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Behaviors of vanadium and chromium in coal-based direct reduction of high-chromium vanadium-bearing titanomagnetite concentrates followed by magnetic separation

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Abstract: The reduction behaviors of $FeO·V_2O_3$ and $FeO·Cr_2O_3$ during coal-based direct reduction have a decisive impact on the efficient utilization of high-chromium vanadium-bearing titanomagnetite concentrates. The effects of molar ratio of C to Fe $n(C)/n(Fe)$ and temperature on the behaviors of vanadium and chromium during direct reduction and magnetic separation were investigated. The reduced samples were characterized by X-ray diffraction (XRD), scanning election microscopy (SEM) and energy dispersive spectrometry (EDS) techniques. Experimental results indicate that the recoveries of vanadium and chromium rapidly increase from 10.0% and 9.6% to 45.3% and 74.3%, respectively, as the $n(C)/n(Fe)$ increases from 0.8 to 1.4. At $n(C)/n(Fe)$ of 0.8, the recoveries of vanadium and chromium are always lower than 10.0% in the whole temperature range of 1100−1250 °C. However, at $n(C)/n(Fe)$ of 1.2, the recoveries of vanadium and chromium considerably increase from 17.8% and 33.8% to 42.4% and 76.0%, respectively, as the temperature increases from 1100 °C to 1250 °C. At $n(C)/n(Fe)$ lower than 0.8, most of the $FeO·V_2O_3$ and $FeO·Cr_2O_3$ are not reduced to carbides because of the lack of carbonaceous reductants, and the temperature has little effect on the reduction behaviors of $FeO·V_2O_3$ and $FeO·Cr_2O_3$, resulting in very low recoveries of vanadium and chromium during magnetic separation. However, at higher $n(C)/n(Fe)$, the reduction rates of $FeO·V_2O_3$ and $FeO·Cr_2O_3$ increase significatly because of the excess amount of carbonaceous reductants. Moreover, higher temperatures largely induce the reduction of $FeO·V_2O_3$ and $FeO·Cr_2O_3$ to carbides. The newly formed carbides are then dissolved in the γ(FCC) phase, and recovered accompanied with the metallic iron during magnetic separation.

Key words: high-chromium vanadium-bearing titanomagnetite concentrates; coal-based direct reduction; magnetic separation; reduction behavior; vanadium; chromium

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1 Introduction

Panzhihua−Xichang (Panxi) region in China is widely recognized by large volumes of vanadium-bearing titanomagnetite, and the proven deposits of titanium and vanadium account for 35.2% and 11.6% of world total reserves, respectively [1]. Vanadium-bearing titanomagnetite at Hongge, China, accounts for 49.5% of the total reserve in Panxi region, China [2]. It is also widely recognized as the biggest chromium-bearing deposit in China [3]. At present, the titanomagnetite concentrates are smelted in the blast furnace to produce hot metal and blast furnace slag [3]. The blast furnace slag contains 22%−25% TiO_2 and 2%−6% metallic iron, and it is rather difficult to be efficiently utilized, resulting in resource depletion [4−6].

To efficiently recover titanium resources from vanadium-bearing titanomagnetite, coal-based direct reduction with subsequent electric furnace smelting has gained considerable attention as an alternative route to the conventional blast furnace process [7,8]. The molten

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iron obtained by electric furnace smelting is oxidized in BOF converter to produce vanadium slag. It is difficult to efficiently recover the vanadium and chromium by roasting−leaching process from the vanadium slag with stable spinel structure [9,10], and the residual hazardous compounds such as V(V) and Cr(VI) in the leaching residue inevitably pose a great threat to the environment [11].

Therefore, a new cleaner production process for the efficient utilization of high-chromium vanadium-bearing titanomagnetite concentrates has been proposed by ZHAO et al [12]. In this process, most of the vanadium and chromium are not reduced and concentrated in the titanium slag during direct reduction. After magnetic separation, vanadium and chromium can be efficiently extracted from the titanium slag using hydrometallurgical processes, so that converter smelting and roast-leach processes can be avoided. However, few studies have been focused on the reduction behaviors of vanadium and chromium in the titanomagnetite concentrates during direct reduction, which have a decisive impact on the elemental distribution of vanadium and chromium between iron concentrate and titanium slag during magnetic separation. Therefore, it is imperative to investigate the reduction behaviors of vanadium and chromium in the concentrates during coal-based direct reduction.

The objectives of the present work are to investigate the reduction behaviors of vanadium and chromium in the isothermal reduction of high-chromium vanadium-bearing titanomagnetite concentrates and their effects on the elemental distribution in the subsequent magnetic separation.

2 Experimental

2.1 Materials

The high-chromium vanadium-bearing titanomagnetite concentrates (<150 μm) used in this work were obtained from Hongge District, southwest China. The chemical composition of the titanomagnetite concentrates is given in Table 1. XRD analysis in Fig. 1 indicates that the titanomagnetite concentrates consist mostly of titanomagnetite (Fe_2TiO_4), with small amounts of ilmenite. The mineralogical investigation indicates that above 97% of the vanadium and chromium in the concentrates were embedded in the titanomagnetite, the octahedral sites of which were occupied by trivalent ions such as V(III) and Cr(III), forming $FeO{\cdot}(Fe,V,Cr)_2O_3$. The pulverized coal is used as a reductant (<150 μm), and the industrial analysis results are listed in Table 2.

Table 1 Chemical composition of high-chromium vanadium-bearing titanomagnetite concentrates (mass fraction, %)

TFe	FeO	TiO_2	V_2O_5	Cr_2O_3	CaO	MgO	Al_2O_3	SiO_2
55.14	27.33	13.60	0.58	1.10	1.10	4.24	3.36	3.12

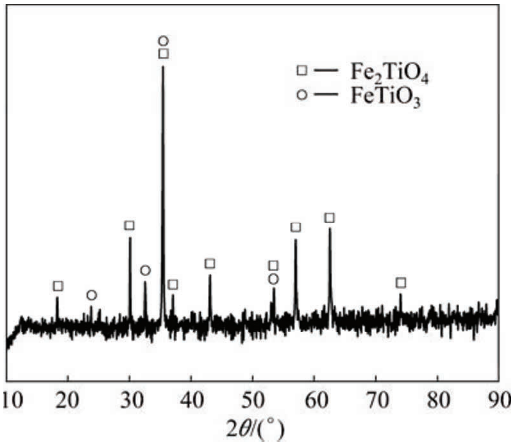

Fig. 1 XRD pattern of high-chromium vanadium-bearing titanomagnetite concentrates

Table 2 Industrial analysis results of pulverized coal (mass fraction, %)

FC_{ad}	V_{daf}	A_d	M_{ad}	S
87.10	4.07	8.83	2.08	0.376

FC_{ad}: Fixed carbon in air dried sample, V_{daf}: Volatiles in air dried sample, A_d: Ash in air dried sample, M_{ad}: Moisture in air dried sample

2.2 Experimental procedures

The reduction experiments were conducted in a temperature controlled Muffle furnace with precise temperature (±1 °C) controls. The titanomagnetite concentrates (120 g) were firstly mixed homogenously with pulverized coal and 2.5% Na_2CO_3 additive. The presence of minor amounts of Na_2CO_3 largely facilitated the carbon gasification reaction and thereby exerted a positive influence on the reduction of the titanomegnetite concentrates, as well as induced the growth of the metallic phases probably because of the formation of a small amount of liquid phases [13−15]. The obtained mixtures were then placed in a capped SiC crucible and heated at various temperatures for 2 h. The crucible was not completely sealed to ensure that the inside pressure was almost equal to the atmospheric pressure. After reduction, the reduced samples were removed and immediately quenched with water to avoid re-oxidation, with subsequent crushing and grinding in a XMB-0.5L steel rod mill (Wuhan Exploring Machinery Factory, China) at ambient temperature for 30 min. The milling medium was made of hardened stainless steel rods.

The magnetic separation was conducted in a DTCXG-ZN50 low intensity magnetic separator (Tangshan DTEE Electrical Equipment Co., Ltd., China)