Reduction Kinetics of FeTiO₃ Powder by Hydrogen

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The reduction kinetics of FeTiO₃ powder by hydrogen has been studied. According to the isothermal reduction experiments at the temperatures of 1023 K, 1073 K, 1123 K and 1173 K, it was found that the reduction products were mainly Fe and TiO₂. During the reduction process, chemical reaction was found to be the rate controlling step. Meanwhile, the particle size distribution of FeTiO₃ powder has a significant influence on the reduction kinetics.

KEY WORDS: FeTiO₃; hydrogen; particle size distribution; chemical reaction; diffusion.

1. Introduction

Most of the metallic titanium and titania white pigment are produced by titanium tetrachloride obtained from the chlorination of high grade titania minerals (e.g. rutile) or titania-enriched slags. However, the resource of rutile is exhausting. And, the production of titania-enriched slags in electric furnace by the reaction of ilmenite with carbon needs a long time and high temperature. Thereby, reducing ilmenite by hydrogen seems to be a promising method to concentrate titania at a low temperature. Meanwhile, the produced moisture is friendly to environment.

The reduction of ilmenite by hydrogen has been studied by many researchers.¹–⁶) However, the kinetic mechanism is still unclear. Because the main component of ilmenite is FeTiO₃, it is important to clear the reduction kinetics of FeTiO₃ first, which is the main aim of the present work.

2. Experiment and Procedures

High purity FeTiO₃ powder (Alfa Aesar, 99.8% purity) was used in this study, and the particle size distribution is shown in Fig. 1. The reduction kinetics of FeTiO₃ powder was studied by using thermogravimetric analyzer. The temperature was controlled within ±2 K. During each isothermal experiment, 60 mg FeTiO₃ was precisely weighted and held in an alumina crucible. Then the furnace was heat to the desired temperature quickly with the protection of Ar gas. After the thermal equilibrium was established, atmosphere was changed to pure hydrogen. Then, reduction mass change was monitored continuously for 1 h. After reacting for 1 h, the reaction was arrested by changing hydrogen to Ar gas, and the furnace was allowed to cool down naturally.

Our aim is to enrich titania and separate Fe from FeTiO₃.

So, the reduction of TiO₂ should be avoided. Therefore, the reduction reaction could be expressed as follows,

\[ \text{FeTiO}_3 + \text{H}_2 = \text{Fe} + \text{TiO}_2 + \text{H}_2\text{O} \]

In order to establish the proper reaction temperature, non-isothermal reduction of FeTiO₃ and TiO₂ by pure hydrogen were done with the heating rate of 10 K/min. The mass changes were shown in Figs. 2 and 3. It can be seen that the weight loss of FeTiO₃ was started from 900 K, before which no change of sample weight was found. Around 1 200 K, there is an obvious change of the weight loss rate, which may result from the reduction of TiO₂. This can be proved by the reduction of TiO₂ in Fig. 3. Therefore, in the temperature range of 900 K–1 200 K, reaction (1) is the main reaction, and the reduction of TiO₂ could be neglected. The XRD pattern of sample after reduction at 1 173 K for 1 h was shown in Fig. 4. It can be seen that the main product phases are Fe and TiO₂. So, in this work, four temperatures of 1 023 K, 1 073 K, 1 123 K and 1 173 K were chose to study the reduction kinetics of FeTiO₃.

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3. Isothermal Experiments Results

Figure 5 presents the cross sectional SEM image of sample reduced at 1 173 K for 60 min, from which it can be seen that the product is dense. The white phase and gray phase in the product are Fe and TiO$_2$, respectively. The unreacted core shrinking model can be used to describe the reduction kinetics of FeTiO$_3$ by hydrogen.\(^{1,7}\) According to unreacted core shrinking model, the reduction of FeTiO$_3$ by hydrogen can be approximately divided into three main steps: diffusion of hydrogen in the gas phase boundary; diffusion of hydrogen in the product layer; chemical reaction at the interface. Generally, the first step is not the rate controlling step. The rate of the first step is strongly affected by the gas flow when the flow is low. So, it is better to understand the influence of gas flow first to decrease the influence of this factor. The isothermal experiments at 1 023 K with hydrogen flows of 40 ml/min, 50 ml/min, 60 ml/min and 70 ml/min were done. Figure 6 shows the variations of reaction fraction $\zeta$ (defined in Eq. (2)) as function of time at different gas flows. When the gas flow is higher than 60 ml/mol, the change of gas flow has no influence on the reduction kinetics. Therefore, all the isothermal experiments will be done with the hydrogen flow of 60 ml/min.
where $\Delta m$ is the weight loss at time $t$; $\Delta m_{\text{max}}$ is the theoretical maximum weight loss; $m_0$ is the initial weight; coefficient of 0.105 is the theoretical maximum weight loss ratio when FeTiO$_3$ is completely reduced to Fe and TiO$_2$.

**Figure 7** shows the reaction fractions as functions of time at different temperature. From Fig. 7, the reduction rate increases sharply as increasing temperature: at 1 023 K for 1 h, the reaction fraction was about 75%, while the fraction increases sharply as increasing temperature: at 1 173 K. Next, the kinetic for the reduction reaction of FeTiO$_3$ by hydrogen will be discussed.

### 4. Reduction Kinetics

#### 4.1. Kinetic Model

It is indicated that for a gas-solid reaction, if it is controlled by chemical reaction, the reaction fraction can be expressed as Eq. (3), while if it is controlled by the gas diffusion in the product layer, the reaction fraction can be expressed as Eq. (4).

\[
\zeta = 1 - \left( 1 - \frac{k' \cdot \exp \left( \frac{-E_{\text{rea}}}{RT} \right)}{R_0^3} t \right)^3 \quad \text{(3)}
\]

\[
\zeta = 1 - \left( 1 - \sqrt{\frac{k'' \cdot \exp \left( \frac{-E_{\text{diff}}}{RT} \right)}{R_0^2} t} \right)^3 \quad \text{(4)}
\]

where $k'$ and $k''$ are constants for a fixed material; $E_{\text{rea}}$ and $E_{\text{diff}}$ are activation energies; $R$ is the gas constant, 8.314 J/(mol-K); $T$ is the absolute temperature, K; $t$ is time, s; $R_0$ is the initial radius of particle, $\mu$m.

Equations (3) and (4) assume that all particles in powder have the same radiiuses, but not consider the real PSD (particle size distribution) of powder. From Fig. 1, it can be seen that the radiiuses of particles have significant differences. It was found that the PSD of powder greatly affects the kinetic behavior of gas-solid reaction. After considering the PSD, kinetic formulae are given as follows,

\[
\tilde{\xi} = \int_{R_1}^{R_2} \frac{4}{3} \pi R_0^3 \cdot \zeta \cdot N \cdot f(R_0) dR_0
\]

\[
\tilde{\xi} = \int_{R_1}^{R_2} \frac{4}{3} R_0^3 \cdot \zeta \cdot f(R_0) dR_0
\]

\[
\tilde{\xi} = \int_{R_1}^{R_2} \frac{4}{3} R_0^3 \cdot f(R_0) dR_0
\]

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\]

where $f(R_0)$ just equal to the factor $\int_{R_1}^{R_2} R_0^3 \cdot f(R_0) dR_0$ which also represents the volume percentage of particle having the radius of $R_0$. When combining Eqs. (3) and (4) with Eq. (6), the corresponding reaction fraction of powder can be expressed as Eqs. (7) and (8), respectively.

\[
\tilde{\xi} = \int_{R_1}^{R_2} \frac{4}{3} R_0^3 \cdot \zeta \cdot f(R_0) dR_0
\]

\[
\tilde{\xi} = \int_{R_1}^{R_2} \frac{4}{3} R_0^3 \cdot f(R_0) dR_0
\]

\[
\tilde{\xi} = \int_{R_1}^{R_2} \frac{4}{3} R_0^3 \cdot f(R_0) dR_0
\]

Now, Eqs. (3), (4), (7) and (8) will be used to deal with the kinetic curves in Fig. 6.

### 4.2. Results and Discussion

Two parameters are needed to be optimized for every kinetic formula: $k'$ and $E_{\text{rea}}$ for Eq. (3); $k''$ and $E_{\text{diff}}$ for Eq. (4); $k'$ and $E_{\text{rea}}$ for Eq. (7); $k''$ and $E_{\text{diff}}$ for Eq. (8). It should be pointed out that when using Eqs. (7) and (8), the integration is approximately replaced by a series sum.

**Figures 8, 9, 10 and 11** are the comparisons of experimental data with the calculated data by Eqs. (3), (4), (7) and (8), respectively. It can be seen from Figs. 8 and 9 that the diffusion controlled kinetic formula (Eq. (4)) can not describe the reduction of FeTiO$_3$ by hydrogen, even if taking into consideration the influence of PSD. When using the chemical reaction controlled kinetic formula (Eq. (3)), it can be seen from Fig. 10 that good consistence is obtained. After considering the PSD, the calculated results become much better (shown in Fig. 11). Mean deviation $\Delta$ defined as

\[
\frac{1}{N} \sum_{i=1}^{N} \left| \frac{\xi_{\text{exp},i} - \xi_{\text{cal},i}}{\xi_{\text{exp},i}} \right|
\]

where $N$ is the number of data points;
\( \xi_{\text{exp}} \) and \( \xi_{\text{cal}} \) are the measured fraction and calculated reaction fraction, respectively, used to assess the different kinetic formulae quantitatively. Table 1 shows the mean deviations for different formulæ, which also indicates that the calculation results of chemical reaction considering PSD best represent the reduction kinetic curves. According to the above analyses, the reduction of FeTiO\(_3\) powder is controlled by the chemical reaction step, and the particle size distribution greatly affects the reduction kinetics. The optimized values for parameters \( k' \) and \( E_{\text{rea}} \) in Eq. (7) are \( 2.566 \times 10^{-6} \text{ m/s} \) and 136.4 kJ/mol, respectively.

5. Conclusions

The isothermal experiments of reducing FeTiO\(_3\) powder by using pure hydrogen is studied in this work. It is found that in the temperatures range of 1,023 K–1,173 K, the products are Fe and TiO\(_2\) after reaction for 1 h. Chemical reaction is the controlling step for the reduction of FeTiO\(_3\) powder; meanwhile, the particle size distribution has a significant influence on the reduction kinetics. The activation energy for reduction reaction is 136.4 kJ/mol.

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