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Catalytic effect of alkali chlorides on carbothermic reduction of pre-oxidized ilmenite①

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[Abstract] A computer-monitoring thermogravimetric system was used to study the effect of alkali chlorides(MCl, M = Li, Na, K and Cs) on the carbothermic reduction of pre-oxidized ilmenite in the course of a linear rise in temperature from 600 ℃ to 1 000 ℃. The experimental results indicate that all the alkali chlorides can speed up the reduction process of pre-oxidized ilmenite, moreover, KCl is the most effective catalyst of the chlorides, while the catalytic effects of LiCl and CsCl are relatively weaker. It seems that the catalytic mechanism of LiCl is different from those of the other alkali chlorides. The cross-sectional morphology of the partially reduced pre-oxidized ilmenite particles and the distribution of potassium ions within them were examined by means of scanning electronic microscopy and electronic probe microanalysis, respectively, which shows that the reduction proceeds topochemically and the alkali ion enriches at the periphery of the particles.

[Key words] thermogravimetry; non-isothermally carbothermic reduction; alkali additives; pre-oxidized ilmenite
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1 INTRODUCTION

Natural ilmenite is an abundant resource for both iron and titanium. Many processes have been developed for upgrading ilmenite to synthetic rutile, and a number of available literatures have reported the studies on reduction of natural ilmenite and titaniferous ores with H_2, CO or solid carbonic materials. Previous investigations indicated that carbonic material was a more effective reducing agent, and carbothermic reduction was one of the most convenient ways to treat this ore when alkali additives were applied as catalysts[1].

This study mainly investigates the effect of alkali chlorides on the kinetics of the reduction of pre-oxidized ilmenite with pure graphite as reducing agent. The experiments were performed in a non-isothermal mode, which permits to clarify the catalytic mechanism and the kinetic behavior of the solid-solid reaction. A computer-monitoring thermogravimetric system and a programmable temperature controller were used to study the carbothermic reduction of pre-oxidized ilmenite. With such an experimental system, both the reduction extent and the corresponding reaction temperature could be precisely monitored and automatically recorded.

2 EXPERIMENTAL

2.1 Experimental apparatus and operation procedures

Fig.1 is a schematic diagram of the experimental apparatus, which consists of three parts: 1) a gas-flow controlling and purification system; 2) a vertical electrical furnace, inside which the temperature is monitored with a programmable temperature controller and recorded with an X-Y functional recorder; 3) an electronic balance converting the mass change of the sample into electronic signals which are read and processed by a computer. The sampling time interval was short enough to reveal the details of the carbothermic reduction.

Pre-treated ilmenite, graphite and alkali chlorides were weighed separately and then fully mixed, with graphite being more than the stoichiometric requirement. For each of the four kinds chlorides (see below), 2%, 5% or 10% (without specific notation, hereafter the percent mark stands for mass percent) of the total sample mass of alkali chloride was added in each run. During reduction process, nitrogen gas was kept to flow through the quartz tube to prevent the oxidation of the reduced sample and graphite. The temperature inside the electrical furnace was adjusted and displayed by the programmable temperature controller during reduction process. While temperature rose linearly, the reduction extent of the sample was monitored by a computer and when temperature reached 1 000 ℃, the temperature controller automatically stopped power supply, and the experiment was consequently completed.

The morphology of the partially reacted particles and the distribution of metallic ions were examined by

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Fig.1 Schematic diagram of experimental apparatus

both scanning electric microscopy and electronic probe microanalysis, respectively, and the results are shown below.

2.2 Materials and their properties

It is well known that pre-oxidation of the ilmenite is favorable for the following reduction operation[2~5]. During pre-oxidation, the ilmenite ($FeTiO_3$) is converted to pseudobrookite (Fe_2TiO_5) and rutile (TiO_2) at temperature above 800 ℃ according to the following reaction[6]:

$$2FeTiO_3(s) + \frac{1}{2}O_2(g) = Fe_2TiO_5(s) + TiO_2(s) \qquad (1)$$

In order to promote the reduction rate, all the ilmenite used in the experiments was pre-oxidized at 1 000 ℃ with pure oxygen for more than 5 h. The reduction experiments were conducted with pre-oxidized natural ilmenite particles and high purity graphite (99.99 %) powder. Chemical composition of the ilmenite is listed in Table 1. As confirmed by X-ray diffraction analysis, the pre-oxidized natural ilmenite consists mainly of Fe_2TiO_5, $MgTiO_3$ and TiO_2 etc[7~9].

Table 1 Chemical composition of ilmenite ore (%)

TiO_2	Fe_2O_3	MgO	CaO	MnO
46.28	42.84	4.48	1.14	0.59
Al_2O_3	SiO_2	V_2O_5	P_2O_5	SO_2
1.04	2.80	0.09	0.06	0.35

As alkali additives can catalyze the carbothermic reduction of metallic oxides[10,11]. Anhydrous reagent-grade sodium chloride, potassium chloride, lithium chloride and cesium chloride were used as catalysts. The salts used as catalysts had a minimum purity of 99.8 %.

Ultra-high purity grade nitrogen (99.99 %) was used to maintain an inert atmosphere in the reaction chamber. Before being fed into the reaction system, the nitrogen gas was further dehydrated with silica gel.

2.3 Experimental conditions

The main experimental conditions are:

Heating-up speed	0.24 $K \cdot s^{-1}$
Temperature range	100 ~ 1 000 ℃
N_2 flow rate	1.66×10^{-5} $m^3 \cdot s^{-1}$
Size of pre-oxidized ilmenite powders	0.125 ~ 0.154 mm
Size of graphite powders	< 0.02 mm
Amount of pre-oxidized ilmenite	10.00 g
Amount of graphite	2.25 g

3 RESULTS AND DISCUSSION

3.1 Effects of amount of alkali additives on reduction rate

The overall reduction reaction can be mainly expressed as Eqn.(2). The reduction conversion is defined based on the following assumption: that all of the iron components in the sample are converted into metallic iron, and the further reduction of TiO_2 is neglected.

$$\frac{2m+n}{3}Fe_2TiO_5(s) + (m+n)C(s) = \frac{2}{3}(2m+n)Fe(s) + \frac{2m+n}{3}TiO_2(s) + mCO_2(g) + nCO(g) \qquad (2)$$

The effect of potassium chloride on the mass loss of the sample is shown in Fig.2, which indicates that the addition of KCl can notably promote the reduction process. Moreover, as the amount of KCl increases, the catalytic effect becomes more obvious.

The effects of NaCl, LiCl and CsCl on the

Fig.2 Mass loss of ilmenite samples during non-isothermally carbothermic reduction with different amounts of KCl reduction rate were shown in Figs.3 ~ 5 respectively, which imply that their kinetic behaviors are similar to which observed for potassium chloride (The amount of the additives are also the same) .

3.2 Effect of alkali chlorides

In order to compare the effectiveness of different kind of chloride, the experimental results with the same amount of alkali additive are presented in Fig. 6, which shows that under the experimental conditions, it is obvious that potassium chloride had the most pronounced effect on the reduction rate.

Fig.3 Mass loss of ilmenite samples during non-isothermally carbothermic reduction with different amounts of NaCl

Fig.4 Mass loss of ilmenite samples during non-isothermally carbothermic reduction with different amounts of LiCl

Fig.5 Mass loss of ilmenite samples during non-isothermally carbothermic reduction with different amounts of CsCl

Fig.6 Mass loss of ilmenite samples during non-isothermally carbothermic reduction with different types of alkali chlorides(5 %)

In terms of reduction extent at the same temperature and within the same time interval, the alkali chlorides can be ranked as the following order with regard to their catalytic effect on the carbothermic reduction becoming weaker

KCl > NaCl > LiCl > CsCl

Furthermore, according to the initial reaction temperature, the catalytic effects of these alkali additives can also be ranked as the order mentioned from Fig.2 to Fig.5 .

3.3 Behavior of alkali ion

Fig.7 shows the morphology and ion distribution maps of particles, which were reduced nonisothermally to almost 40 %. From Fig.7 we can see that the reduction of pre-oxidized ilmenite proceeds almost topochemically, and parts of the potassium ion enters the unreacted particles and the rest enriches at the periphery of the partially reacted particles. This phenomenon implies that the potassium ion might also take part in the carbothermic reduction of the pre-oxidized ilmenite.

4 CONCLUSIONS

1) The addition of alkali chloride can significantly accelerate the reduction of pre-oxidized ilmenite, and increase the amount of alkali chloride results in a larger mass loss of the sample under the experimental conditions.

2) The catalytic effect of the alkali additives can be ranked as the following order: KCl > NaCl > LiCl > CsCl.

3) The carbothermic reduction of pre-oxidized ilmenite proceeds topochemically, and potassium ion enriches at the periphery of the particle.

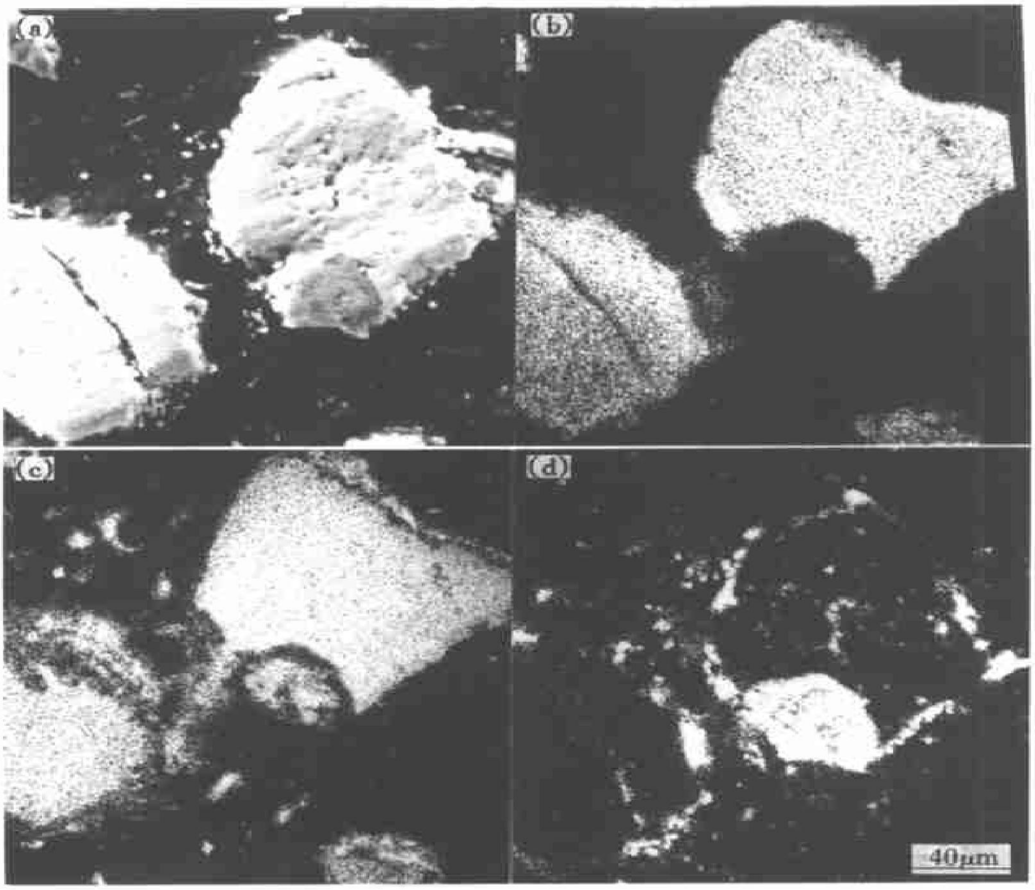

Fig.7 Morphologies and distributions of Ti, Fe, K ions within partially reduced pre-oxidized ilmenite particles
(a) —Morphology of pre-oxidized ilmenite particles; (b) —Distribution of titanium ion; (c) —Distribution of iron ion; (d) —Distribution of potassium ion

[REFERENCES]

[1] Mohanty B P and Smith K A. Alkali metal catalysis of carbothermic reduction of ilmenite [J]. Trans Inst Min Metal, 1993, 102: 163 - 172.

[2] Poggi D, Charette G G and Rigaud M. Reduction of ilmenite and ilmenite ores [J]. Titanium Sci Tech, 1972, 1: 247 - 259.

[3] Jones D. Optical microscopy and electron probe microanalysis study of ilmenite reduction [J]. Trans Inst Min Metal (Sec C: Mineral Process Extr Metall), 1974, 83 (1): 1 - 9.

[4] Patterson M C L and Cameron J. Limitation in gaseous reduction, oxidation and upgrading of Allarol lake ilmenite [J]. Trans Inst Min Metal (Sec C: Mineral Process Extr Metal), 1985, 94: 215 - 223.

[5] Fetisov V B, Leonfyev L I, et al. The reduction of oxidized ilmenite concentrates [J]. Russ Met, 1968, 2: 35 - 57.

[6] Ostberg G. Solid state reduction of ilmenite [J]. Jernkont Ann, 1960, 144 (1): 46 - 76.

[7] Taylor H S and Neville H A. Catalysis in the interaction of carbon with steam and with carbon dioxide [J]. J Am Chem Soc, 1921, 43: 2055 - 2071.

[8] Barnes C and Pickles C A. A thermogravimetric study of the catalytic effect of alkali carbonates on the reduction of ilmenite [J]. High Temp Tech, 1988, 6 (4): 195 - 201.

[9] Karkhanavala M D and Momin A C. The alteration of ilmenite [J]. Econ Geol, 1959, 54: 1095 - 1102.

[10] Rao Y K and Han H G. Catalysis by alkali carbonates of carbothermic reduction of magnetite concentrates [J]. Ironmaking and Steelmaking, 1984, 11 (6): 308 - 318.

[11] Rao Y K. Catalysis in extractive metallurgy [J]. J Metals, 1983, 35(7): 46 - 48.

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