



Short communication

Decomposition of solid alumina in the presence of carbon in vacuum

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ABSTRACT

The decomposition of solid Al₂O₃ in the presence of C was researched at 1873 K–2073 K in vacuum, using α-Al₂O₃ powders as the raw materials and the graphite crucible as C source. There was no direct contact between the Al₂O₃ and the C. The results showed that the Al₂O₃ decomposed into gaseous species, and the C making up the graphite crucible was reacted to form CO. The coupled reaction was proposed: Al₂O₃ decomposed into gaseous Al-containing species (mainly Al and Al₂O) and O₂, and then C reacted with O₂ to form CO to maintain low O₂ partial pressure, making the decomposition of solid Al₂O₃ in vacuum possible. With a decrease in temperature, the gaseous products Al, Al₂O and CO formed the condensates containing a lot of fibrous materials. The condensates mainly consisted of Al₄O₄C, Al₄C₃, Al₂O₃ and Al, and the content of Al₄O₄C was the highest.

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The carbothermal reduction of Al₂O₃ in the atmosphere requires high temperatures above about 2273 K, at which the unreacted Al₂O₃ raw material and the Al, Al₄C₃ and Al₄O₄C products can form a melt. Decreasing the partial pressures of the gaseous products by operating under vacuum or in a gas flow (such as Ar and N₂) can reduce the required temperature, making the carbothermal reduction of solid Al₂O₃ occur.

The carbothermal reduction of solid Al₂O₃ is involved in the fabrication of some ceramic materials such as Al₄O₄C [1–3], Al₄C₃ [4,5], AlN [6,7] and AlON [8–10]. So far its mechanism remains controversial.

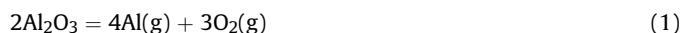
For a long time, it was widely believed that solid Al₂O₃ directly reacts with C to form Al oxycarbides and carbide (Al₂OC, Al₄O₄C and Al₄C₃) [2,11–13].

Nowadays, it has been generally accepted that the carbothermal reduction of solid Al₂O₃ can generate gaseous Al, Al sub-oxides and CO. The gaseous species containing Al and CO should account for the formation of the deposits/condensates with high content of Al₄O₄C and Al₄C₃ [5,11,14–17]. However, the opinions are divided on how the gaseous species containing Al are formed. One viewpoint was that they are formed from the direct solid-solid reaction between Al₂O₃ and C [18–20], while another was that they are

formed from the decomposition of Al₂O₃ [13,21,22].

In our previous experiments on the carbothermal reduction of solid Al₂O₃ in vacuum [15,16], the deposits with high content of Al₄O₄C and Al₄C₃ were formed on the surfaces of the pressed pellets of Al₂O₃ and C, and the reacted pellets still consisted of Al₂O₃ and C. Furthermore, the interfaces between the residual Al₂O₃ particles and C flakes were clear, and there was no indication that the direct solid-solid reaction occurred. Instead, it was speculated that the gaseous Al and Al sub-oxides might be formed from the decomposition of Al₂O₃ and the deposits should be formed from the gaseous species containing Al and CO.

The decompositions of the metal oxides usually generate pure metal and O₂, and it was proposed that Al₂O₃ decomposed into gaseous Al and O₂ [13]. Katsov [23] found that the basic vapor components at Al₂O₃ atomization were Al, Al₂O and AlO, and the relation between these components was determined by the content of O₂. Accordingly, it was reasonable to deduce that solid Al₂O₃ decomposes to form Al and Al sub-oxides, certainly accompanied by the generation of O₂. As the gaseous species containing Al in the Al–O–C system mainly include Al, Al₂O, AlO and Al₂O₂ [24], the possible decompositions of Al₂O₃ are shown as Equations (1)–(4).



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It is well known that Al is very easy to be oxidized, and thus the decomposition of Al_2O_3 requires quite high temperatures and low O_2 partial pressures. The equilibrium O_2 partial pressures at 2000 K for Reactions (1)–(4) is 1.37×10^{-4} Pa, 6.68×10^{-5} Pa, 1.45×10^{-4} Pa and 1.45×10^{-6} Pa, respectively, calculated according to Reference [15]. In the presence of a reducing agent C, the C reacts with O_2 to decrease dramatically the O_2 partial pressure, resulting in that the decomposition temperature of Al_2O_3 decreases significantly, just as Lvov [25] thought in the carbothermal reduction of metal oxides. C acted as a role to reduce O_2 partial pressure. The combination of C with O_2 is shown as Equation (5).

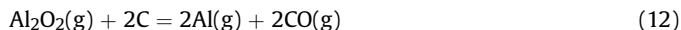


Coupling Equations (1)–(4) with Equation (5), the total reactions to form gaseous species containing Al were obtained, as shown by Equations (6)–(9).



The four reactions can be used to represent the carbothermal reductions of Al_2O_3 to form gaseous species containing Al. They cannot occur at temperatures below 2273 K under the atmospheric pressure. This is to say, even if in the presence of C, Al_2O_3 in the solid state cannot decompose. The Gibbs free energy change (ΔG) of them is a function of temperature and the pressures of the gaseous products, and decreasing the pressures can decrease the required temperatures; therefore, they can occur at lower temperatures in vacuum. The thermodynamic analysis demonstrated that the required temperatures for Reactions (6) and (7) are considerably lower than Reactions (8) and (9) at the same total pressure [15].

It was needed to explore the possibility of Al sub-oxides further reacting with C to be reduced to Al. The possible reactions are shown by Equations (10)–(12).



ΔG at reduced pressures is plotted vs temperature (T) in Fig. 1, calculated according to References [26,27]. On the condition that the partial pressures of CO and Al are both 20 Pa, Reaction (10) can occur thermodynamically at temperatures above 1839 K and 1932 K at the Al_2O partial pressure of 10 Pa and 1 Pa, respectively, and cannot occur at temperatures below 2000 K at 0.1 Pa; the lowest temperature required for Reaction (11) is 692 K, 764 K and 852 K at the AlO partial pressure of 10 Pa, 1 Pa and 0.1 Pa, respectively; that for Reaction (12) is 1400 K, 1442 K and 1487 K at the Al_2O_2 partial pressure of 10 Pa, 1 Pa and 0.1 Pa, respectively. AlO and Al_2O_2 are almost impossible to be formed in Al_2O_3 -C system at temperatures below 1487 K at practical pressures [15], therefore, in Al sub-oxides only Al_2O may be stable at temperatures below 2000 K in vacuum. In consistence with this, Heyrman, et al. [28] found that Al, Al_2O

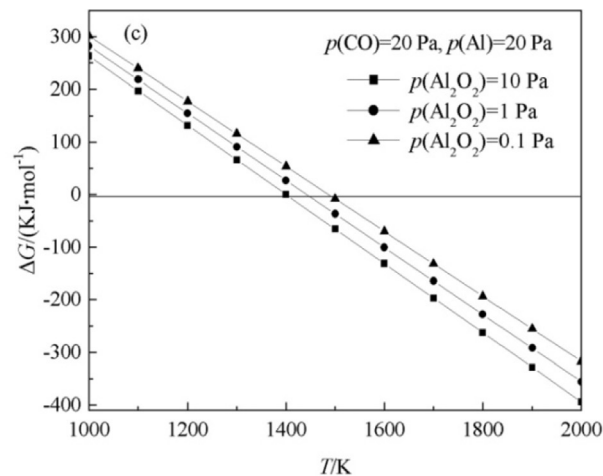
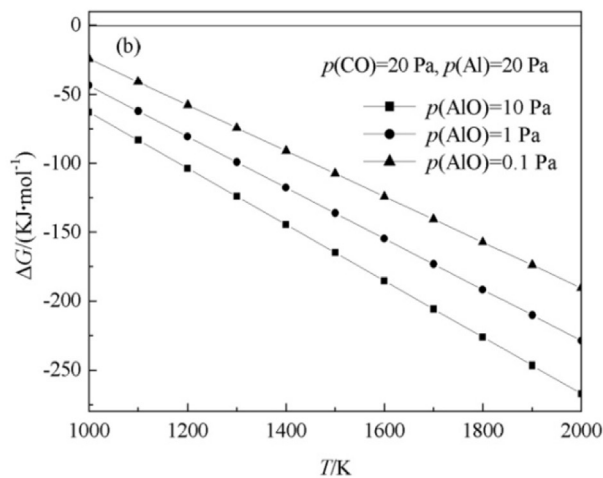
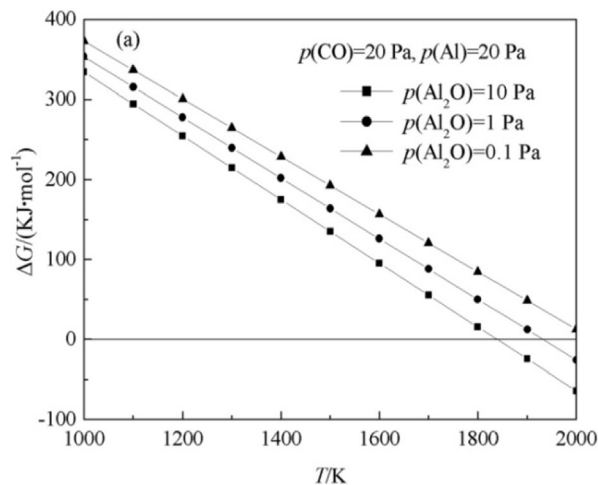


Fig. 1. ΔG vs T : (a) Reaction (10); (b) Reaction (11); (c) Reaction (12).

and CO was only vaporizing species in the Al_2O_3 -graphite system in the temperature range 1200 K–1700 K. Lihrmann [24] proposed

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