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Carbothermic Reduction Mechanism of Vanadium-titanium Magnetite

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Abstract: To achieve the high-efficiency utilization of vanadium-titanium magnetite (VTM), reduction experiments were conducted to determine the carbothermic reduction mechanism of VTM. Effects of volatile matter, temperature, time, and carbon ratio (molar ratio of fixed carbon in coal to oxygen in iron oxides of VTM) on reduction degree were investigated. Results show that reduction degree increases with increasing volatile matter in coal, temperature, time, and carbon ratio. Phase transformation, microstructure, and reduction path were analyzed by X-ray diffraction, scanning electron microscopy, energy-dispersive X-ray spectroscopy, and FactSage 6.0. The thermoravimetry-differential scanning calorimetry-quadrupole mass spectrometer method was used for kinetic analysis of the main reduction process. Results indicate that the kinetic mechanism follows the principle of random nucleation and growth ($n=4$), and the activation energy values at 600-900 and 900-1350 ℃ are 88.7 and 295.5 kJ/mol, respectively.

Key words: vanadium-titanium magnetite; carbothermic reduction; mechanism; phase transformation; kinetics

Vanadium-titanium magnetite (VTM) is an important and abundant mineral in China. Its reserves reach up to 10 billion tons in the Panxi region of Sichuan Province, China. With the continual depletion of high-grade iron ores and titanium-containing ores, the development and utilization of VTM is highly significant[1-4].

Over the past several decades, many studies on the reduction of ilmenite and VTM have been conducted. Scholars[5-7] have investigated the reduction mechanism and kinetics of ilmenite with carbon at low temperatures. In Wouterlood's experiments[5], results show that ilmenite is reduced at 900-1 200 ℃, and the reduction consists of a fast first stage (Fe^{3+} to Fe^{2+}) and a slower second stage (Fe^{2+} to Fe). In El-Guindy and Davebport's experiments[6], reaction is observed to start at around 950 ℃, and gas diffusion is the rate-controlling step at 1075-1140 ℃. Meanwhile, many research groups[8-15] investigated the reduction mechanism and kinetics of ilmenite and VTM with a gaseous reducing agent (CO, H_2). Results show that ilmenite and VTM are reduced to metallic iron and titanium sub-oxides, and that titanium exerts a strong influence on the mechanism and reduction rate of iron. However, information on the reduction of VTM with coal is insufficient[16-18]. In particular, the reduction mechanism and reaction kinetics at high temperatures have not been studied thoroughly. Considering that the coal-based direct reduction is an important method of utilizing VTM, the reduction mechanism as well as kinetics of VTM and coal at higher temperature are necessary to clarify for further application.

In the current study, the effects of volatile matters, temperature, time, and carbon ratio (molar ratio of fixed carbon in coal to oxygen in iron oxides of VTM) on the reduction degree of VTM and coal at 1250-1350 ℃ were presented. The reduction mechanism including phase transformation, morphology, and reduction path was also discussed. Reaction thermodynamics and kinetics during reduction were analyzed as well.

1 Experimental

1.1 Raw materials

The chemical compositions of VTM and reduction coal are presented in Table 1. The particle sizes of VTM and reduction coal are sieved to a size less than 0.074 mm. High-purity argon gas (99.99 vol. %) was

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Table 1 Chemical compositions of VTM and industrial analysis of coal mass%

VTM								Coal				
TFe	FeO	V_2O_5	TiO_2	CaO	SiO_2	MgO	Al_2O_3	A_{ad}	V_{daf}	M_{ad}	S_{td}	FC
53.91	31.13	0.52	13.03	0.68	3.20	2.71	3.82	14.00	33.70	1.36	0.02	50.94

Note: FC—Fixed carbon; M_{ad}—Moisture.

used as a protective atmosphere. Pulverized coal was used as a reductant in experiments. As shown in Table 1, it is high in volatiles (V_{daf}) but low in ash (A_{ad}) and total sulfur (S_{td}).

The X-ray diffraction (XRD) pattern of VTM is shown in Fig. 1. The main mineral compositions are magnetite ($(Fe,Mg)Fe_2O_4$), titanomagnetite ($Fe_xTi_{3-x}O_4$), ilmenite ($FeTiO_3$) and vanadium spinel (FeV_2O_4).

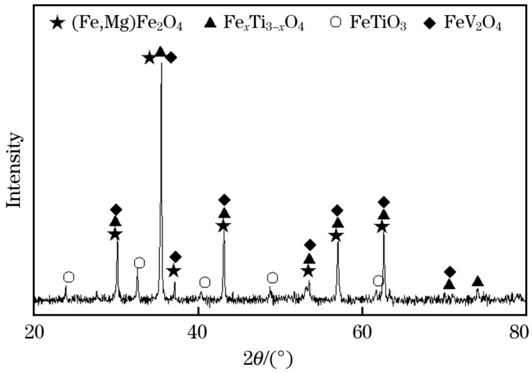

Fig. 1 XRD pattern of the VTM

1.2 Experimental procedure

The experiments include non-isothermal and isothermal reduction. The sample is produced from VTM concentrate and reduction coal, and the carbon ratio is 1.0. The schematic of the experimental apparatus is shown in Fig. 2.

The equipment consists of a vertical tube furnace, a computer monitoring system, and a thermocouple. After heating the furnace to a required temperature in argon atmosphere, a sample of VTM and coal mixture was placed in the reactor, which was then moved to the hot zone of the furnace. When the experiments were finished, the sample was withdrawn from the furnace and cooled; mass loss was measured, and reduction degree was calculated as a mass fraction of oxygen removed from metallic oxides. Phase transformation during reduction was analyzed using XRD, and the morphology of reduction sample was observed by scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS). Reduction kinetics was determined by mass-loss measurements.

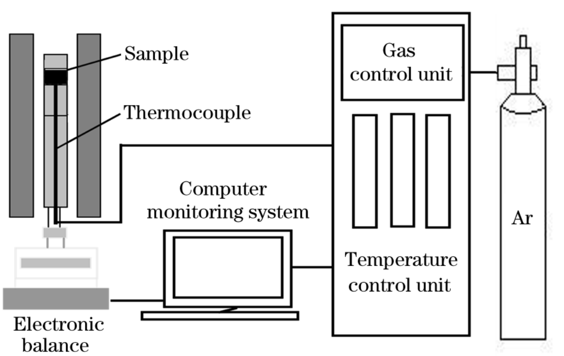

Fig. 2 Schematic diagram of experimental apparatus

1.3 Reactions between VTM and reduction coal

The major reactions between VTM and reduction coal are volatilization, carbon-solution loss, carbon-stream reactions, metal-oxide reduction, and carburization. The chemical formulas representing these possible main reactions are as follows.

$$Coal \rightarrow (CO, CO_2, H_2, H_2O, C_aH_b) \quad (1)$$

$$C + CO_2(H_2O) \rightarrow CO + CO(H_2) \quad (2)$$

$$Fe_3O_4 + 4CO(H_2) \rightarrow 3Fe + 4CO_2(H_2O) \quad (3)$$

$$Fe + 2CO \rightarrow (Fe-C) + CO_2 \quad (4)$$

$$(V_2O_3)_a \cdot (TiO_2)_b \cdot (FeO)_c + cCO(H_2) \rightarrow aV_2O_3 + bTiO_2 + cFe + cCO_2(H_2O) \quad (5)$$

$$(V,Ti)_nO_{2n-1} + (2n-1)CO \rightarrow n(V,Ti) + (2n-1)CO_2 \quad (6)$$

1.4 Reduction degree definition

The mass loss of sample during reduction is mainly attributed to the mass loss of oxygen, fixed carbon, and volatiles. The gas resultants mainly consist of CO in theory, and the reduction degree R of VTM with coal is calculated by Eq. (7).

$$R = \frac{O_{remove}}{O_{total}} = \frac{W_{V\text{-}O} + \frac{M_O}{M_{CO}} W_{CO}}{O_{total}} = \frac{W_{V\text{-}O} + \frac{M_O}{M_{CO}}(W_0 - W_t - W_V - W_{V\text{-}O})}{O_{total}} = \frac{4}{7} \cdot \frac{W_0 - W_t - W_V + \frac{3}{4} W_{V\text{-}O}}{O_{total}} \quad (7)$$

where, O_{total} is the total mass of removable oxygen in metallic (Fe, V, and Ti) oxides; O_{remove} is the mass of removed oxygen; $W_{V\text{-}O}$ is the mass of oxygen re-