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Behavior of titanium dioxide in alumina carbothermic reduction-chlorination process in vacuum

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Abstract: Behaviors of TiO_2 in the alumina carbothermic reduction and chlorination process in vacuum at different temperatures were investigated experimentally by means of XRD, SEM and EDS. In the preparation of materials, the molar ratio of Al_2O_3 to C was 1:4, and 10% TiO_2 and excess $AlCl_3$ were added. The results show that TiC is produced by C and TiO_2 after TiO_2 transforms from anatase into rutile gradually. In the temperature range of 1 763−1 783 K, the compounds of Ti and Al are not found in slags and condensate. The purity of aluminum reaches 98.35%, and TiO_2 does not participate in alumina carbothermic reduction process and chlorination process in vacuum.

Key words: titanium dioxide; alumina; carbothermic reduction; chlorination

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1 Introduction

It is known that aluminum is not produced from bauxite directly. The process producing aluminum industrially includes alumina refining and aluminum electrolysis. But the development of electrolysis process is limited by some factors such as expensive raw materials, serious environmental pollution and large electrical energy consumption [1]. In recent years, extracting aluminum from alumina or bauxite by subhalide decompositions process has been studied [2−4]. The mechanism of this process includes carbothermic reduction, chlorination and subhalide decomposition [5]. The recovery rate and the content of aluminum may change obviously when bauxite is used as material [6]. Because of the presence of impurities such as silica, iron oxide and titanium dioxide, the content of alumina in bauxite is different (25%−80%). The content of titanium dioxide is less than 11% roughly [7]. The disproportionations of titanium dioxide in the aluminium extraction with subfluorides in vacuum have been studied [8]. If titanium dioxide less than 10% (mass fraction) was added in raw materials, the recovery rate of aluminum increases with increasing the content of titanium dioxide [6]. On the other hand, it is confirmed that the reactions of TiO_2 and C could occur as [9]: $TiO_2 \rightarrow Ti_nO_{2n-1} (n>4)$, $Ti_nO_{2n-1} \rightarrow Ti_4O_7$, $Ti_4O_7 \rightarrow Ti_3O_5$, $Ti_3O_5 \rightarrow Ti_2O_3$, $Ti_2O_3 \rightarrow TiC_xO_y$ and $TiC_xO_y \rightarrow TiC$. Ti_3AlC_2, $TiAl_3$, Ti_3Al, Ti_2AlC, Ti_3AlC and Ti_3AlC_2 could be successfully obtained by the reaction of TiC, Ti, Al_4C_3 and Al [10−12]. But specific effects of titanium dioxide in alumina carbothermic reduction process at different temperatures in chlorination process have not been studied systematically.

The aim of the present work is to investigate the definite behavior of TiO_2 in alumina carbothermic reduction and chlorination process. The behaviors of TiO_2 at different temperatures were studied by XRD analysis. The surface morphology and composition

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of condensation product were examined by SEM and EDS.

2 Experimental

2.1 Raw material

Analytical grade alumina, graphite, titanium dioxide and anhydrous aluminum chloride were used as raw materials in the experiments.

2.2 Experimental method

Alumina (15 g) and graphite (6 g) as starting materials were mixed on a molar ratio of 1:4 of Al_2O_3 to C with addition of 10% TiO_2. They were then made into pieces of *d* 20 mm × 5 mm under pressure of 2−6 MPa. The pieces and $AlCl_3$ were put in different graphite crucibles (shown in Fig. 1). The heating rate of the system was about 20 K/min. In the alumina carbothermic reduction process, the system needs to be kept at 993, 1 193, 1 393, 1 493, 1 593, 1 713 and 1 763 K for 30 min, respectively. Afterward, $AlCl_3$ sublimated at 373−403 K and was transported to the carbothermic reduction slag for 40−90 min, then chlorination process started. At high temperature, AlCl(g) was produced and moved into upper condensing towers. Meanwhile, AlCl(g) decomposed into $AlCl_3$(g) and Al(l) at low temperature. The schematic diagram of vacuum furnace is shown in Fig. 1.

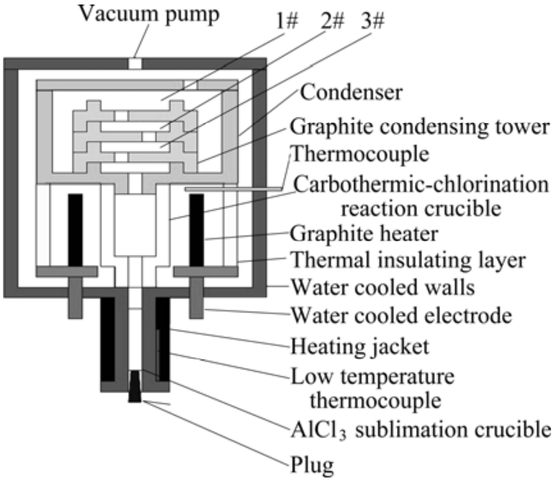


Fig. 1 Schematic diagram of vacuum furnace

To identify the effect of TiO_2 on carbothermic reduction, another powder mixture without TiO_2 powders was prepared and kept at 1 763 K for 30 min in the same way. The molar ratio of Al_2O_3 to C in the mixture remained 1:4.

2.3 Analysis methods

The crystalline phase of the products was identified by X-ray diffraction instrument (Rigaku Corporation, D/max−3B). The structural features and chemical composition were characterized by scanning electron microscopy and EDAX (Philips, Holland), respectively.

3 Results and discussion

3.1 Behavioral analysis of TiO_2 in alumina carbothermic reduction process at different temperatures

The XRD patterns of the slags after alumina carbothermic reduction process at different temperature are shown in Fig. 2. Because the location and intensity of

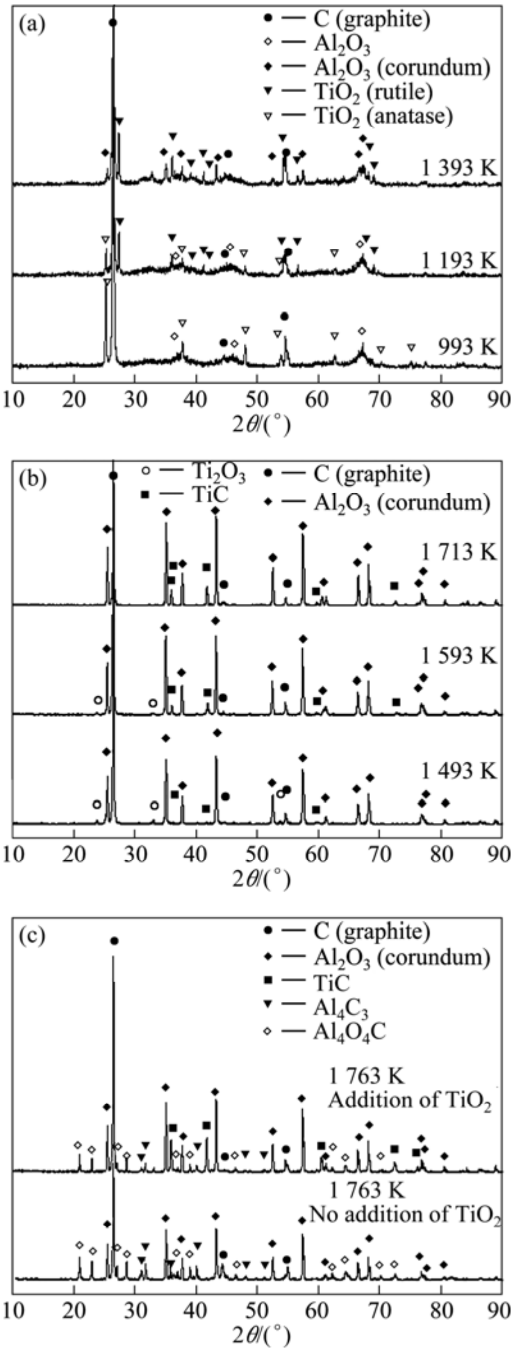


Fig. 2 XRD patterns of slag after carbothermic reduction at different temperatures

diffraction peaks of γ-Al_2O_3, η-Al_2O_3, θ-Al_2O_3, κ-Al_2O_3 and δ-Al_2O_3 are similar, it is difficult to determine the specific crystalline forms of alumina. But there is obvious difference between corundum (α-Al_2O_3) and other alumina [13]. Only Al_2O_3 and α-Al_2O_3 are marked in Fig. 2.

It can be seen from Fig. 2(a) that the slag contains alumina, graphite and anatase at 993 K. Diffraction peaks of rutile already appear at 1 193 K. The experimental result is consistent with that in Ref. [14], which indicates that the phase transformation of TiO_2 occurs at 1 193 K or below. With increasing temperature from 1 193 to 1 393 K, the intensity of diffraction peaks of rutile increases, while that of significantly anatase becomes weaker than that at 993 K and finally disappears.

Besides, it is observed that the diffraction peak of α-Al_2O_3 appears and original alumina is consumed completely at 1 393 K. The experimental result is consistent with that in Ref. [15], which reaches the changing conditions of α-Al_2O_3. It was reported that the crystalline transformations of many materials may be affected by some elements and compounds [16−17]. But in this process, the crystalline transformations of TiO_2 and Al_2O_3 do not involve with each other.

In Fig. 2(b), graphite and α-Al_2O_3 remain unchanged at 1 493−1 713 K. Ti_2O_3 and TiC are generated, while rutile disappears at 1 493 K. The intensity of TiC increases with increasing temperature from 1 493 to 1 713 K. Ti_2O_3 reduces and disappears gradually. Only Ti_2O_3 and TiC are detected while other intermediates fail to be detected, according to Ref. [8], because the reactions of these intermediate products may be too fast, and the interval of temperature range of experimental research is too broad and other factors.

A graph of Gibbs free energy change (ΔG_T) related to temperature (T) under 120 Pa is drawn to clarify these processes (Fig. 3). Because of being short of thermodynamic data on Ti_nO_{2n-1} (n>10) and TiC_xO_y, only $TiO_2 \rightarrow Ti_4O_7$, $Ti_4O_7 \rightarrow Ti_3O_5$, $Ti_3O_5 \rightarrow Ti_2O_3$, $Ti_2O_3 \rightarrow TiC$ are analyzed in these processes:

$$4TiO_2+C=Ti_4O_7+CO(g) \tag{1}$$

$$3Ti_4O_7+C=4Ti_3O_5+CO(g) \tag{2}$$

$$2Ti_3O_5+C=3Ti_2O_3+CO(g) \tag{3}$$

$$Ti_2O_3+5C=2TiC+3CO(g) \tag{4}$$

As shown in Fig. 3, these process reactions begin at 1 250 K or below, but the experiments show that all these begin above 1 393 K. This is because the reaction rate of solid-solid phase reaction is not only relative with temperature, but also with activation energy, distribution of grain, contact area of reactant and etc [18].

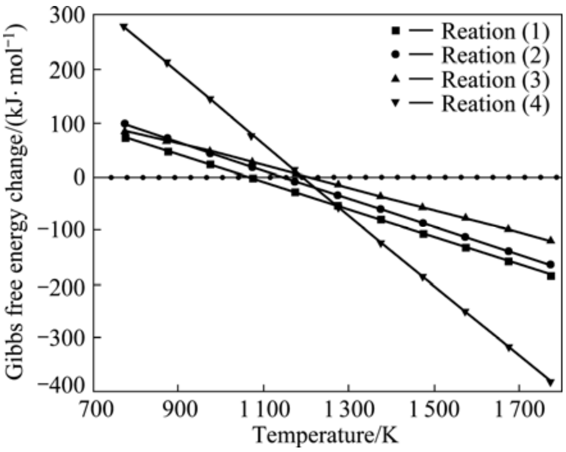


Fig. 3 Relationship between Gibbs free energy change and temperature under 120 Pa

The XRD patterns of the slags kept at 1 763 K for 30 min with and without the addition of TiO_2 are shown in Fig. 2(c). The intermediates (Al_4C_3 and Al_4O_4C) which are very important to the chlorination process [6] are generated by reactions between graphite and alumina at 1 763−1 783 K in vacuum (15−120 Pa). As seen in Fig. 2(c), the intermediates are produced by graphite and alumina whether adding TiO_2 or not. No compounds of Ti and Al are detected (Ti_3AlC_2, Al_3Ti, Ti_2AlC and so on).

Although TiC is produced by the reaction between graphite and TiO_2, this process is completed before alumina carbonthermic reduction. The intermediates (Al_4C_3 and Al_4O_4C) generated in alumina carbothermic reduction process are not apparently different with or without the addition of TiO_2. Compounds of Ti and Al are not detected in alumina carbothermic reduction process. Titanium-containing materials are not involved in this process.

3.2 Behavioral analysis of TiO_2 in chlorination process

Intermediates could be participated in chlorination process at 1 763−1 783 K in vacuum (15−120 Pa) [6]. Figure 4 shows the XRD pattern of the slags obtained after chlorination process during which TiO_2 is added. The materials contained in slags are the same as the materials after carbothermic reduction. The compounds of Ti and Al are also not detected after chlorination process, which implicates that TiC is not involved in chlorination process.

During the chlorination process, AlCl(g) is generated, which would decompose at low temperature, then aluminum is produced [6]. As shown in Fig. 5, aluminum appears in every condensing tower. Element C is detected in the condensate because the condensing

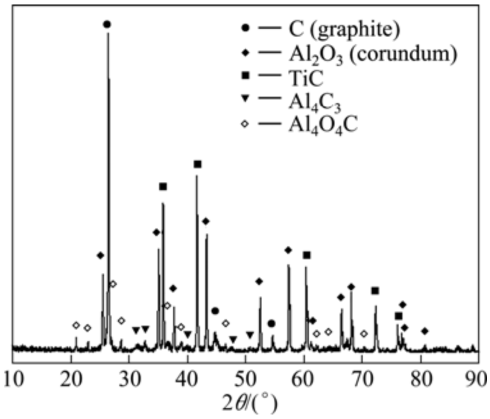


Fig. 4 XRD pattern of slag after carbothermic reduction-chlorination process

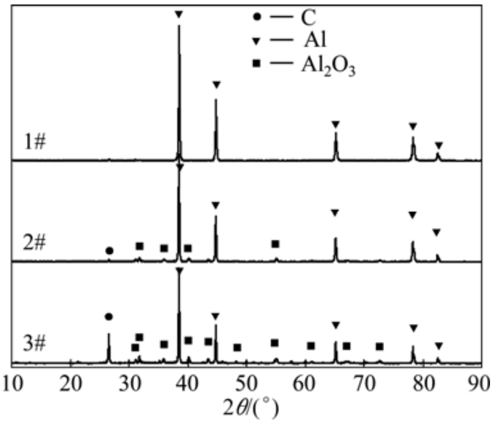


Fig. 5 XRD patterns of condensates from different condensing tower

towers are made from graphite. Al_4C_3 in condensing towers may be produced by the reaction between Al and C as:

$$4Al+3C{=\!=}Al_4C_3 \tag{5}$$

As shown in Fig. 6, the Gibbs free energy change (ΔG_T) of reaction (5) is below zero when the system temperature is below 1 773 K. Below and above the melting point of aluminum (993.4 K), the Gibbs free energy change of reaction (5) is evident. Because the temperature gradient in the condenser is obvious, the condensates in $2^{\#}$ condensing tower contain less Al_4C_3 than those in $3^{\#}$. Aluminum in $1^{\#}$ condensing tower is pure.

Figure 7 shows the SEM image and EDS analysis of condensates obtained from $1^{\#}$ condensing tower. The product aluminum has a filar structure. As shown in the EDS image, it is obvious that the contents of aluminum and oxygen in condensates are 98.35% and 1.65% (mass fraction), respectively. The titanium-containing compound is not detected in the condensate, which indicates that it is not involved in the subhalide decomposition process.

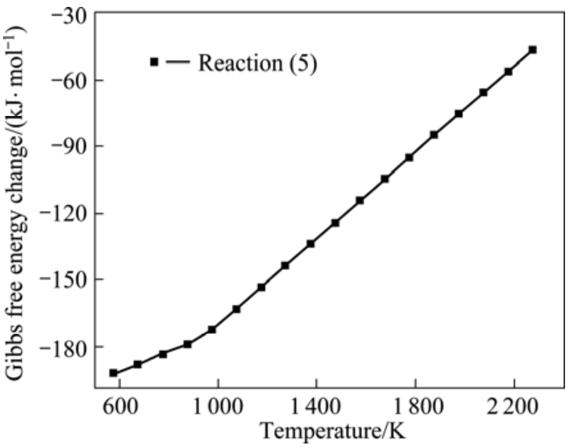
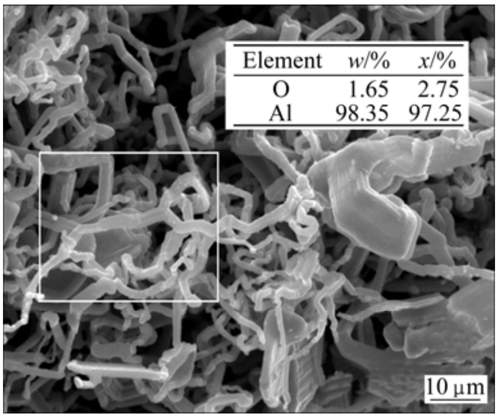


Fig. 6 Relationships between Gibbs free energy change and temperature



Element	w/%	x/%
O	1.65	2.75
Al	98.35	97.25

Fig. 7 SEM image and EDS analysis of condensation product

4 Conclusions

1) In the carbothermic reduction process, after TiO_2 transforms from anatase into rutile gradually, TiC is produced by the reaction between TiO_2 and C. In the range of 1 763−1 783 K, Al_3C_4 and Al_4O_4C are generated by alumina and graphite with TiC. The compounds of Ti and Al in slag are not detected.

2) In chloride reaction process at 1 763−1 783 K, TiC remains unchanged and the intermediates participate in the reaction. Aluminum is generated and its purity is 98.35%. Compounds of Ti and Al in slag or titanium-containing materials in the condensate are not found.

3) The experimental results indicate that TiO_2 is not involved in the alumina carbothermic reduction-chlorination process.

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氧化铝真空碳热还原−氯化工艺中二氧化钛的行为分析

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摘 要：在不同温度下氧化铝真空碳热还原和氯化反应的过程中，利用 XRD、SEM 和 EDS 检测手段分析 TiO_2 的行为。在制备材料时，Al_2O_3 和 C 的摩尔比为 1:4，并添加 10% TiO_2 和过量的 $AlCl_3$。结果表明，TiO_2 从锐钛矿型转化为金红石型后与 C 反应生成 TiC。在 1 763−1 783 K 的温度区间，在残渣和冷凝物中没有发现 Ti 和 Al 的化合物。生成铝的纯度达到 98.35%，且 TiO_2 不参与氧化铝真空碳热还原和氯化过程。

关键词：二氧化钛；氧化铝；碳热还原；氯化反应

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