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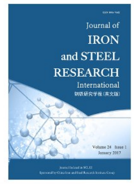

Reduction behavior and mechanism of Hongge vanadium titanomagnetite pellets by gas mixture of H_2 and CO

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ABSTRACT

Hongge vanadium titanomagnetite (HVTM) pellets were reduced by H_2-CO gas mixture for simulating the reduction processes of Midrex and HYL-III shaft furnaces. The influences of reduction temperature, ratio of $\varphi(H_2)$ to $\varphi(CO)$, and pellet size on the reduction of HVTM pellets were evaluated in detail and the reduction reaction kinetics was investigated. The results show that both the reduction degree and reduction rate can be improved with increasing the reduction temperature and the H_2 content as well as decreasing the pellet size. The rational reduction parameters are reduction temperature of 1050 ℃, ratio of $\varphi(H_2)$ to $\varphi(CO)$ of 2.5, and pellet diameter in the range of 8－11 mm. Under these conditions (pellet diameter of 11 mm), final reduction degree of 95.51% is achieved. The X-ray diffraction (XRD) pattern shows that the main phases of final reduced pellets under these conditions (pellet diameter of 11 mm) are reduced iron and rutile. The peak intensity of reduced iron increases obviously with the increase in the reduction temperature. Besides, relatively high reduction temperature promotes the migration and coarsening of metallic iron particles and improves the distribution of vanadium and chromium in the reduced iron, which is conducive to subsequent melting separation. At the early stage, the reduction process is controlled by interfacial chemical reaction and the apparent activation energy is 60.78 kJ/mol. The reduction process is controlled by both interfacial chemical reaction and internal diffusion at the final stage, and the apparent activation energy is 30.54 kJ/mol.

1. Introduction

The Hongge mining area in Panxi region of southwest China is endowed with 3.55 billion tons of vanadium titanomagnetite resources with high content of chrome[1,2], and it is also recognized as the largest chromium-bearing deposit, which amounts to 9 million tons, accounting for 68% of the chromium reserve in China[3]. Since the chemical composition and phase structure of Hongge vanadium titanomagnetite (HVTM) are much more complicated than those of other vanadium titanomagnetites, it is more difficult to achieve high-efficiency utilization[3], and therefore, HVTM has not been put into practical industrial production. With the continuous consumption of high-grade iron ore resources, large-scale development and utilization of HVTM is becoming highly significant[4].

At present, most vanadium titanomagnetite is smelted in blast furnaces at Panzhihua Iron and Steel Corporation, China[5]. In the blast furnace process, concentrates are sintered or pelletized and smelted to produce hot metal and slag, and the slag is more difficult to be utilized efficiently in traditional separation processes[6,7]. The hot metal obtained from blast furnaces is oxidized to produce vanadium slag, where chromium also exists in the form of spinel. It is more difficult to obtain vanadium and chromium efficiently by sodium salt roasting-water leaching process because of stable spinel structure, which also causes serious environment degradation in soil and water[8-10].

In order to utilize the HVTM efficiently, a new process is proposed for comprehensive utilization of HVTM. In this process, HVTM was firstly pelletized, reduced in shaft furnace, and then melting separated to produce metal phase and molten slag. The metal phase was used as raw materials for steel making or

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casting and slag needed further treatment for recovering titanium, vanadium, and chromium. The focus of the present study is on the simulation of the direction reduction process of the HVTM pellets in shaft furnace. The factors that affect the reduction degree and rate, phase composition and morphology change were investigated. Furthermore, the reaction kinetics was discussed. The results can provide a theoretical basis and technical support for the comprehensive utilization of HVTM, and increase the recovery rates of vanadium, titanium, and chromium.

2. Experimental

2.1. *Experimental materials*

In this experiment, the green pellets were prepared and dried for 5 h at 105 ℃ in a drying cabinet. The dried pellets were preheated at 900 ℃, roasted at 1200 ℃ for 15 min in a muffle furnace with an air stream blown in, and then cooled to ambient temperature. The chemical composition of pellets, whose compressive strength was about 2893 N on average, is shown in Table 1.

The mineralogical components of the product pellets were investigated by X-ray diffraction (XRD) analysis (Fig. 1). As shown in Fig. 1, the dominant iron phase is Fe_2O_3 and the majorities of titanium and chromium mainly exist in the form of solid solution Fe_9TiO_{15}, $(Fe_{0.6}Cr_{0.4})_2O_4$, and $Fe_{0.7}Cr_{1.3}O_3$. Besides, chromium is also combined with vanadium in a solid solution $(Cr_{0.15}V_{0.85})_2O_3$. The scanning electron microscopy (SEM) and energy-dispersive spectrometry (EDS) results are shown in Fig. 2. The gases (H_2, CO, CO_2, and N_2) used in the investigation are of 99.99% purity.

Table 1
Chemical composition of HVTM pellets (mass%)

TFe	FeO	CaO	SiO_2	MgO	Al_2O_3	TiO_2	V_2O_5	Cr_2O_3
54.40	0.81	0.73	4.20	2.43	2.38	9.11	0.61	1.48

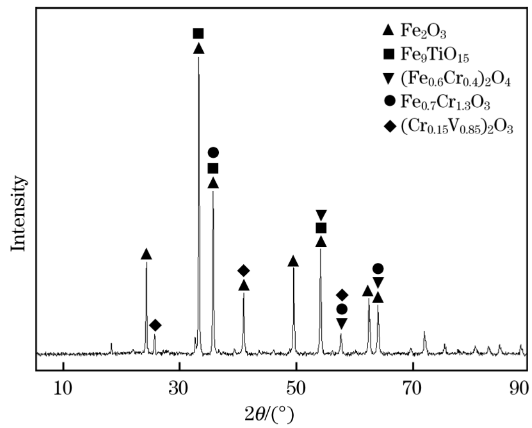

Fig. 1. XRD pattern of HVTM pellets.

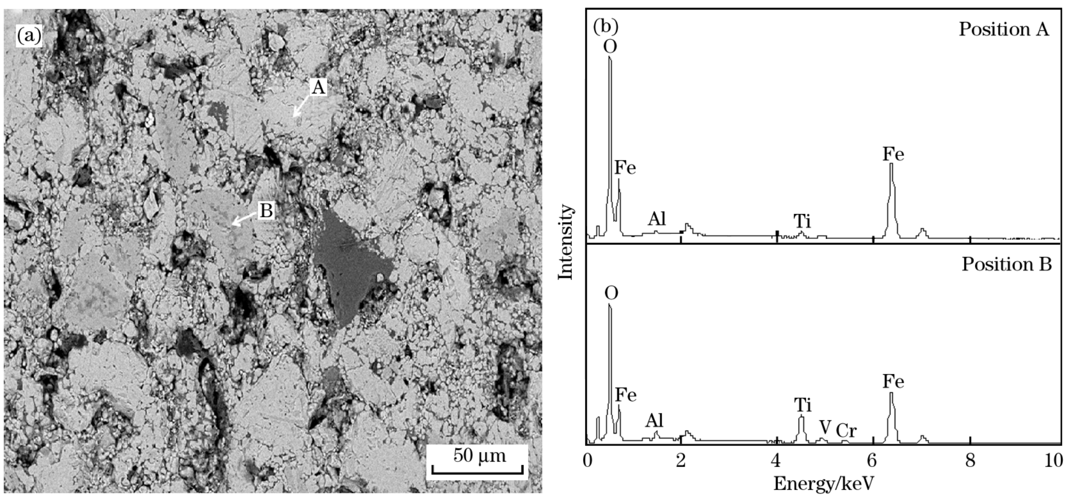

Fig. 2. SEM image (a) and EDS analysis (b) of HVTM pellets.

2.2. *Apparatus and procedure*

Reduction experiments were conducted in a high-temperature electric resistance furnace to simulate the shaft furnace production process. The schematic diagram of experimental apparatus is shown in Fig. 3. It consists of the main body, a temperature control cabinet, a water drier, and an electronic balance with a detection precision of 1 mg. The gas composition ($90\%(H_2+CO)+5\%N_2+5\%CO_2$) was obtained according to the rules of Midrex and HYL-III shaft furnaces and controlled by mass flow controller.

In each experiment, when the shaft furnace was heated to the preset temperature in a pure nitrogen atmosphere, the crucible containing twenty oxidized pellets was put into the furnace and connected to an electronic balance for continuous measurement of the mass loss as a function of time. After stabilization