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### Reductive kinetics of Panzhihua ilmenite with hydrogen

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Abstract: The hydrogen reduction of Panzhihua ilmenite concentrate in the temperature range of 900–1050 °C was systematically investigated by thermogravimetric analysis (TG), X-ray diffraction (XRD) and scanning electron microscopy (SEM) methods. It was shown that the products of the Panzhihua ilmenite reduced at 900 °C were metallic iron and rutile. Above 1000 °C, ferrous pseudobrookite solid solution was generated. During the reduction process, element Mg gradually concentrated to form Mg-rich zone which can influence the metallization process. The reduction reaction proceeded topochemically and its related reduction kinetics were also discussed. The kinetics of the reduction indicated that the rate-controlling step was the diffusion process. The apparent activation energy of the hydrogen reduction of Panzhihua ilmenite was calculated to be 117.56 kJ/mol, which was larger than that of synthetic ilmenite under the same reduction condition.

Key words: Panzhihua ilmenite; synthetic ilmenite; hydrogen reduction; kinetics; rate-controlling step; magnesium migration

#### **1** Introduction

The mineral ilmenite (nominally FeTiO<sub>3</sub>) is one of the primary mineral resources for producing titanium dioxide and Ti [1-3]. Panzhihua ilmenite in Sichuan, southwest of China, is one of the largest ilmenite reserves over the world with an estimated ilmenite reserve of about  $8.7 \times 10^8$  t, which accounts for more than 90% of the total titanium resource of China and over 35% of the world [4-6]. Panzhihua ilmenite concentrate is a rock-type mineral that contains low-grade titania and high content of impurities (especially high content of MgO), which make it difficult to upgrade the ilmenite ore [7]. Due to its high impurity content, the reducibility of ilmenite is low and Panzhihua ilmenite is unsuitable for the chlorination process to produce TiO<sub>2</sub> pigment [8,9]. In a traditional method, ilmenite ore is smelted with carbon in electric furnace for preparing titanium-bearing slag. The smelting process always requires a long time and a high temperature, and the slag-forming reagents added to produce a fluid titaniarich slag will dilute the concentration of titanium dioxide in the slag and have deleterious effects on the subsequent processes of extracting titania [10,11]. Therefore, it would be beneficial to develop a direct reduction processs that produces solid titania-rich slag and metallic iron, and the metallic iron can be removed from the reduced products by either leaching or mechanical separation.

In recent decades, there has a rising interesting in the direct reduction of ilmenite ores, and hydrogen has been investigated as the predominant reductant for the direct reduction of ilmenite ores [12–15]. Furthermore, many studies on the reduction of synthetic ilmenite ores by hydrogen were reported. ZHAO and SHADMAN [16] as well as VIJAY et al [17] examined the reduction process of synthetic ilmenite by hydrogen. It was suggested that intrinsic chemical reaction and diffusion of gaseous species through product layer were the ratecontrolling factors during the reduction process. The temporal profiles of conversion had a sigmoid shape and presented three different stages, i.e., original induction

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stage, medium acceleration stage, and final deceleration stage. VRIES et al [18,19] employed a pressurized thermogravimetric microbalance to investigate the reduction of synthetic ilmenite pellets in the temperature range of 550–900 °C and pressure range of  $(1.2-10)\times10^5$  Pa. However, these isothermal experiments of reduction of Bama ilmenite using H<sub>2</sub>–Ar gas mixtures were carried out by WANG et al [20].

However, the kinetics of reduction of Panzhihua ilmenite by hydrogen is still unclear because of high content of impurities in the ilmenite. In the present work, the influences of temperature and hydrogen content on the reduction rate and degree were investigated, and the reduction kinetics was also discussed. The activation energy of reduction reaction was calculated, and the hydrogen reduction mechanism of ilmenite concentrate was discussed based on the experimental results.

#### 2 Experimental

#### 2.1 Materials

The chemical composition of Panzhihua ilmenite concentrate used in the present work is shown in Table 1. For comparison, synthetic ilmenite was prepared from the mixture of Fe,  $Fe_2O_3$ , and  $TiO_2$  with an appropriate molar ratio at 1200 °C by roasting for 30 h. Figure 1 further indicates the crystalline phases of the synthetic ilmenite and Panzhihua ilmenite. As shown in Fig. 1, the main crystalline phases of the natural ilmenite are magnesian ilmenite ((Fe,Mg)TiO<sub>3</sub>) with a small amount of titanomagnetite (Fe<sub>2</sub>TiO<sub>4</sub>-Fe<sub>3</sub>O<sub>4</sub>). The natural ilmenite and synthetic ilmenite powders were ground by planetary ball mill and screened to obtain similar particle size fractions in the range of 26–104 µm. Then, approximately 1.2 g ilmenite powder was pressed into a cylindrical pellet sized 8 mm in diameter and 5 mm in thickness.

 Table 1 Chemical composition of Panzhihua ilmenite (mass fraction, %)

TiO <sub>2</sub>	FeO	Fe <sub>2</sub>	$_{2}O_{3}$	MgO	SiO <sub>2</sub>
45.48	32.11	7.41		6.85	3.34
Al <sub>2</sub> O <sub>3</sub>	CaO	MnO <sub>2</sub>	$V_2O_5$	S	Р
2.18	1.67	0.68	0.09	0.04	0.15

#### 2.2 Experimental procedure

#### 2.2.1 Thermogravimetric (TG) analysis

The schematic diagram of the thermogravimetric apparatus for the hydrogen reduction experiments is shown in Fig. 2. It consists of a vertical furnace and a computer monitor system used for recording the mass variations during the process. In a typical experiment, an alumina crucible was hung on the central section of furnace chamber by a sapphire extension wire. The sample was put into the alumina crucible and then preheated to a specific temperature in argon atmosphere. Then, in the isothermal period, the reactant gases ( $H_2$ -Ar mixture) were blown into the reaction area. Both of hydrogen and argon gases were measured and controlled by high-accuracy mass flow-meters. At the end of the experiment, pure argon gas was purged into the crucible. Finally, the sample was cooled in inert atmosphere.



**Fig. 1** XRD patterns of Panzhihua natural ilmenite (a) and synthetic ilmenite (b)



Fig. 2 Schematic diagram of TG apparatus

#### 2.2.2 Characterization of reduced ilmenite

The morphology of the reduced pellet was examined using a JEOL JSM-6700F scanning electron microscope (SEM). The elemental composition was analyzed by energy-dispersive X-ray (EDX) spectroscopy attached to the SEM and also by inductively coupled plasma (ICP). The phase constitution was determined by Rigaku D/Max-2550 X-ray diffractometer (XRD).

#### **3 Results and discussion**

As the gas product during the hydrogen reduction process is only water vapor, the reduction degree can be calculated based on the total mass loss during the reduction. Therefore, the experimental results are presented in the form of the mass loss of sample against reduction time. The mass loss fraction is defined as

$$w = \frac{m_0 - m_t}{m_{\text{cal}}} \times 100\% \tag{1}$$

where  $m_0$  is the mass of the initial sample,  $m_t$  is the mass of sample after reduction time *t*, and  $m_{cal}$  is the mass loss obtained by theoretical calculation.

#### 3.1 Effect of hydrogen content on reduction process

The Panzhihua ilmenite pellets were reduced at 1000 °C with 10% $H_2$ -Ar, 30% $H_2$ -Ar, and 50% $H_2$ -Ar mixture (volume fraction) gas, respectively. For each experiment, the temporal profile of conversion was determined by monitoring the sample mass using a recording electrobalance. As shown in Fig. 3, an increase in  $H_2$  content results in an increase in the reduction rate and a decrease in the time required to attain certain fractional mass loss.



Fig. 3 Reduction degrees of Panzhihua ilmenite concentrate reduced by  $H_2$ -Ar mixture gas with various hydrogen contents at 1000 °C

# **3.2 Effect of reduction temperature on reduction** process

Isothermal mass loss measurements were performed in the temperature range of 900–1050 °C. Figure 4 shows the influences of temperature on the reduction of Panzhihua ilmenite (Fig. 4(a)) and synthetic ilmenite (Fig. 4(b)) by H<sub>2</sub>–Ar mixture gas. The reduction rate and degree increase sharply when the temperature increases, and the reduction reaction can finish approximately at 900 °C for 200 min and at 1000 °C for 150 min with 50% H<sub>2</sub>–Ar mixture gas (volume fraction). The reduction rate of Panzhihua ilmenite is lower than that of the synthetic ilmenite, which may be attributed to the high content of impurities in the natural ilmenite. It is known that magnesium atom can dissolve in the ilmenite to form solid solution. Actually, the Panzhihua ilmenite can be expressed as (Fe,Mg)TiO<sub>3</sub>, which is a kind of solid solution mineral. Therefore, it is considered that the lower reduction rate of Panzhihua ilmenite may be mainly attributed to the magnesium oxide containing in the ilmenite.



**Fig. 4** Reduction degrees of ilmenite samples reduced by 50%H<sub>2</sub>-Ar mixture gas at different temperatures: (a) Panzhihua ilmenite; (b) Synthetic ilmenite

The reduction of Panzhihua ilmenite and synthetic ilmenite using pure H<sub>2</sub> was also investigated. As shown in Fig. 5(a), the reduction of Panzhihua ilmenite concentrate by using pure hydrogen at 900 °C for 200 min is incomplete and the reduction degree is approximately 70%. When the reduction temperature increases to 1000 °C, the reduction degree can reach about 92% within 200 min, which shows that higher temperature can improve the reduction rate. When the temperature is above 900 °C, the reaction proceeds rapidly in the initial stage. However, the reaction speed decreases after being reduced for 50 min. As shown in Fig. 5(b), the reduction rate of synthetic ilmenite by  $H_2$  is higher than that of Panzhihua ilmenite concentrate under the same conditions. The reduction degree approaches 98% at 1050 °C within 100 min.



Fig. 5 Reduction degrees of ilmenite samples reduced by pure  $H_2$  at different temperatures: (a) Panzhihua ilmenite; (b) Synthetic ilmenite

#### 3.3 Phase transformation during reduction process

XRD analysis results of the reduced Panzhihua ilmenite samples are given in Fig. 6 and Table 2.

The phases of the sample reduced at 900 °C include iron, magnesian ilmenite and rutile. The diffraction peak intensities of ilmenite and magnesian ilmenite decrease apparently when iron phase appears. The magnesian ilmenite phase is not obvious in the XRD pattern of the sample reduced at 1000 °C. Moreover, with increasing the temperature, the peak intensity of rutile decreases evidently, which suggests that rutile can hardly generate from the solid-solution mineral as an independent phase above 1000 °C. The increase in the peak intensity of ferrous pseudobrookite solid solution phase ((Fe,Mg)Ti<sub>2</sub>O<sub>5</sub>) indicates that M<sub>3</sub>O<sub>5</sub> phases are formed, where M represents the combination of elements such as iron, magnesium and titanium. It was reported that the thermodynamic activity of iron could be lowered due to the formation of M<sub>3</sub>O<sub>5</sub> solid solution [21]. The reported results indicated that the reduction of TiO<sub>2</sub> may occur as long as iron metallization is completed [16,20]. However, the iron in Panzhihua ilmenite can hardly achieve complete metallization due to the formation of stable

solid solution. Therefore, during the reduction process for ilmenite, the reduction of  $TiO_2$  is inhibited.



Fig. 6 XRD patterns of initial sample (a) and obtained samples reduced by pure  $H_2$  at 900 °C (b), 1000 °C (c) and 1050 °C (d) for 200 min

**Table 2** Phase composition of Panzhihua ilmenite reduced by pure  $H_2$  at different temperatures for 200 min

Temperature/°C	Phase		
Initial sample	Ι		
900	Fe, I, R		
1000	Fe, P		
1050	Fe, P		

Fe representing metallic iron; I representing ilmenite; R representing rutile; P representing ferrous pseudobrookite

#### 3.4 Morphology of reduced ilmenite concentrate

Figure 7 shows the micromorphology of the initial Panzhihua ilmenite particle (Fig. 7(a)) and the ilmenite after being reduced at 1000 °C with pure hydrogen for 200 min (Fig. 7(b)). It can be seen that the initial Panzhihua ilmenite particle has a compact structure with no obvious gaps. And several small slivers can be observed on its surface. In contrast, a lot of pores are formed on the surfaces of the ilmenite particles reduced by pure hydrogen at 1000 °C (Fig. 7(b)). The formation of the porous structure may be attributed to the removal of oxygen component containing in the ilmenite particle during the reduction process.

The reduced Panzhihua ilmenite samples embedded in epoxy resin were cut and polished. Figure 8 shows the cross section micromorphologies of the samples reduced by pure hydrogen at 1000 °C for different reduction time. Obviously, two phases are observed, the bright one is the metallic iron and the dark gray one may be attributed to the phase enriched in titania. EDX mapping images of Ti, Mg, O and Fe are also shown in Figs. 8(a), (b) and (c). It is worth noticing that the magnesium moves gradually and then forms an enrichment core. This phenomenon could be explained by the barrier effect [22]. During the



Fig. 7 SEM images of Panzhihua ilmenite before (a) and after (b) being reduced by pure hydrogen at 1000 °C for 200 min



**Fig. 8** Micromorphologies of cross section of Panzhihua ilmenite reduced by pure hydrogen at 1000 °C for 30 min (a), 60 min (b) and 90 min (c) (The insets are their corresponding EDX mapping images of Ti, Mg, O and Fe, respectively)

reduction process, magnesium diffused ahead of the reaction interface to form a magnesium barrier zone in which  $Fe^{2+}$  was replaced by  $Mg^{2+}$ , inhibited hydrogen diffusion in the pellet and hence the activity of  $Fe^{2+}$  was lower. The lower activity of the  $Fe^{2+}$  would make its

reduction process more difficult. Figure 9 shows the schematic diagram showing the barrier effect of magnesium. Moreover, as magnesium oxide can form a more stable solid solution with titanium and iron oxides, magnesium oxide thus has larger barrier effect than other



Fig. 9 Schematic illustration of barrier effect of magnesium during reduction process

impurities such as silicon oxide and aluminium oxide.

#### 3.5 Reduction kinetics

Based on the results of thermogravimetric and micromorphology analyses, it can be concluded that the hydrogen reduction of ilmenite concentrate is a topochemical reaction. According to the reaction kinetics, the relationship between the reduction time (t) and reverse degree (R) can be expressed as [20]

$$\frac{(C_0 - C_{eq})}{r_0^2 \rho_0} t = \frac{1}{6D_e} [3 - 2R - 3(1 - R)^{2/3}] + \frac{1}{kr_0} [1 - (1 - R)^{1/3}]$$
(2)

where  $C_0$  and  $C_{eq}$  are the hydrogen contents on ilmenite surface and in equilibrium, respectively, k is the reaction rate constant,  $D_e$  is the effective diffusion coefficient,  $r_0$ is the characteristic initial radius of ilmenite pellet, and  $\rho_0$  is the initial oxygen content in the ilmenite.

According to the solid-state kinetics [22-24], Eq. (3) is controlled by chemical reactions at the interface, Eq. (4) is controlled by diffusion, and Eq. (5) is controlled by both chemical reactions and diffusion.

$$1 - (1 - R)^{1/3} = kt$$
 (3)

$$1 - (2/3)R - (1 - R)^{2/3} = kt \tag{4}$$

$$3k_1[1-(1-R)^{1/3}]+(3/2)k_2[1-(2/3)R-(1-R)^{2/3}]=t$$
(5)

where k,  $k_1$  and  $k_2$  are the rate constants at different rate-controlling steps.

Based on the results shown in Figs. 4 and 5 and applying Eq. (2), three cases for rate controlling step were examined. It is found that the diffusion of hydrogen gas in the reduced layer was the rate controlling step under all experimental conditions owing to the better linear correlation of  $1-(2/3)R-(1-R)^{2/3}$  to time. The relationship between  $1-(2/3)R-(1-R)^{2/3}$  and time is shown in Figs. 10 and 11 for 50% H<sub>2</sub> and pure H<sub>2</sub> gas, respectively.

Figure 12 shows the relationship between the calculated reaction rate constant and reciprocal



**Fig. 10** Relationship between  $1-(2/3)R-(1-R)^{2/3}$  and time for reduction by 50%H<sub>2</sub>-Ar mixture gas: (a) Panzhihua ilmenite; (b) Synthetic ilmenite

temperature according to the Arrhenius equation. With the extra step of curve-fitting, it is found that the natural logarithm of reaction rate constant (ln *k*) is linearly associated with reciprocal temperature. The apparent activation energies of Panzhihua ilmenite concentrate reduced by 50% H<sub>2</sub> and pure H<sub>2</sub> are calculated to be 128.65 and 117.56 kJ/mol, respectively. And the apparent activation energies of synthetic ilmenite reduced by 50% H<sub>2</sub> and pure H<sub>2</sub> are determined to be 74.42 and 77.80 kJ/mol, respectively. Therefore, the reduction of Panzhihua ilmenite requires higher energy to cross the energy barrier than that for the synthetic ilmenite.



**Fig. 11** Relationship between  $1-(2/3)R-(1-R)^{2/3}$  and time for reduction by pure H<sub>2</sub>: (a) Panzhihua ilmenite; (b) Synthetic ilmenite



Fig. 12 Calculated interface reaction rate constant as function of reciprocal temperature

#### **4** Conclusions

1) In the temperature range of 900–1050 °C, the reduction speed and reduction degree of Panzhihua ilmenite and synthetic ilmenite by  $H_2$ -Ar mixture gas increase with the increase of temperature and hydrogen

content. The products of the Panzhihua ilmenite reduced at approximately 900 °C are metallic iron and rutile. Above 1000 °C, ferrous pseudobrookite solid solution is generated.

2) Compared with synthetic ilmenite, the reduction speed and reduction degree for Panzhihua ilmenite are relatively low due to the impurities containing in the ilmenite. During the reduction process, magnesium containing in the Panzhihua ilmenite can influence the reduction of iron.

3) The reductive kinetics is controlled by the hydrogen diffusion in the reduced layer under the experimental conditions. The apparent activation energy of the hydrogen reduction of Panzhihua ilmenite is evidently larger than that of the synthetic ilmenite. The apparent activation energies of Panzhihua ilmenite concentrate reduced by 50%  $H_2$  and pure  $H_2$  are calculated to be 128.65 and 117.56 kJ/mol, respectively.

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## 攀枝花钛铁矿的氢气还原动力学

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摘 要:采用 TG、XRD 和 SEM 等分析手段,系统研究了 900~1050 ℃ 条件下攀枝花钛铁矿的氢气还原过程。结 果表明:在 900 ℃ 恒温还原过程中,还原产物为铁和金红石,当温度高于 1000 ℃时,亚铁板钛矿开始形成。在 还原过程中,元素镁会逐渐富集并影响金属化过程。同时,讨论了局部化学反应和相关的还原动力学过程,反应 控速步骤为扩散过程。由计算可知,在所选实验条件下,氢气还原攀枝花钛铁矿的表观活化能为 117.56 kJ/mol, 高于合成钛铁矿还原过程中的表观活化能。

关键词:攀枝花钛铁矿;合成钛铁矿;氢气还原;动力学;控速步骤;镁元素迁移

(Edited by Wei-ping CHEN)