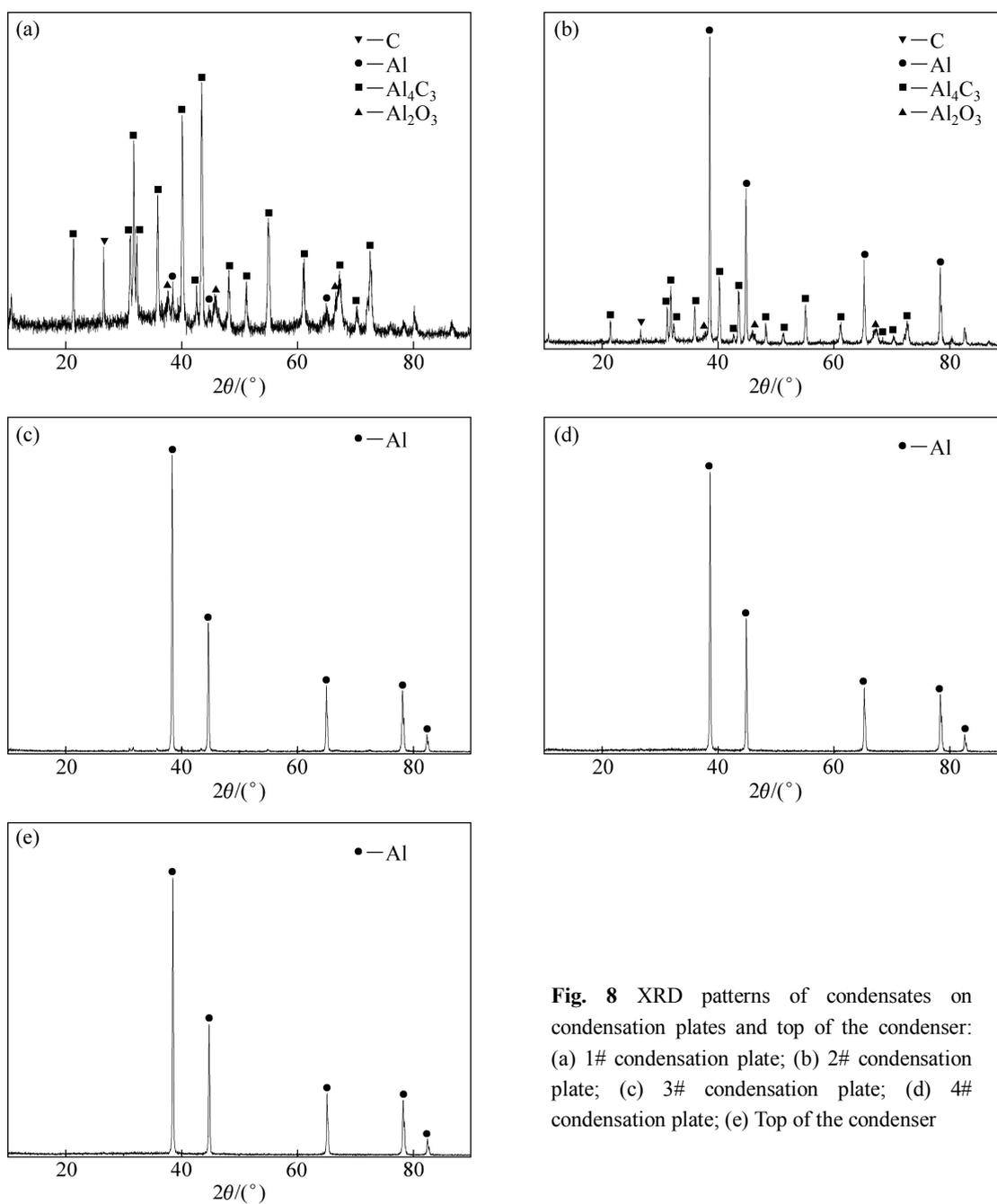


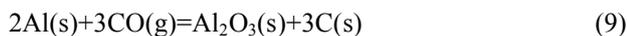
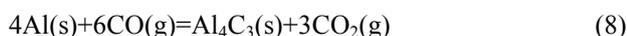
Fig. 8 XRD patterns of condensates on condensation plates and top of the condenser: (a) 1# condensation plate; (b) 2# condensation plate; (c) 3# condensation plate; (d) 4# condensation plate; (e) Top of the condenser

chlorination–disproportionation, besides back-reactions the gaseous products reacted with $\text{AlCl}_3(\text{g})$ to form $\text{AlCl}(\text{g})$, and consequently the gas from crucible into the condenser consisted of CO , AlCl and AlCl_3 unreacted. The gas condensed continuously with decreasing temperature as it went through the condensation plates and the top of the condenser to the cover of the furnace.

The XRD patterns of the condensates on the condensation plates and on the top of the condenser in the presence of $\text{AlCl}_3(\text{g})$ at 1743 K for 30 min are shown in Fig. 8. $\text{AlCl}(\text{g})$ into condenser should disproportionate to form Al and $\text{AlCl}_3(\text{g})$, and thereby the condensates should consist of Al . However, the condensates on 1# and 2# condensation plates contained C , Al_4C_3 and Al_2O_3 besides Al . The C should be formed by the disproportionation of CO according to reaction (7) because Al could absorb CO to catalyze its disproportionation to C and CO_2 .



The Al_4C_3 and Al_2O_3 should be formed by the back-reactions of Al and CO according to reactions (8) and (9).



From Fig. 8, the diffraction peaks assigned to C , Al_4C_3 and Al_2O_3 in the condensates grew weak with decreasing temperature. It was indicated that the extent of the disproportionation of CO and the backward reactions of Al and CO decreased as the temperature decreased.

AlCl_3 condensed on the water-cooled cover of the furnace where the temperature approximated to the room temperature, due to the low sublimation temperature of AlCl_3 in vacuum [19].

5 Conclusions

1) AlCl in the carbothermal reduction–chlorination–disproportionation of alumina in vacuum should be formed by two successive reaction steps. In the first step, alumina reacts with carbon to generate $\text{Al}_2\text{O}(\text{g})$ or $\text{Al}(\text{g})$. In the second step, the $\text{Al}_2\text{O}(\text{g})$ or $\text{Al}(\text{g})$ reacts with $\text{AlCl}_3(\text{g})$ to form $\text{AlCl}(\text{g})$.

2) AlCl disproportionates to aluminum and $\text{AlCl}_3(\text{g})$ at lower temperatures. The aluminum can absorb CO to catalyze its disproportionation to C and CO_2 , and react backward with CO to form Al_4C_3 , Al_2O_3 , C and CO_2 . The extent of the disproportionation of CO and the backward reactions of Al and CO decreases as the $\text{AlCl}(\text{g})$ disproportionation temperature decreases. AlCl_3 condenses at a temperature approximated to the room temperature.

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氧化铝的真空碳热还原-氯化-歧化反应

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摘要: 通过 XRD 物相分析和热力学分析研究氧化铝的真空碳热还原-氯化-歧化反应。以氧化铝和石墨为原料, 在真空下、1643–1843 K 的温度范围内进行实验。结果表明, $\text{AlCl}_3(\text{g})$ 与氧化铝碳热还原产生的 $\text{Al}_2\text{O}(\text{g})$ 或 $\text{Al}(\text{g})$ 反应生成 $\text{AlCl}(\text{g})$, 该 $\text{AlCl}(\text{g})$ 在较低温度下歧化分解为金属铝和 $\text{AlCl}_3(\text{g})$; 当压力为 100 Pa、温度为 980 K 时, $\text{AlCl}(\text{g})$ 的歧化反应率达到 90%。生成的金属铝可以吸附催化 CO 歧化为 C 和 CO_2 , 并可以与 CO 二次反应形成 Al_4C_3 、 Al_2O_3 、C 和 CO_2 , 导致铝产物中含有 C、 Al_4C_3 和 Al_2O_3 。产物铝中所含的这些杂质随着 $\text{AlCl}(\text{g})$ 歧化反应温度的降低而减少。 $\text{AlCl}_3(\text{g})$ 在接近室温的温度下冷凝下来。

关键词: 碳热还原; Al_2O_3 ; AlCl ; 真空; 歧化

(Edited by YUAN Sai-qian)