Reduction of the Mixture of Titanomagnetite Ironsand and Hematite Iron Ore Fines by Carbon Monoxide

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1. Introduction

Reduction of New Zealand ironsand by carbon monoxide and the effects of preoxidation were studied by authors of this paper in Refs. 1) and 2). The New Zealand ironsand predominantly consists of titanomagnetite (TTM, Fe$_{3-x}$Ti$_x$O$_4$, with x = 0.27±0.02), and contains about 57 mass% of total iron,1) with the price of about 2/3 of the conventional hematite iron ores.3) The titanium in TTM ironsand affects the applications of the ironsand for ironmaking processes in many ways. It has been reported that the reduction of TTM ironsand is much slower than that of magnetite or hematite iron ores due to the spinel cubic structure and higher thermodynamic stability of TTM phase resulted from the substitution of titanium in the lattice.1,2,4–7) The complete reduction of iron oxides in TTM ironsand by carbon monoxide is possible at high temperatures around 1 373 K, under high reducing potential.1,4,6,7) Although it has been reported that the preoxidation increases the reducibility of the ironsand,5,7) the high content of titanium oxide in the ironsand is not preferable for the further ironmaking processes, because the titanium oxides in TTM ironsand form TiN, TiC and TiO, which have very high melting points and, in large amounts,8) can decrease the sulphide capacity and the viscosity of slags during the processes.9)

The researches on the alternative application of the ironsand, such as a sub-source in the current Direct Reduced Iron (DRI) process are not sufficient. This paper presents results of reduction of TTM ironsand with or without mixing with hematite iron ore fines in a fixed bed reactor, and suggests an alternative application of the TTM ironsand as a sub-resource for DRI processes.

2. Experimental

The TTM ironsand examined in this paper was from Waikato North Head, New Zealand and the hematite iron ore fines was from Mt. Newman, WA, Australia. The chemical compositions of the TTM ironsand and the hematite iron ore fines are presented in Table 1. Both iron ores were screened to have a size about 100 μm. After the screening, the mean diameters of the particles of the TTM ironsand and the hematite iron ore fines were 100.0±5.0 μm, and 105.0±10.0 μm, respectively. The specific surface area of the ores was 1.2 m$^2$/g for the TTM ironsand and 1.6 m$^2$/g for the hematite iron ore fines.

Reduction experiments were conducted using a laboratory fixed bed with Thermal Gravimetry Analysis system (TG-171, Cahn Instrument Incorporation, CA, USA). Experimental set-up is given in Fig. 1. A sample of 2 grams was located in an unreactive porous isolite crucible. After a sample was put into the crucible, the reactor was purged argon and the microbalance was stabilized. Then the sample was heated up to required temperature in argon atmosphere, and the reducing gas mixture was introduced to the reactor. The weight change during the reduction was measured and recorded in every ten seconds. After certain reaction time, the sample was cooled by turning off the power under Ar gas atmosphere.

The reducing gas, CO–Ar gas mixture, was prepared with highly purified argon and carbon monoxide using mass flow controllers. The gases were purified before mixing by passing through traps filled with Mg chips and CaSO$_4$ to remove oxygen and moisture. The total flowrate of the reducing gas mixture was held at 1.67×10$^{-2}$ m$^3$/s after preliminary experiments for the determination of the inlet-gas flowrate.

The degree of reduction was calculated by the following equation:

$$\text{Reduction percentage} = \frac{m_{\text{initial}} - m_{\text{final}}}{m_{\text{initial}}} \times 100\%$$

Table 1. Chemical compositions of the TTM ironsand and the hematite ore fines.

| Element | Fe$_{3-x}$Ti$_x$O$_4$ | Fe$_{2+}$ | Fe$_{3+}$ | TiO$_2$ | Al$_2$O$_3$ | MgO | SiO$_2$ | CaO | Mn |
|---------|---------------------|---------|---------|--------|-----------|-----|--------|-----|-----|
| Ironsand| 57.2 | 24.2 | 33.0 | 7.43 | 3.59 | 2.94 | 2.17 | 0.67 | 0.51 |
| Hematite ore| 62.7 | 62.7 | 0.08 | 2.61 | 4.81 | 0.64 |

Fig. 1. Experimental setup.
where, $W_i$ is the initial oxygen amount of an unreduced sample; $\Delta W_i$ is the weight decreased of a sample reduced for time, $t$, at a reducing temperature. The specific surface areas and the size distributions of the raw particles were measured by BET method (ASAP 2000 V2.02) and CILAS 1064 Liquid, respectively. The morphology of samples after the reduction was observed by Scanning Electron Microscopes (SEM, HITACHI S-4500 and JEOL JSM-5900).

3. Results and Discussion

The reduction curves of the TTM ironsand and the hematite iron ore fines in the temperature range from 1 273 to 1 373 K, using 70vol%CO–30vol%Ar gas mixture, were presented in Fig. 2. The reduction rate of the TTM ironsand increased with the increase in the temperature, while that of the fine hematite iron ore decreased with the increase in the temperature. At 1 373 K, except the initial stage of the reduction, the reduction of the TTM ironsand proceeded faster than that of the hematite iron ore fines, achieving the complete reduction after 45 min reaction. The SEM images (Fig. 3) of the reduced hematite iron ore fines at different temperatures showed that the reduced iron particles tended to be sintered and stuck with neighboring particles with the increase in temperature. These show that the decrease in the reduction rate of the hematite iron ore fines was due to the sintering of the reduced metallic iron. It is well-known fact that the sintering occurs by the formation of metallic iron at temperatures above 1 273 K. On the other hand, during the reduction of the TTM ironsand, the sticking phenomenon was not found in the particles even after 60 min of the reaction. The SEM images (Fig. 4) of the raw and the completely reduced ironsand particles, after 60-min reaction at 1 373 K, showed that the change in the size and the outer morphology of the particles were negligible before and after the reduction. The non-sticking behavior of the TTM ironsand during reduction is likely due to the titanium oxides dispersed in the ironsand. Previous study by the authors showed that titanium was distributed uniformly in the particles before and after reduction, in the form of titanium oxides.10–12) It has been known that the sintering and sticking particles is due to the mass transfer from a particle volume or from the grain boundary between particles. The titanium oxides in the ironsand particles might act as a barrier against the mass transfer of metallic iron from the bulk of the particle to the interface, resulting in the non-sticking during the high-temperature reduction process.

The reduction of the mixtures of the TTM ironsand and the hematite iron ore fines were examined at 1 373 K, using 70vol%CO–30vol%Ar gas mixture. The reduction curves and the degree of the reduction at different times versus different content of the TTM ironsand are plotted in Fig. 5 (a) and 5(b). The average particle diameters after the reduction of the ore mixtures are presented in Table 2. The average particle size and the deviation increased with the increase in the amount of the hematite iron ore fines. The particle size of the reduced hematite iron ore fines was not measurable due to the serious sticking.

The apparent increase in the initial reduction rate with the increase in the content of the hematite iron ore fines is because the initial reduction rate of the TTM ironsand, which involves the reduction of TTM to wustite, is much lower than that of the hematite iron ore particles. With the mixing of 30–75 mass% of the hematite iron ore fines into the ore mixture, the time required for the complete reduction of the iron oxide in the ore mixture could be slightly reduced by about 10%. However, when the content of the hematite iron ore fines was higher than 75 mass% in the ore mixture, the reduction rate decreased, especially after 80% reduction achieved. It is due to the sintering and sticking of the particles during the reduction, as shown in Table 2.

The present paper suggests an alternative application of TTM ironsand by the reduction experiments of the ore mix-
ture. Further detailed experimental investigations combined with mathematical modeling must be carried out for the evaluation of the quantitative parameters for ironmaking industries.

4. Conclusion

To develop the applications of TTM ironsand for DRI processes, the reduction of the mixture of TTM ironsand and hematite iron ore fines by carbon monoxide were examined at 1373 K.

In the reduction experiments at 1373 K, the TTM ironsand showed high-resistance against sintering and sticking between particles, while the hematite iron ore fines sintered and stuck to a bulk resulting in the low reducibility at the temperature.

The mixing of 30–75 mass% of the hematite iron ore fines with the TTM ironsand could save the time for the complete reduction. The mixing also decreases the titanium oxide content in the final product, as much as the amounts of the mixed hematite iron ore. The introduction of the mixture of conventional hematite iron ore fines and TTM ironsand would be beneficial for the current ironsand reduction process.

Table 2. The average particle diameters of the samples containing different amount of the TTM ironsand, after the 50-min reduction at 1373 K.

| TTM ironsand (mass%) | 100  | 75   | 50  | 30  | 15  |
|----------------------|------|------|-----|-----|-----|
| Average diameter (μm)| 98.0±5.0 | 98.0±5.0 | 100.0±5.0 | 105.0±10.0 | 130.0±25.0 |

Fig. 4. SEM images of TTM ironsand particles (a) raw and (b) after 60-min reduction by 70vol%CO–30vol%Ar at 1373 K.

(b) Relationship between the degree of reduction and the amount of TTM ironsand.

Fig. 5. Reduction of the ore mixtures by 70vol%CO–30vol%Ar at 1373 K. (a) reduction curves and (b) relationship between the degree of reduction and the amount of TTM ironsand.

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