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Effect of wet grinding on carbothermic reduction of ilmenite concentrate

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ABSTRACT

High titania slag has become a good raw material in the development of titanium. Ilmenite is reduced first and then smelted in an electric arc furnace to separate iron from the high titania slag. Therefore, enhanced reduction of ilmenite concentrate can reduce smelting time and energy consumption. Wet grinding method, which is often used to reduce particle size and improve the balling ability of ilmenite, was proposed to enhance the reduction. The effect of wet grinding on the carbothermic reduction of ilmenite was investigated. The wet grinding treatment was found to result in a high reduction rate and improve metallisation. The metallisation degree of reduced ilmenite concentrate increased as the time of wet grinding increased. Under the constant reduction conditions, the degree of metallisation improved from 68.58% to 87.32% while the FeO content decreased from 10.62 to 5.28% as the wet grinding time increased from 10 to 60 min.

1. Introduction

As natural rutile and high-grade titania mineral resources decrease worldwide, ilmenite has become one of the important raw materials for the titanium industry because of its titania content (Wu and Zhang, 2006; Pistorius and Coetzee, 2003). Grades of ilmenite contain 45 to 65.8 mass percent TiO_2 and ilmenite is regarded as a significant resource in the production of rutile, which can be used directly as a pigment to manufacture titanium (Deng and Luo, 1998; Miller, 1957). However, ilmenite is a type of low-grade titania ore. Therefore, ilmenite is commonly preferred to enrich titania as high titania slag and is processed in an electric arc furnace (EAF) to fully utilise it (Zhao and Guo, 2005; Pourabdoli et al., 2006). Separating iron from ilmenite is an expensive process (Chen et al., 1997) because of the long reduction and smelting time, which results in high power consumption of usually 2000 kW h to 2500 kW h for each tonnage of titania slag.

In the past decades, a considerable number of studies (Tripathy et al., 2012; Wang et al., 2008; Kucukkaragoz and Eric, 2006; Gupta et al., 1989) have reported on ilmenite reduction. However, enhancement of ilmenite reduction is less studied. The possible technical routes for enhancing ilmenite reduction can be classified into two methods, namely, addition of additives to raw materials and mechanical activation treatment methods. For example, Gupta et al. (1989) examined the effect of ferric chloride ($FeCl_3$) addition to the reduction of ilmenite. Adding $FeCl_3$ to ilmenite–graphite mixtures significantly increased the reduction rate. No reduction occurred in the absence of $FeCl_3$, whereas the reaction occurred rapidly at 1273 K with 10% $FeCl_3$. Run et al., 2013 and Ranganathan et al. (2012) reported on the effect of ferrosilicon addition to the reduction of ilmenite. The metallisation ratio and the particle size of iron in the reduced samples increased as Fe–Si amount and reduction time increased. If molten Fe–Si alloy was present during reduction, it could enhance the rate of reduction and the agglomeration of iron. Huang et al. (2004) studied the effect of wet grinding on the pelletising process and the pellets. The strength of wet, preheated and fired pellets was all improved. Chen et al. (1997) reported the results of carbothermic reduction of ilmenite by mechanical activation. After ball milling an ilmenite–carbon mixture at room temperature, the ilmenite was reduced to rutile and metallic iron during subsequent low-temperature annealing. A long milling time lowed to the reduction temperature and increased the reduction rate further. High milling intensity also lowed to the reduction temperature further. Welham and Williams (1999) reported that milling was a non-equilibrium process, in which physical energy was transferred into a powder by crystalline damage, the formation of defects and localised heating during impact, thereby increasing the enthalpy and entropy of the system.

The low strength of ilmenite pellet, long reduction time, slow reduction rate and high energy consumption are the major problems in the

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Table 1
Main chemical components of ilmenite concentrate (wt.%).

TiO_2	Fe_2O_3	FeO	CaO	MnO	MgO	SiO_2	Al_2O_3	V_2O_5
45.64	6.53	36.45	1.12	0.855	3.22	3.65	1.02	<0.10

smelting of Panzhihua ilmenite with the EAF processes. Few studies have reported the effect of wet grinding on the carbothermic reduction of ilmenite concentrate. This study investigated the effect of mechanical activation on carbothermic reduction of ilmenite concentrate.

2. Experimental procedures

2.1. Raw materials

Ilmenite concentrate was supplied by Panzhihua Iron and Steel (Group) Co. The chemical composition and particle size distribution of the concentrate are listed in Tables 1 and 2, respectively. The X-ray diffraction pattern of ilmenite concentrate showed that FeTiO3, Fe3O4 and MgTiO3 were the main minerals, as showed in Fig. 1. Coke was used as a reducing agent; its composition is shown in Table 3. The average particle size of coke was approximately 74 μm.

2.2. Experimental apparatus and methods

5000 g of ilmenite concentrate was mixed with excess amount of coke (14%mass% of ilmenite) in each experiment to ensure sufficiently reduction of iron oxides in the concentrate. Previous finding (Huang et al., 2012) suggested that coke was important to provide sufficient carbon for full reduction of iron oxides in the ilmenite concentrate. The grinding machine was a laboratory scale mill made of rubber liners, with an inner diameter of 0.5 m and an inner volume of 0.1 m^3. Wet grinding was performed by steel balls, which average size was approximately 30 mm. The ball movement was controlled by adjusting the rotation speed. The rotation speed was set at 48 rpm in the experiments. The mixtures of ilmenite concentrate and coke with 4% moisture were ground for 4, 10, 30 and 60 min at room temperature.

After wet grinding, the ilmenite concentrate powder was dried at 393 K for 2 h. The size distribution, specific surface area, surface morphology and lattice distortion of ilmenite concentrate were then measured. The size distribution and the average particle size were determined using the OMEC particle analyser (PIP9.1). The specific surface area of powders was determined using a Gemini VII 2390 surface area analyser with N_2 gas at liquid nitrogen temperature, in which the sample was degassed at 200 °C under vacuum for 1 h before measurement. A TESCAN VEGA 2 scanning electron microscope (SEM) was employed to study the powder morphology.

The mixture of powdered ore and coke was then briquetted by using a mould press; each briquette was approximately 30 mm in size and 50 g in weight. The briquettes were dried before being used in the experiment. The samples were placed in a corundum crucible, which was then placed in a vertical tube furnace and introduced into the isothermal zone of the furnace once the desired temperature was reached. Each sample was reduced for 30 min at 1653 K under an argon atmosphere. A schematic of the reduction experimental apparatus is shown in Fig. 2. After reduction, the briquettes were broken into two halves, and the cross section was observed under SEM (TESCAN VEGA 2 SEM, 15 kV beams) and optical microscopy (50 iPOL). The

Table 2
Particle size distribution of ilmenite concentrate (raw material).

Particle size (μm)	+150	−150–+110	−110–+75	−75–+44	−44–+37	−37
Content (wt.%)	0.9	2.4	23.8	44.5	12.8	15.6

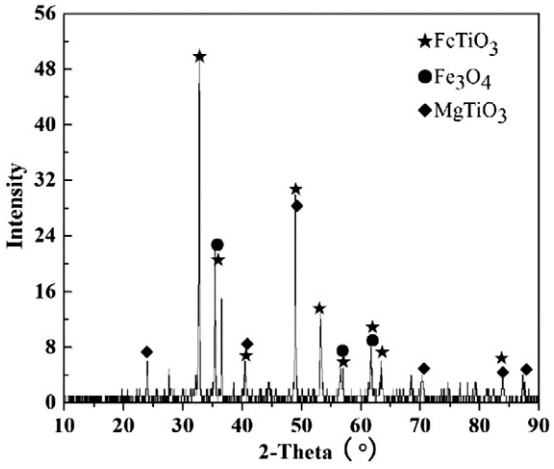

Fig. 1. XRD pattern of Panzhihua ilmenite concentrate.

cross section surface of the samples is platted and rinsed in acetone by an ultrasonic cleaner and then dried before SEM observation, but the cross section surface of sample needs polishing process for optical microscopy analysis. For optical microscopy, samples mounted in 'Metset' mounting plastic were ground on silicon carbide papers to 800 grades and polished successively with 6, 3, and 1 μm 'Hyprez' diamond lapping compound. Chemical and thermo gravimetric analyses were performed on powder samples. The TFe, Fe^{2+} and metallic iron (MFe) contents of reduced sample were analysed using wet chemical method. The metallisation degree of the reduced samples was defined as the following equation:

$$\text{Metallisation} = \frac{\text{MFe}}{\text{TFe}} \times 100\% \quad (1)$$

where, TFe and MFe are the contents of total iron and metallic iron in the reduced samples, respectively. The thermo gravimetric analysis was conducted using a Shimadzu TA 50I in flowing high-purity argon dried by passing through a column of magnesium perchlorate. The gas flow rate was 80 mL/min. The samples were supported on a platinum pan suspended in the isothermal zone of the reactor, which was purged with argon for 45 min before being placed in the hot furnace. A sample which weighed 40 mg was heated at a rate of 20 K/min, and the temperature was raised to approximately 1400 °C. The weight of the sample and the adjacent temperature were continuously recorded. The temperature was not constant instead it was ramped up to 1400 °C.

3. Results and discussion

3.1. Wet grinding

3.1.1. Particle size and specific surface area after wet grinding

The effect of grinding time on the particle size distribution of ilmenite concentrate is shown in Fig. 3. As the grinding interval increased, the particle size distribution shifted to the left, which means that the particle size decreased gradually. When the grinding time is more than 10 min; a second sub-population peak appears at approximately 100 μm or above, which probably resulted from the agglomeration of fine particles.

Table 3
Proximate analysis and S and P contents of coke.

Component	Fixed carbon	Ash	Volatile	S	P
wt.%	83.66	14.12	2.22	0.65	0.125