Reduction Extraction Kinetics of Titania and Iron from an Ilmenite by H$_2$–Ar Gas Mixtures

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(Received on August 6, 2008; accepted on November 13, 2008)

Reduction of an ilmenite concentrate as a natural concentration containing 49.78 mass% TiO$_2$ and 27.96 mass% total Fe by H$_2$–Ar gas mixtures was investigated from 1 073 to 1 273 K. Both the reduction degree and reduction rate increased with the increase of temperature and hydrogen content. The reduction degree of the ilmenite decreased due to the presence of impurities including manganese and silicon oxides in the ilmenite concentrate. During the reduction, the formation of manganese and silicon oxide-enriched zones prevented complete reduction of Fe$^{2+}$. The reduction products were characterized using X-ray diffraction, scanning electronic microscope with energy disperse spectroscopy and optical microscopy analysis, respectively. The main phases in reduced products were reduced iron, rutile, reduced rutiles, pseudobrookite and Ti$_3$O$_5$. The reduction reaction proceeded topochemically and the reduction kinetics was discussed. It was found that the rate controlling step was the diffusion of hydrogen gas in the reduced layer.

KEY WORDS: ilmenite; reduction; hydrogen; kinetics; rate controlling step.

1. Introduction

Over the past decades, the solid-state reduction of ilmenite has been receiving a great deal of attention as an important process in industry because the sources of high grade titanic mineral are exhausting. In titanium industry, as ilmenite ore is smelted with carbon in the electric furnace, pig iron and titania-enriched slag are produced in this process. Long time and high temperature are usually necessary to precede the reaction with carbon. On the other hand, hydrogen can be more effective to reduce ilmenite at lower temperature in gas–solid reactors such as fluidized bed. The produced moisture is friendlier to environment than the gas products of carbothermic reduction of ilmenite. In recent years there has been a rising interest in the solid-state reduction of ilmenite ores with hydrogen, which might partially be associated with the process for winning oxygen from lunar materials.

Vijay et al.$^{7)}$ investigated the reduction of raw and preoxidized ilmenites with hydrogen in a fluidized bed reactor and found the reduction period could be divided into three distinct stages: initial slow induction stage, intermediate acceleratory stage and final slowing down process. The reducibilities of Egyptian and Norwegian ilmenite ores with hydrogen have been studied by Hussein et al.$^{8)}$ The results showed the reduction of preoxidized ilmenite was easier to reduce than that of raw one. Sun et al.$^{9–11)}$ investigated the hydrogen reduction kinetics of natural ilmenite by the thermogravimetry. Diffusion of gaseous species through product layer and intrinsic chemical reaction were found to be the main rate controlling step during reduction. Isothermal experiments of the reduction of titania-contained ironsand were carried out using H$_2$–Ar gas mixtures in a laboratory-scale fixed bed reactor by Park et al.$^{12–14)}$ Itoh et al.$^{15,16)}$ proposed a new rutile extraction process from natural ilmenite ore by oxidation and magnetic separation in the microwave irradiation. Furthermore, many studies on the reduction of iron ores by gas were reported.$^{17–21)}$

The Bama ilmenite has abundant reserves in Guangxi province of China. However, the kinetics of reduction of the Bama ilmenite with hydrogen is unclear. In the present work, the effects of temperature and hydrogen content on the reduction rate and degree were investigated, and the reduction kinetics was discussed.

2. Experimental

The chemical composition of Bama ilmenite concentrate investigated in the present study is shown in Table 1. The ilmenite was ground and screened to particle size fraction from 71 to 150 μm. About 2 g of ilmenite powder was weighed precisely and then mixed with adhesive (honey which was bought from the market) to be pressed into $\phi 9 \times 6$ mm cylindrical pellets in a steel die under 15 MPa.

The schematic diagram of experimental apparatus is shown in Fig. 1. It consists of a shaft furnace, a temperature...
controller, a water detecting device and an electric furnace for eliminating possible oxygen in H₂–Ar mixtures.

In a typical experiment, the pellets were put into the furnace which was purged with argon. The samples on the grid plate (quartz, pore ratio: 0.4, average pore diameter: 0.1 mm) were preheated for 20 min to ensure the removal of adhesive and moisture completely. Then the gas mixture was introduced into the furnace. At the end of the run, the power was shut off and the pure argon was introduced to keep inert atmosphere for the sample cooling. The high purity H₂ and Ar were used in the experiments. The gases were purified before mixing by passing through gas purifier filled with anhydrous magnesium perchlorate. Then they were introduced in an electric furnace to eliminate oxygen. The flow rate of inlet gas was controlled by the rotameter. The moisture in the outlet gas was detected by a humidity sensor (Hanna Instruments (China) HI-8564, a thin film polymer sensor, measurement range: 10.0–95.0%, resolution: 0.1%, precision: >98%) and the degree of reduction was calculated. The outlet gas line from the bottom of the reactor to water detecting device was heated by a heating-tape at about 403 K. The total gas flow rate was 1000 cm³/min.

The phases in ilmenite samples were determined by using XRD (Philips 1140, Cu Kα, 40 mA current, 30 kV voltage). The morphologies of the specimens were observed by SEM (JSM-6301F, USA) equipped with EDS and optical microscope (LEITZ WETZLAR-307, Germany). The degree of reduction was calculated as a mass fraction of oxygen removed during reduction to that in the iron oxides.

3. Results and Discussion

Figure 2 shows the XRD spectrum of Bama natural ilmenite concentrate. The phases detected are mainly ilmenite and partly pseudorutile. Therefore, the main chemical reactions from 1073 to 1273 K can be expressed as reactions (1) and (2).

FeTiO₃ + H₂ = Fe + TiO₂ + H₂O ...............(1)

1/3 Fe₂Ti₃O₉ + H₂ = 2/3 Fe + TiO₂ + H₂O ...........(2)

The reduction degree W was calculated by Eq. (3),

\[ W = \frac{H \cdot w_t - w' \times 100\%}{w_0} \]

where H is humidity of outlet gas after time t, w, is mass of input gas after time t, and w is the theoretical total moisture mass produced by the reduction of ilmenite by hydrogen, according to reactions (1) and (2), and Table 1. If iron oxides were reduced completely, w is calculated to be 0.1044w₀, where w₀ is initial mass of ilmenite sample.

3.1. Effect of Hydrogen Content

Ilmenite specimens were reduced at 1073 and 1173 K with H₂ varying from 10 to 50 vol% in the H₂–Ar mixtures. Changes of the reduction degree of the ilmenite concentrate with time during the reduction are shown in Figs. 3 and 4 at 1073 and 1173 K, respectively. It is clear that the increase in hydrogen content caused a visible increase in reduction degree and rate. As shown in Fig. 4, the effect of hydrogen content on reduction degree was more obvious at 1173 K.

3.2. Effect of Temperature

Figures 5 and 6 show the effect of temperature on the reduction of ilmenite concentrate by H₂–Ar mixtures from 1073 to 1273 K. Figure 7 shows the influence of temperature on the reduction of ilmenite concentrate by pure hydrogen. The reduction rate and degree increase sharply when the temperature increases, and the reduction reaction finished till 90 min with 30 vol% H₂ and till 80 min with 40 vol% H₂ at 1273 K. When the ilmenite concentrate was reduced at 1173 K for 2 h, the reduction degrees were about 80% and 90% with 30 and 40 vol% H₂, respectively. In the temperature range from 1073 to 1173 K, the slopes of the reduction curves slowly and steadily decreased with increasing the reduction degree as shown in Fig. 5. Compared with the result of Park and Ostrovski, the reduction de-
gree of Bama ilmenite concentrate is lower, which could be attributed to the fact that Bama ilmenite concentrate examined in the present experiments are composed of ilmenite, pseudorutile and some of impurities including manganese and silicon oxides, while the raw materials in Park’s experiment are iron sand composed of mainly iron oxides and only 7.34 mass% titania. According to the thermodynamic calculation, iron oxide is usually reduced more easily than ilmenite and pseudorutile. The result of Zhao and Shadman also demonstrated that the reduction degree of Bama ilmenite concentrate was lower than that of pure ilmenite. It is known that manganese oxide could inhibit the reduction of the ilmenite and lead a lower reduction degree. Therefore, it is considered that the lower reduction rate of Bama ilmenite is due to the manganese oxide contained as an impurity. The silica would also inhibit the reduction due to the formation of fayalite during the reduction process which decreases the reactivity of the iron oxide.

As shown in Fig. 7, the reduction of ilmenite concentrate was incomplete and the reduction degree was approximately 72% at 1 073 K for 2 h even though using pure hydrogen as the reductant. After reduced at 1 123 K for 2 h the reduction degree was up to about 94%, which shows that higher temperature can accelerate the rate of reduction reaction. It can be seen that the reduction of the ilmenite concentrate by pure hydrogen tended to be complete for 90 min at 1 173 K, for 70 min at 1 223 K, for 50 min at 1 273 K, which shows that the reduction time is shortened with the increase of temperature. At constant temperature more than 1 123 K, the reduction reaction proceeded rapidly in the initial stage in the reduction process. However, the reaction rate decreased after reducing for 20 min.

### 3.3. Phases of Reduced Products

The phases in ilmenite concentrate reduced for 120 min by pure hydrogen were analyzed by XRD. The results were shown in Fig. 8. The intensity of iron peaks increased obviously with increasing temperature. The phases of the sample reduced at 1 123 K mainly contained reduced iron, il-
menite, rutile and pseudobrookite. In the pattern of the sample reduced at 1 173 K, ilmenite phase was not observed and reduced rutiles phase appeared. The intensity regarding rutile and pseudobrookite phases increased with the increase of reduction temperature from 1 123 to 1 223 K. The Ti₃O₅ phase appeared in the sample reduced at 1 223 and 1 273 K. Moreover the intensity of pseudobrookite decreased evidently, which suggested that pseudobrookite was reduced and decomposed. Increase in the intensity of Ti₃O₅ phase suggested that the reduction reaction was enhanced at 1273 K. These results show that high temperature is effective for occurrence and proceeding of the reduction of ilmenite. The reduction rate can be enhanced and the reduction degrees increase with increasing temperature. The results are consistent with the above analysis of Sec. 3.2.

3.4. SEM and EDS Analysis

The SEM micrographs of the samples reduced for 2 h with pure hydrogen at 1 273 K are shown in Fig. 9. The micrographs revealed two distinct regions which appeared as bright and dark gray phases. X-ray Kα mappings of iron, titanium and oxygen are shown in Figs. 9(a), 9(b) and 9(c), respectively. It could be seen that the bright phase and dark gray one were mainly iron phase and titanium oxides, respectively. From the micrographs there were many pores in titanium oxides due to the oxygen removal in iron oxides. During the reduction, iron nuclei formed extensively and grew simultaneously. Furthermore, the small iron masses were unstable and moved to agglomerate. Therefore, the coalescence of iron was evident. Thermodynamically, this phenomenon was attributed to the minimization of the total surface energy. Due to the quick growth of iron nuclei and the coalescence of iron in the reduction process, the produced iron was accumulated. When the iron mass grew up to some extent, the global shape was destroyed. Therefore, iron was mainly in the strip shape and a spot of global iron could also be observed in the reduced samples.

Figure 10 shows SEM micrograph and EDS results of different microzone of the same sample reduced by pure hydrogen at 1 273 K. The EDS analyses of the sample indicated that the phase enriched in titanium was depleted in iron and vice versa. This confirmed the high degree of segregation between iron and titanium oxides occurred in the reduced samples, which is consistent with the above results. The finding has important implications for product separation and recovery of Fe and TiO₂ from ilmenite, particularly for the application of magnetic separation method.

3.5. Morphology of Reduced Ilmenite Concentrate

Figure 11 shows the morphologies of ilmenite concentrate reduced by 30 vol% H₂ at 1 123 K for different time with optical microscope. It can be seen that the iron layer was formed on the surface of the granule after ilmenite concentrate was reduced using 30 vol% H₂ for 30 min at 1 123 K. Beneath the iron layer, the layer of titanium oxides was produced, where a small quantity of iron was distributed. An unreacted core in the granule could be observed in both samples reduced for 30 and 60 min at 1 123 K. The results indicate clearly that the hydrogen reduction proceeded...
from surface to inner part of the granule topochemically. Figure 12 shows a mechanism model of the ilmenite reduced with hydrogen. The reaction was divided into three stages in the reduction process. In the initial stage, the reaction mainly proceeded according to reaction (1), and the reaction rate was fairly slow. In the middle stage, the reaction rate was enhanced because TiO₂ pore opened up and hydrogen transported to the reaction front was enhanced. The unreacted core dwindled as the reduction time was prolonged. At the same time, the thickness of the iron layers and titanium oxides increased gradually. Finally, depletion of FeTiO₃ resulted in a decrease in the rate of reduction. When the unreacted core disappeared the reduction reaction was accomplished. Moreover, the resistance of hydrogen diffusion to the unreacted core enhanced because of the increase of the thickness of the iron layer and titanium oxide, which also caused the decrease of the reduction rate.

3.6. Reaction Kinetics

Based on the observed results, it can be concluded that the reduction of the pellet proceeded topochemically. According to the previous studies, this kind of reaction included the process of diffusion of gaseous species and that of intrinsic chemical reaction. The total reduction time is expressed by Eq. (4), which is valid under the conditions of solid sphere being reacted with gas phase, the effect of gas phase mass transfer being negligible and the reaction rate being controlled by intrinsic interfacial chemical reaction and the diffusion of reactant and product gas species through solid product layer.

\[
t = \frac{r_0 \rho_0}{k(C_0 - C_q)} \left[ 1 - (1 - R)^{1/3} \right] + \frac{r_0^2 \rho_0}{D_c(C_0 - C_q)} \left[ (1/2 - R/3 - (1 - R)^{2/3}/2) \right] \tag{4}
\]

where \( t \) is reduction time (min), \( C_0 \) and \( C_q \) are reduction gas concentration at granule surface and in equilibrium, respectively (mol/cm³), \( k \) is reaction rate constant (cm/min), \( D_c \) is effective diffusion coefficient (cm²/min), \( r_0 \) is characteristic initial radius of ilmenite pellet (cm), \( \rho_0 \) is initial oxygen concentration in the pellet (mol/cm³), and \( R \) is reduction degree.

Based on the results shown in Figs. 5 to 7 and applying Eq. (4), three cases for rate controlling step were examined, namely, (i) chemical reaction control, (ii) diffusion control, and (iii) mixed control. It was found that diffusion of hydrogen gas in the reduced layer was the rate controlling step at all experimental conditions for temperature and hydrogen content. The relationship between \( 1/2 - R/3 - (1 - R)^{2/3}/2 \) and time is shown in Figs. 13 to 15 for 30, 40 and 100 vol% H₂ gas, respectively.

The slopes of lines in the figures were obtained from linear regression analysis, and the effective diffusion coefficient was calculated at each experimental condition from the following relationship,

\[
\text{(Slope)} = \frac{D_c(C_0 - C_q)}{r_0^2 \rho_0} \tag{5}
\]

To estimate the effective diffusion coefficient, \( r_0 \) is assumed to be 0.5 cm resulting the pellet volume equivalent to that of the pellet (φ₉×8 mm), \( \rho_0 \) is assumed to be 0.031 mol/cm³ from the composition and density of FeTiO₃ (61 mass%, 4.72 g/cm³) and Fe₂Ti₃O₉ (39 mass%, 4.13 g/cm³) assumed by ferric and ferrous ratio shown in Table 1. The number of \( C_0 \) in Eq. (5) is \( 1.22x \times 10^{-4}/T(K)\text{mol/cm}^3 \) for \( x \text{vol%H}_2\text{–Ar} \text{gas} (x=30, 40 \text{or} 100) \), and \( C_q \) is assumed to be zero. Figure 16 shows the calculated effective diffusion coefficients as a function of reciprocal temperature. The logarithmic values of effective diffusion coefficients with reciprocal temperature show the linear relationship. The activation energy for the diffusion of hydrogen in reduced layer was calculated to be 163 ±1, 167 ±3 and 147 ±2 kJ/mol for 30, 40 and 100 vol% H₂ gas, respectively. The effective diffusion coefficients and activation energies calculated from the results of reduction by 30 and
40 vol% H₂–Ar gases are quite similar, while the coefficients and activation energy calculated from that by 100 vol% H₂ are lower. The difference of calculated diffusion coefficients is remarkable at higher temperature, and lower diffusion coefficient for 100 vol% H₂ gas at high temperature range causes the lower activation energy. As shown in Fig. 15, the relationship between 1/2 – R/3 – (1 – R)²/3 and time is taken out of the linear relationship at higher temperature. Therefore, the calculated effective diffusion coefficients depart from the linear relationship extended from lower temperature in Fig. 16. It is considered that the reduction behavior by pure hydrogen at higher temperature is beyond the case of simple topochemical unreacted core model expressed by Eq. (4) and the other reduction model should be applied.

4. Conclusions

The reduction kinetics and behavior of the Bama ilmenite by H₂–Ar mixture gas were investigated from 1 073 to 1 273 K. The results can be summarized as follows:

1) Generally, reduction products with pure hydrogen were iron, rutile, reduced rutiles, pseudobrookite and Ti₃O₅. The reduction of the pellet with H₂–Ar gas mixtures proceeded topochemically. Increase of temperature and H₂ content was beneficial to the reduction of ilmenite concentrate.

2) The reduction degree decreased owing to the impurities in Bama ilmenite. It is considered that the manganese and silicon oxides disturbed the complete reduction of Fe²⁺.

3) The hydrogen diffusion in the reduced layer was the rate controlling step at all experimental conditions for temperature and hydrogen content.

Acknowledgements

The present work has been supported by the National Nature Science Foundation of China (No. 50474043).

REFERENCES

1) Y. Wang and Z. Yuan: Int. J. Miner. Process., 81 (2006), 133.
2) Z. Yuan, X. Wang, C. Xu, W. Li and M. Kwauk: Min. Eng., 19 (2006), 975.
3) Y. Liu, T. Qi and J. Chua: Int. J. Miner. Process., 81 (2006), 79.
4) W. Li, Z. Yuan, C. Xu, Y. Pan and X. Wang: J. Iron Steel Res. Int., 12 (2005), No. 4, 1.
5) Y. Zhao and F. Shadman: Ind. Eng. Chem. Res., 30 (1991), 2080.
6) N. Welham: J. Mater. Sci., 36 (2001), 2343.
7) P. Vijay, R. Venugopalan and D. Sathiyanamoorthy: Metall. Mater. Trans. B, 27B (1996), 731.
8) M. Hussein, R. Kammel and H. Winterhager: Indian J. Technol., 5 (1967), 369.
9) K. Sun, R. Takahashi and J. Yagi: ISIJ Int., 33 (1993), 523.
10) K. Sun, M. Ishii, R. Takahashi and J. Yagi: ISIJ Int., 32 (1992), 489.
11) K. Sun, R. Takahashi and J. Yagi: ISIJ Int., 32 (1992), 496.
12) E. Park and O. Ostrovski: ISIJ Int., 44 (2004), 999.
13) E. Park and O. Ostrovski: ISIJ Int., 44 (2004), 74.
14) E. Park, S. Lee, O. Ostrovski, D. Min and C. Rhee: *ISIJ Int.*, 44 (2004), 214.
15) S. Itoh, T. Suga, H. Takizawa and T. Nagasaka: *ISIJ Int.*, 47 (2007), 1416.
16) S. Itoh, S. Sato, J. Ono, H. Okada and T. Nagasaka: *Metall. Mater. Trans. B*, 37B (2006), 979.
17) M. L. Vries, I. E. Grey and J. D. Gerald: *Metall. Mater. Trans. B*, 38B (2007), 267.
18) C. Feilmayr, A. Thurnhofer, F. Winter, H. Mali and J. Schenk: *ISIJ Int.*, 44 (2004), 1125.
19) H. Purwanto, T. Shimada, R. Takahashi and J. Yagi: *ISIJ Int.*, 41 (2001), S31.
20) Y. Iguchi, K. Hori and T. Shibata and S. Hayashi: *ISIJ Int.*, 44 (2004), 984.
21) I. Sohn and R. Fruehan: *Metall. Mater Trans. B*, 36B (2005), 605.
22) K. Suresh, V. Rajakumar and P. Grievson: *Metall. Trans. B*, 18B (1989), 735.
23) H. W. Kang, W. S. Chung, T. Murayama and Y. Ono: *ISIJ Int.*, 38 (1998), 324.
24) A. Habermann, F. Winter, H. Hofbauer, J. Zirngast and J. L. Schenk: *ISIJ Int.*, 40 (2000), 935.
25) M. H. Khedr: *ISIJ Int.*, 40 (2000), 309.
26) J. Szekely and N. J. Themelis: Rate Phenomena in Process Metallurgy, John Wiley & Sons, Inc., New York, NY, (1971), 614.
27) W. L. Roberts, T. J. Campbell and G. R. Rapp, Jr.: Encyclopedia of minerals 2nd ed., Van Nostrand Reinhold, New York, (1990), 394, 496.