Journal of Alloys and Compounds 619 (2015) 443–451

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

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

Kinetics and mechanism of hydrogen reduction of ilmenite powders

Jie Dang, Guo-hua Zhang *, Kuo-chih Chou

State Key Laboratory of Advanced Metallurgy, University of Science and Technology Beijing, Beijing 100083, China

ARTICLE INFO

Article history:
Received 23 April 2014
Received in revised form 28 August 2014
Accepted 7 September 2014
Available online 16 September 2014

Keywords:
Kinetics
Isothermal
Non-isothermal
Ilmenite
Hydrogen reduction

ABSTRACT

Both isothermal and non-isothermal reduction experiments of Panzhihua ilmenite powders by pure hydrogen were carried out using a thermo-gravimetric (TG) analyzer. Results of X-ray Diffraction (XRD), Scanning Electron Microscope (SEM) and Energy Dispersive Spectroscopic (EDS) analyses showed that in the temperature range of 1146–1201 K, the main products were metallic iron, TiO_2 and $MgTiO_3$ with the iron being embedded in TiO_2 matrix. It was found that the reduction reaction was controlled by the chemical reaction at the reaction interface and the apparent activation energy was extracted to be 98.35–99.02 kJ/mol by using a new kinetic model. However, under the non-isothermal condition, as gradually increasing the temperature to 1493 K, TiO_2 and $MgTiO_3$ could be reduced, and the final products were metallic iron and $Mg_xTi_{3-x}O_5$ (x was in the range of 0.45–1).

1. Introduction

As sources of high-grade titanium minerals (*e.g.* rutile) are being exhausted worldwide, more attentions must be paid to processes of dealing with low-grade minerals such as ilmenite [1–2]. Among the titanium containing minerals, ilmenite is the most abundant one in nature [3]. Furthermore, Panzhihua ilmenite, located in Sichuan, Southwest China, is one of the largest ilmenite resources over the world with an estimated ilmenite reserve of about 870 million tons, which accounts for more than 90% of the total reserve of China and over 35% of the world [4–6]. However, it contains a low-grade of TiO_2 and high contents of impurities (especially MgO). Therefore, Panzhihua ilmenite is unsuitable for the chlorination process to produce TiO_2 pigment. On the other hand, the sulfate process employed to manufacture TiO_2 pigment faces severe environmental challenges [7]. The conventional smelting route, which is used to smelt ilmenite ores with carbon in high-temperature furnaces to produce pig iron and titania-enriched slags, also has many disadvantages. Firstly, the smelting process always requires a long time and a high temperature [8]. Secondly, slag-forming reagents added to produce a fluid titania-enriched slag will dilute the concentration of titanium dioxide in the slag and have deleterious effects on the subsequent processes of extracting titania [9–11].

The gas-based reduction of ilmenite seems to be a promising method to obtain titanium oxides and direct reduction iron at a low temperature, since it is a much more environmentally friendly method [12,13]. Recently, many investigations have been done on this process [2,14–22]. Zhao and Shadman [9] studied the reduction kinetics and mechanism of synthetic ilmenite by hydrogen and concluded that at temperatures below 1149 K, the conversion-time curve has a sigmoidal shape. Wang et al. [11] investigated the hydrogen reduction of Bama's ilmenite pellets and found that the reduction reaction proceeded topochemically with the diffusion of hydrogen in the reduced layer to be the rate controlling step. Sun et al. [23] also studied the hydrogen reduction of natural ilmenite in a fluidized bed, and found that both the mass transport of the reactants and the intrinsic chemical reaction played important roles. Though many attentions have been paid on the mechanism of reducing ilmenite by hydrogen, most of the researches were focused on pellets samples and the fundamental information on the reduction kinetics and mechanism of powders is still not sufficient. In the present work, the reduction of Panzhihua ilmenite powders by hydrogen was investigated under both isothermal and non-isothermal conditions to elucidate the reduction kinetics and mechanism.

2. Materials and experimental procedure

2.1. Materials

Chemical compositions of Panzhihua ilmenite concentrate are presented in Table 1. The powder size distribution was measured by the laser interferometer (SEISHIN LMS-30) with the density function being shown in Fig. 1, in which the vertical coordinate of right upper black dot of every small zone represents the total volume fraction of the powders in this zone. The average particle size is calculated to be 40.870 μm. The XRD analysis (Fig. 2) indicates that Panzhihua ilmenite

* Corresponding author. Tel.: +86 1062333703; fax: +86 1062332570.
E-mail addresses: jiedang2011@gmail.com (J. Dang), ghzhang_ustb@163.com (G.-h. Zhang), kcc126@126.com (K.-c. Chou).

http://dx.doi.org/10.1016/j.jallcom.2014.09.057
0925-8388/

concentrate is mainly composed of a $FeTiO_3$ based solid solution, into which other elements are dissolved by substituting Fe or Ti lattices. Here, $Fe(Mg)TiO_3$ is used to approximately represent this solid solution for the large content of Mg impurity.

2.2. Experimental procedure

The weight change of ilmenite powders during reduction was monitored by using an HCT-2 thermal analysis system, which included a thermo-gravimetric microbalance. Fig. 3 shows the schematic diagram of the apparatus. In each experimental run, the sample of about 20 mg was used and filled into an alumina crucible. After the crucible with the sample was placed in the heating furnace, argon was introduced into the system to get the air out of the furnace. In the isothermal experiment, the furnace was first heated from room temperature (around 303 K) up to the desired reduction temperature at a heating rate of 10 K/min in argon atmosphere. When the thermal balance was stabilized, the argon gas was switched to pure hydrogen, and the weight loss due to the reduction was then monitored continuously. After reacting for a certain time, hydrogen was changed to argon again, and the sample was cooled to the room temperature.

In non-isothermal experiments, pure hydrogen was first introduced into the furnace to get the air out then the furnace was heated from room temperature to 1493 K in hydrogen atmosphere at a heating rate of 4, 7 or 10 K/min, respectively.

In all the experimental runs, a constant flow rate of 60 ml/min (298 K, 1 bar; about 0.318×10^{-2} m/s at 298 K) was kept during the reduction. This level was found to be sufficient for diminishing the diffusion resistance of gas in the gas-boundary layer. Hydrogen and argon used in the experiments were in high purity (<5 ppm O_2). The flow rate of gas was controlled by gas flow controllers (Alicant, Model MC-500SCCM-D). XRD (Model, TTRIII, Japan) measurements were carried out for samples. The morphologies of these samples were observed by using the SEM (Model S250MK3, CAMBRIDGE) technique.

3. Results

Since the starting temperature of reducing TiO_2 by pure hydrogen is at around 1220 K [19], therefore, below 1220 K, only the reductions of Fe^{2+} and Fe^{3+} to Fe will be occurred, and the theoretical maximum mass loss of the sample after a complete reduction is calculated to be $0.0994m_0$ (where 0.0994 is the weight fraction of oxygen combined with iron; m_0 is the initial mass of ilmenite powders). When the temperature is higher than 1220 K, Ti^{4+} will also be reduced, and the theoretical maximum mass loss of the sample after a complete reduction is calculated to be $0.1283m_0$ under the assumptions that Fe^{2+} and Fe^{3+} are completely reduced to Fe, and TiO_2 is reduced to Ti_3O_5.

3.1. Isothermal reduction

Isothermal reduction of Panzhihua ilmenite concentrate powders by hydrogen was studied in the temperature range of 1146–1201 K. The time dependences of the mass loss at three temperatures between 1146 and 1201 K are presented in Fig. 4, from which it is apparent that the mass loss increased with the increases of temperature and time, and the reduction reaction would be completed for about 28 min at 1146 K but 14 min at 1201 K.

3.2. Non-isothermal reduction

Fig. 5 shows the non-isothermal reduction curves at three different heating rates, viz, 4, 7 and 10 K/min. From Fig. 5, it can be obtained that the maximum mass loss of non-isothermal reduction is near $0.12m_0$, which is larger than that of isothermal reduction experiments (near $0.0994m_0$) but less than $0.1283m_0$, resulting from the reduction of the majority of TiO_2 and $MgTiO_3$. Furthermore, it can be clearly seen that in the later stage of the reduction, the reaction rate decreased, which indicated that reductions of TiO_2 and $MgTiO_3$ by hydrogen were more difficult than $FeTiO_3$.

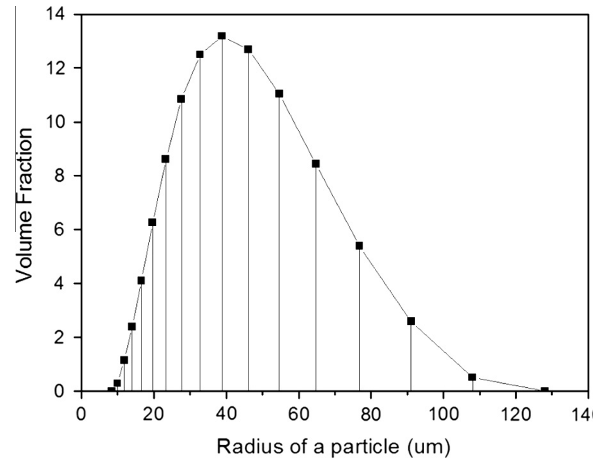

Fig. 1. Powder size distribution of Panzhihua ilmenite concentrate.

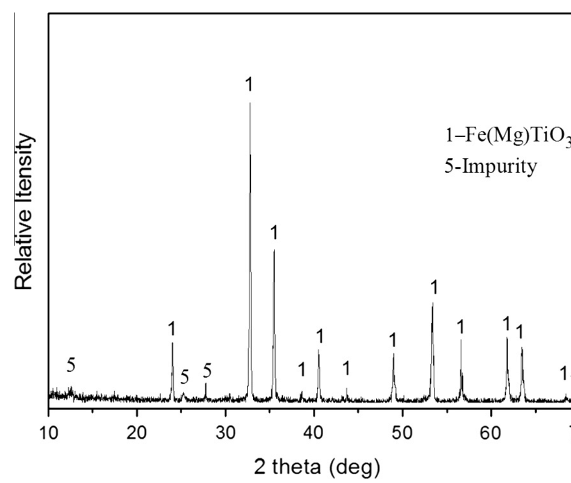

Fig. 2. XRD patterns of Panzhihua ilmenite concentrate.

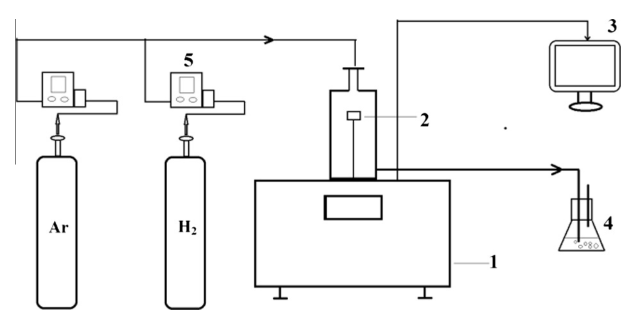

Fig. 3. Schematic diagram of the experimental apparatus for TG analysis. 1. HCT-2 thermo-gravimetric analyzer, 2. Alumina crucible, 3. Data collector, 4. Exhausted gases, 5. Gas flow controller.

Table 1
Chemical compositions of Panzhihua ilmenite concentrate.

Composition	$Fe_2O_3^C$	FeO^C	CaO^X	$V_2O_5^X$	$Al_2O_3^X$	SiO_2^X	MgO^X	TiO_2^X
Mass%	9.02	32.49	0.90	0.13	1.42	3.48	7.66	43.27
Composition	MnO^X	$Cr_2O_3^X$	Na_2O^X	SO_3^X	ZnO^X	$P_2O_5^X$	$In_2O_3^X$	Total
Mass%	0.66	0.03	0.27	0.59	0.02	0.03	0.03	100

Superscript: C-chemical analysis (acid – base titration); X-X-ray fluorescence analysis.