Effects of the Content and Particle Size of Char in the Composite on the Carbothermic Reduction of Titanomagnetite at 1 100°C

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The effects of molar ratio of C/O and the particle size of char on carbothermic reduction of titanomagnetite (TTM) were investigated from a kinetic viewpoint at 1 100°C employing thermogravimetric analysis (TGA) and quadruple mass spectrometry (QMS). An increase in molar ratio of C/O results in a higher rate of carbon gasification, leading to an increase in final fraction reduction of TTM since excessive amount of char in TTM and char composite shifted the equilibrium in carbothermic reduction of TTM from the wustite/Fe equilibrium to that by the carbon gasification. With decreasing the particle size of char, the carbothermic reduction of TTM was improved by the activation of carbon gasification.

KEY WORDS: titanomagnetite; carbothermic reduction; molar ratio of carbon to oxygen; particle size.

1. Introduction

Due to the depletion of high grade hematite ores, it has been attempted to utilize magnetite ores in the conventional blast furnace ironmaking or direct reduced iron (DRI) production.15 The gas-based DR processes, such as, MIDREX or HYL III is becoming more and more competitive due to low price of shale gas. Nevertheless, coal-based DRI processes such as rotary kiln or rotary hearth furnace are still receiving great attention for producing virgin iron.16 However, extensive understanding of DRI production technology using magnetite ores is still demanded.

The fundamental researches about the mechanism and kinetics of carbothermic reduction of iron oxides were extensively carried out. Rao25 found that the carbothermic reduction of Fe₂O₃ by graphite proceeds much more rapidly in mixtures with proportionately higher carbon content. Srinivasan and Lahiri26 showed that a decrease in C/Fe₂O₃ ratio results in a lower rate of carbon gasification, leading to a decrease in the partial pressure of CO inside the sample. Fruehan27 confirmed the reduction rate of Fe₂O₃ by graphite increases with decreasing particle size and increases with the increasing carbon content. Kashiwaya et al.28 showed that the ratio of reduction rate to gasification rate increased as the distance of hematite and graphite decreases in the study on the coupling phenomena between reduction and gasification. Recently, Chen et al.29 reported that the Boundouard reaction proceeds at a much faster rate to provide the redundant CO with increasing pulverized coal content.

In most of the studies, the compositional change in the off gas with varying the carbon content in the composite has not been clearly shown in terms of QMS analyses. The current study aims to obviously evaluate the rates of reduction and gasification affected by the variation of the carbon content and particle size of char in the composite.

2. Experimental

Table 1 shows the chemical compositions of titanomagnetite (TTM) used in this study (about 190 μm in diameter). From the mass percent of FeO and Fe₂O₃ in Table 1, the oxygen content combined with Fe was calculated to be about 21.64 mass%, which is the theoretical loss in mass per 100 g of TTM for complete reduction. The char used in the current study was prepared by heating a coal at 950°C for 3 h in N₂ atmosphere and it was analyzed to contain 2.63 mass% of volatile matter (VM) and 10.1 mass% of ash as shown in Table 2.

Pulverized titanomagnetite (about 30 μm in diameter) and char (about 10 μm in diameter) with a corresponding molar ratio of carbon in char to removable oxygen in TTM were homogeneously mixed using a ball mill. The pellets were formed into cylindrical shape (10 mm in diameter and 7 mm in height) weighing 1.5 g (±0.10 g) by a hydraulic press under the pressure of 50 MPa for 1 min with distilled water added to ensure complete compactness. The pellet was placed into a cylindrical Al₂O₃ crucible (14 mm in diameter and 20 mm in height) which was then suspended and connected using a Pt wire to the balance part of a thermogravimetric analysis (TGA) apparatus. The isothermal reduction experiments were performed rapidly by heating up the TGA furnace at 100°C/min to 1 100°C. The flow rate of Ar carrier gas was preliminarily determined to be 250 mL/min.

3. Results and Discussion

3.1. Evaluation of Fractional Reduction of Titanomagnetite (TTM) and Variable Char Composite by TGA

It is generally known that the reduction of iron oxide by carbon occurs through the gaseous intermediates CO and CO₂ as represented by Eqs. (1) and (2).31 Under the assumption that all the CO gas generated by carbon gasification was used for the reduction in the titanomagnetite, the overall reduction can be expressed by Eq. (3):

\[ \text{TTM} + \text{CO(g)} = \text{reduced TTM} + \text{CO}_2(g) \]  \hspace{1cm} (1)

\[ \text{C(s)} + \text{CO}_2(g) = 2\text{CO(g)} \]  \hspace{1cm} (2)

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The stoichiometric amount of char was estimated to reduce all the removable oxygen combined with Fe in the TTM based on the following reduction reaction considering that the TTM contains 0.2164 g in 1 g of TTM and that the

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fixed carbon of the char is 87.32 mass%:

\[
\text{Amount of required char (g)} = 0.2164 \times \frac{MW_c}{MW} \times \frac{100}{87.32} = 0.1859 \text{ g} \quad \quad (4)
\]

where \(MW_i\) represent the molecular weight of component \(i\).

Since one oxygen atom in TTM is removed together with one carbon atom with the progress of reduction based on Eq. (3), the weight change of TTM can be calculated by Eq. (7) in terms of the weight change by TGA:

\[
\Delta W_{\text{TGA}} = \Delta W_{\text{TTM}} + \Delta W_{\text{char}} \quad \quad (5)
\]

\[
\Delta W_{\text{TTM}} : \Delta W_{\text{char}} = 16 : 12 \quad \quad (6)
\]

\[
\Delta W_{\text{TTM}} = \Delta W_{\text{TGA}} \times (16/28) \quad \quad (7)
\]

The fractional reduction of TTM can be evaluated by the weight change of TTM with respect to the oxygen content combined with Fe in TTM as represented by Eq. (8). In particular, the initial mass of TTM, \(W_{\text{TTM,0}}\), should be calculated taking into account of the corresponding molar ratio of the carbon in char to the removable oxygen in TTM by Eq. (9):

\[
\text{Fractional reduction} = \frac{\Delta W_{\text{TTM}}}{W_{\text{TTM,0}} \times 0.2164} \quad \quad (8)
\]

\[
W_{\text{TTM,0}} = W_{\text{(TTM+char,i)}} \times \frac{1}{1+(\text{molar ratio, C/O}) \times 0.1859} \quad \quad (9)
\]

where the molar ratio, C/O was varied from 0.50 to 1.25 as shown in Table 3.

On the other hand, the fractional reduction can also be determined by considering the fraction of oxygen removed, which can be estimated by the composition of off gases in terms of QMS. That is, the composition of the off gas was analyzed to compare the rates of reduction and gasification as shown in Fig. 1. The rates of reduction (RDR) and gasification (RCS) were evaluated by the balances of oxygen and carbon in the product gases in Ar atmosphere of fixed flow rate, respectively:

\[
\text{RDR (mol/min)} = \frac{[\text{CO (mL/min)} + 2 \times \text{CO}_2 (\text{mL/min})]\times \frac{1 \text{ mol}}{22451 \text{ mL}}}{16} \quad \quad (10)
\]

\[
\text{RCS (mol/min)} = \frac{[\text{CO (mL/min)} + \text{CO}_2 (\text{mL/min})]\times \frac{1 \text{ mol}}{22451 \text{ mL}}}{16} \quad \quad (11)
\]

where CO and CO$_2$ mean the flow rates of respective gases in mL/min.

\[
\text{Fractional reduction} = \frac{\Delta W_{\text{TTM}}}{W_{\text{TTM,0}} \times 0.2164} = \frac{\sum \text{RDR} \times \Delta t (\text{mol}) \times 16 \text{ g/mol}}{W_{\text{TTM,0}} \times 0.2164} \quad \quad (12)
\]

The fractional reduction of TTM was obtained by integrating RDR in Eq. (8) with time, which was plotted with RDR and RCS in Fig. 1. It indicates that the fractional reduction evaluated by TGA is in approximate accordance with that estimated by QMS. Since RDR is slightly faster than RCS in the progress of reduction as shown in Fig. 1, one carbon atom could ultimately remove more than one oxygen atom in Eq. (3), which might be ascribed to the slight difference in the fractional reduction values evaluated by TGA and QMS.

3.2. Effect of Molar Ratio of C/O in the Composite on the Maximum Rates of Reduction and Gasification

The isothermal reduction of TTM with char at 1100°C was performed as shown in Fig. 1. The fastest reduction rate was observed in between 0.20 and 0.30 of fractional reduction where the apparent reduction rate constant (\(k\)) is the largest. This reduction stage corresponds to the state where TTM, magnetite and metallic Fe coexist. The specific fractional reduction of 0.21 can be calculated for the stage where all the Fe$_3$O$_4$ in TTM reduces to wustite with respect to the reduction completion of TTM and char composite considering that FeO in ulvospinel is not easily reducible since it is tightly bonded with TiO$_2$.

The molar ratio of carbon in char to the removable oxygen was varied from 0.5 to 1.25 as shown in Fig. 2(a). The final fractional reduction increased with increasing the molar ratio of C/O although the reduction rates adjacent to the fractional reduction of 0.21 are not different each other. It is believed that this is because the final fractional reduction was determined by the carbon requirement for carbothermic reduction. Before the fractional reduction reaches about 0.5, the four cases in the molar ratio of C/O are the identical conditions. In particular, to explain the effect of the change in char amount added, the maximum rates of reduction and gasification were plotted against the molar ratio of C/O as shown in Fig. 2(b). With increasing the molar ratio of C/O, the rate of gasification was improved, which then resulted in the increase of \(P_{\text{CO}_2}\) inside the pellet. Then this contributed to the further increase of TTM reduction, which results in the increase of \(P_{\text{CO}_2}\). After all, this leads to the further improvement of gasification. In summary, the molar...
ratio of C/O in carbothermic reduction of TTM change in parallel with $p_{\text{CO}}/p_{\text{CO}_2}$. That is, $p_{\text{CO}}/p_{\text{CO}_2}$ tend to approach the equilibrium of wustite/Fe in TTM for low molar ratio of C/O and the char gasification equilibrium for high values of the ratio considering that the char gasification is the rate controlling step in the progress of reduction, which is clear in Fig. 1. This indicates that the carbon should be added to the pellet in excessive amount for shifting the equilibrium in carbothermic reduction of TTM from the wustite equilibrium to that dominated by the carbon gasification.

3.3. Effect of Particle Size of Char on the Reduction of TTM

Surface area ($A$) of $n$ spherical particles of average diameter ($d_{av}$) can be evaluated by the following simple relationship:

$$A = n \times 4\pi \left( \frac{d_{av}}{2} \right)^2 = n \times \pi d_{av}^2 \quad \text{......... (13)}$$

Assuming that the particle size follows the Gaussian distribution with average diameter ($d_{av}$), then the number of particles occupying the volume ($V$) can simply be calculated by the following relationship for the mass ($m$) and density ($\rho$) of the particles:

$$n = \frac{V}{(4\pi / 3) \times (d_{av} / 2)^3} = \frac{6m}{\rho \pi d_{av}^3} \quad \text{......... (14)}$$

Therefore, the combination of Eqs. (13) and (14) leads to $A/m = 6/(\rho d_{av})$. That is, the specific surface area of particles is inversely proportional to the average diameter of particles.

As shown in Fig. 3, with decreasing the diameter of char particle, that is, with increasing the specific surface area, the maximum rate of gasification (RCS) was increased, which led to increase of $p_{\text{CO}}$. The enhancement of reduction rate by decreasing the particle size indicates that the carbon gasification reaction is at least one of the rate controlling steps even at 1100°C, which can be explained by the variation of RDR and RCS with time in Fig. 1. That is, the rate of reduction is slightly larger than the rate of gasification at 1100°C in the progress of carbothermic reduction of TTM, which strongly indicates that the carbon gasification reaction might be clearly the rate controlling step throughout the course of reduction. This is in contrast to the previous result by Otsuka and Kunii. They reported that carbon gasification reaction may be rate controlling throughout the course of reduction, the final stages being probably controlled by the reduction of wustite by CO.

4. Conclusions

Through the carbothermic reduction in titanomagnetite by char at 1100°C, the following conclusions were obtained.

(1) It was confirmed that the fractional reductions of TTM evaluated by TGA was in approximate agreement with those estimated by QMS.

(2) An increase in molar ratio of C/O results in a higher rate of carbon gasification, leading to an increase in final fractional reduction of TTM since excessive amount of char in TTM and char composite shifted the equilibrium in carbothermic reduction of TTM from the wustite equilibrium to that dominated by the carbon gasification.

(3) Through the analysis of off gas with QMS, it was clarified that the decrease in the particle size of char in the composite of TTM and char increased the rate of gasification reaction, which contributed to the improvement of TTM reducibility.

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