Powder Technology 326 (2018) 137–145

Contents lists available at ScienceDirect

Powder Technology

journal homepage: www.elsevier.com/locate/powtec

Influence of TiO_2 addition on the oxidation induration and reduction behavior of Hongge vanadium titanomagnetite pellets with simulated shaft furnace gases

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ARTICLE INFO

Article history:
Received 26 July 2017
Received in revised form 3 December 2017
Accepted 14 December 2017
Available online 16 December 2017

Keywords:
Titanium
Hongge vanadium titanomagnetite
Oxidation induration
Reduction behavior
Mechanism

ABSTRACT

This study investigated the oxidation induration of Hongge vanadium titanomagnetite pellets (HVTMP) with different TiO_2 additions, and its influence on subsequent reduction behavior with simulated shaft furnace gases. The results showed that the addition of TiO_2 decreased the compressive strength and increased the porosity of the HVTMP, and eventually had a detrimental effect on the oxidation induration process. The oxidation induration mechanism was further elucidated by the means of XRD and SEM. When more TiO_2 was added, the reduction degree and rate of the HVTMP decreased due to the generation of Fe_2TiO_5 during the oxidization induration process, which was unfavorable for the subsequent reduction process. The morphology structure confirmed that the growth of metallic iron whiskers was suppressed with an increase in TiO_2, which resulted in the decrease of reduction swelling. Furthermore, the reduction swelling and compressive strength of the reduced HVTMP exhibited a reverse linear relationship. The current study not only provides experimental evidence to establish a correlation between TiO_2 addition and oxidation reduction behavior, but also provides both a theoretical and technical basis for the effective utilization of Hongge vanadium titanomagnetite either in blast furnace or shaft furnace.

1. Introduction

There is abundant vanadium titanomagnetite (VTM) throughout the world, and it contains plentiful valuable elements [1,2]. Hongge VTM (HVTM), deposited in the Panzhihua-Xichang area (Sichuan, China), is one of the largest VTM resources, it is not only rich in valuable elements including iron, titanium, and vanadium, but also contains a high content of chromium. The chromium reserve is 900 Mt., accounting for 68% of the total resource in China [3,4]. Therefore, it is very rewarding to study the utilization of this special mineral resource.

At present, VTM is mainly smelted in blast furnace (BF) to produce hot metal and slag in which the titanium content (in terms of TiO_2) varies from 22 to 25 wt% [5,6]. However, BF slag cannot be utilized effectively through traditional separation techniques [7,8]. Compared with BF process, many new processes have been developed based on direct reduction containing coal to improve the utilization of VTM, HVTM, and other minerals [9–18]. E. H. Wu [9] studied the smelting-separation process for metallized pellets of VTM. L. S. Zhao [12] investigated the reduction behavior of vanadium and chromium during coal-based direct reduction of HVTM followed by magnetic separation. It was found that the recovery rates of vanadium and chromium increased with the increase of n(C)/n(Fe) and reduction temperature. X. W. Lv [16] reported on the reduction behavior of VTM in microwave and the distribution of the elements during the smelting process. However, the recovery rates of titanium, vanadium, and chromium are still low among these processes. Besides, the coal-based direct reduction is relatively inefficient, with long reduction time and slow reduction rate [19]. As a result, HVTM has not yet been exploited and utilized on a large scale.

In order to utilize HVTM efficiently, a novel clean smelting process has been proposed by the authors' laboratory, which evidently increases the recovery rates of valuable elements [20]. In this process, gas-based direct reduction of HVTM pellets (HVTMP) is an essential procedure. It is generally known that in both BF and gas-based shaft furnace, the use of oxidized pellets as the burden presents many advantages, such as uniform size, high physical strength, and low degradation [21–23]. In the past few decades, a considerable number of studies have reported on the oxidation and gas-based reduction of VTM, HVTM, and other minerals [24–35]. F. Pan [24] analyzed the structural changes and elements migration during the oxidation process of VTM. It was observed that the compact structure changed into porous one during the oxidation process, and the nano-sized sheets transformed into molten particles on the surface with gradually increasing the oxidation temperature. W. Li [27] investigated the correlations between roasting characteristics of HVTMP and its subsequent reduction behaviors.

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https://doi.org/10.1016/j.powtec.2017.12.050
0032-5910/

They found that the increase of roasting temperature and time of HVTMP accelerated its subsequent reduction, however, the reduction rate decreased when the pellets roasted at 1250 °C were used. S. Saikat [31] studied the oxidation behavior and phase characterization of titaniferous magnetite ore of eastern India. They concluded that ilmenite phase transformed to hematite and titanium dioxide at lower temperature, whereas ferric-pseudobrookite phase was found at higher temperature. Notably, titanium is one of the main valuable elements in HVTM, but no published studies have investigated the influence of TiO_2 on the oxidation induration process of HVTMP has not been reported, let alone its subsequent reduction behavior and mechanism with simulated shaft furnace gases. Therefore, the oxidation induration and reduction behavior affected by titanium need examined more closely, in order to optimize the process parameters and enhance reduction.

As one part of ongoing work to develop a novel clean smelting process for HVTM, the objective of the present study was to investigate the influence of TiO_2 on the oxidation induration of HVTMP and its reduction behavior, using simulated shaft furnace gases. For this purpose, the compressive strength, porosity, phase composition, and microstructure of HVTMP with different TiO_2 additions during oxidation induration were investigated. Then, for the prepared HVTMP, the reduction behavior was studied in detail, particularly the reduction degree, phase composition, reduction swelling and compressive strength, were studied in detail. These results not only provide experimental evidence to establish a correlation between TiO_2 addition and oxidation reduction behavior, but also provide both a theoretical basis and technical support for the comprehensive utilization of HVTM.

2. Experimental

2.1. Materials

In this study, the HVTM was sourced from the Panxi-Honge region of China, its main chemical composition is depicted in Table 1. It can be seen that the HVTM has a low content of total iron grade and a high content of Cr_2O_3. In order to analyze the sample conveniently, only iron, titanium, vanadium, and chromium were marked in the XRD patterns. Fig. 1 shows that the main phases are magnetite (Fe_3O_4), titanomagnetite ($Fe_{2.75}Ti_{0.25}O_4$), coulsonite (Fe_2VO_4), and chromite ($FeCr_2O_4$). The chemical reagent TiO_2 was analytically pure, and the binder used in this study was bentonite. The particle sizes of all the raw materials, including HVTM, bentonite and TiO_2, were 100% passing 0.074 mm.

2.2. Procedures

The main procedure of preparing HVTMP included milling, balling, drying, oxidation roasting, and cooling. The milling operation of HVTM with bentonite and TiO_2 was conducted in a planetary ball mill. The rotational speed of the mill was kept constant at 200 rpm for 2 h. The TiO_2 addition levels in the HVTM were: 0 wt%, 3 wt%, 6 wt%, and 9 wt%. The bentonite was fixed at 1 wt% of the mixture of HVTM and TiO_2. After milling, the mixtures were mixed with water and balled into green pellets in an experimental balling disc pelletizer. The green pellets ranging from 11.5 to 12.5 mm in diameter were dried in an oven at 105 °C for 5 h. Oxidation roasting experiments were carried out in a muffle furnace. In each experiment, when the muffle furnace reached the preheating temperature of 900 °C, air was introduced to the furnace to maintain an ample oxidizing atmosphere. The dried pellets were first preheated for 10 min and then the temperature was increased to the roasting temperature of 1200 °C and maintained for 20 min [25]. After oxidation roasting, the roasted pellets were taken out from the furnace and cooled to room temperature naturally.

All gas-based direct reduction experiments were conducted using a reduction shaft furnace. Before starting each experiment, the furnace was first heated to the target temperature in a nitrogen atmosphere, and then the pellets were placed into the constant temperature zone of the furnace. When the temperature was steady, the simulated shaft furnace gases (64.3%H_2 + 25.7%CO + 5%CO_2 + 5%N_2 gas mixtures) were introduced into the furnace at a total gas flow rate of 4 L min^{-1}, and the reduction started [20]. After a certain period of reaction time, the pellets were removed from the furnace quickly and cooled down in a high flow rate of an argon atmosphere to the ambient temperature.

The reduction ratio was evaluated as the fraction of oxygen removed from the HVTMP. However, the oxides containing Ti, V, and Cr could barely be reduced under the experimental temperature and atmosphere conditions of this study. Therefore, the reduction degree (R) was

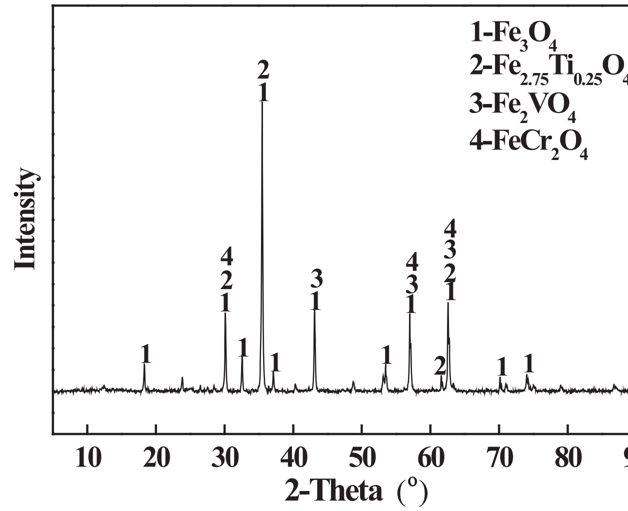

Fig. 1. XRD patterns of HVTM.

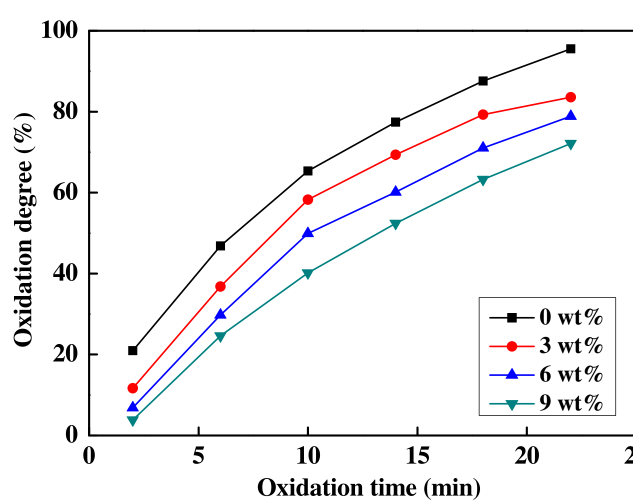

Fig. 2. Effect of oxidation time on the oxidation degree of HVTMP with different TiO_2 additions.

Table 1
Chemical composition of HVTM (wt%).

TFe	FeO	CaO	SiO_2	MgO	Al_2O_3	TiO_2	V_2O_5	Cr_2O_3	S	P
54.54	26.25	0.98	4.88	2.98	2.50	9.26	0.62	1.48	0.48	0.01