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Kinetic study on carbothermic reduction of ilmenite with activated carbon

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Abstract: The carbothermic reduction of Panzhihua ilmenite with various additions of activated carbon was investigated by isothermal experiments over the temperature range of 1373 to 1773 K in the argon atmosphere. According to the reaction kinetics recorded by the infrared gas analyzer, it was found that the amount of carbon addition had little influence on the reaction rates at various temperatures except 1473 K. When the reaction temperature was above the eutectic temperature of 1427 K of Fe−C binary system, part of carbon would dissolve into Fe to form a liquid phase, which made the liquid Fe as a diffusion channel of carbon to diffuse to the reaction interface. The carbothermic reduction above 1573 K obeyed the shrinking-core model. The mass fraction of TiC could be determined by the standard addition technique.

Key words: ilmenite; carbothermic reduction; activated carbon; titanium carbide; solid−liquid interface

1 Introduction

As is known to all, ilmenite is one of the major sources for titanium. In China, more than 90% (mass fraction) of ilmenite is located in Panzhihua, Sichuan Province. The content of titanium dioxide in ilmenite is higher than 40%. Although the ilmenite is expressed as $FeO{\cdot}TiO_2$, it can also accommodate many other components in its structure, for instance, Fe_2O_3, MgO, Al_2O_3, MnO and CaO [1]. With the exhaustion of the high grade titanium ores, such as rutile, more attention has been paid on ilmenite [2−7]. Nowadays, ilmenite is widely used as an alternative raw material for rutile in producing titanium metal and titanium containing compounds, for example, titanium sponge, synthetic rutile, titanium tetrachloride, titanium carbide, titanium nitride and so on. Therefore, the carbothermic reduction of ilmenite has a crucial influence on the commercial productions of synthetic rutile, titanium carbide, titanium nitride or titanium carbonitride.

Carbothermic reduction of ilmenite was investigated by Welham and Williams from the ambient temperature to 1773 K in Ar atmosphere [8]. It is demonstrated that iron and rutile initially appeared during the carbothermic reduction. Then, rutile was reduced to a series of oxides (Ti_nO_{2n-1}, n>3), Ti_3O_5, Ti_2O_3 and TiC in sequence. REZAN et al [9] studied the carbothermic reduction and nitridation of ilmenite in $50\%H_2$−$50\%N_2$ (volume fraction) atmosphere and N_2 atmosphere, respectively. It is found that Ti_2O_3 did not appear as an intermediate reaction product if the nitrogen was present. In addition, the reduction rate in $50\%H_2$−$50\%N_2$ atmosphere was significantly faster than that in pure nitrogen. GUPTA et al [10,11] studied the kinetics of ilmenite with graphite from 1273 to 1373 K in Ar atmosphere. The reduction reaction rate of ilmenite was increased significantly by the addition of $FeCl_3{\cdot}6H_2O$. It is thought that the addition of $FeCl_3{\cdot}6H_2O$ promoted the nucleation of iron. WELHAM and WILLIS [12] and EL-HUSSINY and SHALABI [13] studied the carbothermic reduction of ilmenite in N_2 atmosphere from 973 to 1673 K and 1073 to 1423 K, respectively. The diffusion of the solid-state carbon was regarded as the rate determining step for both carbide formation from oxide and nitridation of carbide. However, part of carbon would dissolve into Fe to form a

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liquid phase when the experimental temperature was above the eutectic temperature of Fe−C binary system 1427 K. This led to a solid−liquid reaction in the reduction process, which was ignored by many researchers. The reduction kinetic and mechanism of solid−liquid reaction during the carbothermic reduction is still not sufficient.

In the present work, the carbothermic reduction of Panzhihua ilmenite was investigated under isothermal conditions to illustrate the reaction kinetics and reaction mechanism. The solid−liquid reaction interface was proposed for the first time in the carbothermic reduction of ilmenite, which played an important role in the dynamic diffusion.

2 Experimental

2.1 Carbothermic reduction of ilmenite with activated carbon

The ilmenite was supplied by Panzhihua Iron and Steel (Group) Co., Ltd, China. It was analyzed by the National Analysis Center for Iron and Steel (NACIS), as listed in Table 1. The activated carbon (analytical reagent, >97%) was supplied by Sinopharm Chemical Reagent Beijing Co., Ltd, China. Both ilmenite and activated carbon were characterized using X-ray diffraction (XRD, Rigaku Ultima IV) with Cu K_α radiation (λ=1.5406 Å). The accelerating voltage and the applied current were 40 kV and 40 mA, respectively. XRD patterns of ilmenite and activated carbon are shown in Fig. 1. The ilmenite and the activated carbon were mixed evenly with the addition of polyvinyl alcohol solution (PVA, 2%, mass fraction) in an agate mortar. Then, the mixtures were made into cylindrical briquettes (diameter 18 mm, thickness 4 mm) using a stainless steel mold under a pressure of 230 MPa. All cylindrical briquettes were roasted in an electric resistance furnace (BLMT−1973 K) at 673 K for 2 h under a flowing Ar atmosphere (300 mL/min) to get rid of the PVA. The mass of each cylindrical briquette was 2 g. As shown in Table 2, the mass ratios of activated carbon to ilmenite were set to be 0.276, 0.316 and 0.395, respectively. The reaction temperatures were 1373, 1473, 1573, 1673 and 1773 K, respectively.

Table 1 Chemical compositions of ilmenite (mass fraction, %)

FeO	Fe_2O_3	TiO_2	MgO	SiO_2
36.85	5.59	45.34	5.76	3.46
Al_2O_3	CaO	MnO	Total	
1.35	0.96	0.69	100	

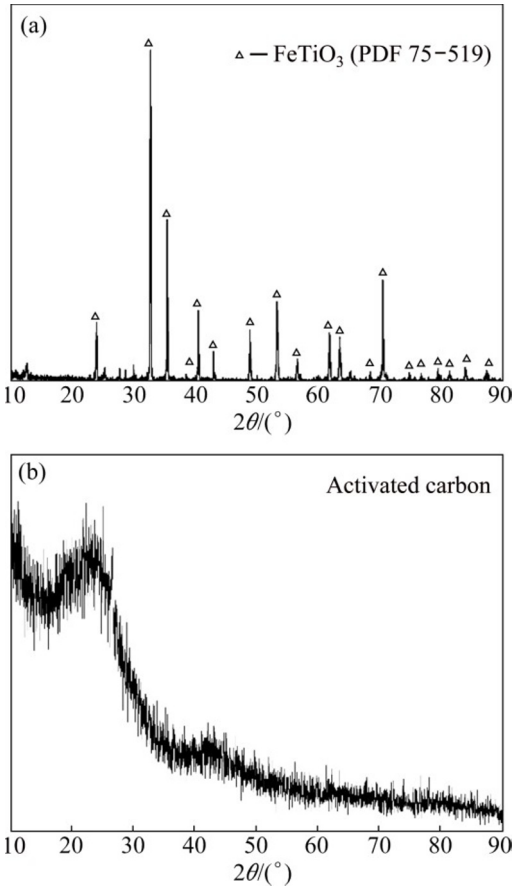

Fig. 1 XRD patterns of ilmenite (a) and activated carbon (b)

Table 2 Experimental conditions of carbothermic reduction

Group	Mass ratio of activated carbon to ilmenite	Reaction temperature/K
A1	0.276	1373
A2	0.276	1473
A3	0.276	1573
A4	0.276	1673
A5	0.276	1773
B1	0.316	1373
B2	0.316	1473K
B3	0.316	1573
B4	0.316	1673
B5	0.316	1773
C1	0.395	1373
C2	0.395	1473
C3	0.395	1573
C4	0.395	1673
C5	0.395	1773

A schematic diagram of the experimental apparatus is shown in Fig. 2. It consists of a mass flowmeter (Alicat 21-1-10-0-500-Km0410), an electric resistance furnace and an infrared gas analyzer (XLZ−1090). CO_2, CO and O_2 can be analyzed by the infrared gas analyzer over ranges of 0−30 % (±0.1%), 0−40% (±0.1%) and