Effect of Types of Carbonaceous Material and CaO Addition on Reduction Behavior of Pre-reduced Iron Ore–Carbon Composite

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Utilization of iron ore-carbon composite for blast furnace has a possibility of the method to decrease carbon dioxide emission from iron and steel industry. Major iron ores consist of Fe₂O₃, Fe₃O₄, and FeOOH, which require several reduction steps through FeO to form metallic iron. When graphite and pure FeO obtained by pre-reduction are used for the raw material of composite, the reduction of iron oxide proceeds at lower temperature than that using conventional iron ore. In the actual process, raw materials such as iron ores and coke contain impurities of silica, alumina and sulfur. Furthermore, limestone is used as fluxing materials to control basicity of slag. In this study, the effect of types of carbonaceous materials and CaO addition on the reduction behavior of the composite using FeO prepared by pre-reduction was examined. Reduction temperatures of FeO composite using coke and biomass char were higher than that using graphite. The reason can be explained by the effect of sulfur contained in the carbonaceous materials. The addition of CaO which reacted with sulfur led to lowering the reduction temperature.

KEY WORDS: iron ore-carbon composite; catalytic effect; wüstite; reduction mechanism; sulfur.

1. Introduction

In the ironmaking process, reduction of their carbon dioxide emissions has been required. The utilization of iron ore-carbon composites is one of the method to contribute to the decrease in the carbon dioxide emissions.¹,²) Such composites are used in a commercial blast furnace, which is prepared by using steel dusts.¹) The operational data showed that the maximum amount of used composite was 54 kg/THM (ton of hot metal), and it decreases in carbon consumption of 0.36 kg-C/THM for every 1 kg-C/THM input as the composite. It is well known that the reduction rate of the composite is usually controlled by the gasification reaction of carbonaceous materials and/or heat supply.²)

Therefore, catalytic effect of metallic iron can accelerate the carbothermic reduction in the composite.³)

Reduction of iron oxide is a step reaction of Fe₂O₃→Fe₃O₄→FeO→Fe. Several steps are required to obtain metallic iron from Fe₂O₃/Fe₃O₄. It means that utilization of catalytic effect of metallic iron, Fe, at lower temperature is difficult. If FeO is used as a primary iron source, Fe will be formed much lower temperature.⁴) However, FeO is not a stoichiometric compound and is not available as a natural mineral since it is unstable below 840 K. In order to use FeO as raw materials for the ironmaking process, therefore, pre-reduction is necessary, and it may result in an increasing carbon dioxide emission. On the other hand, reduction from Fe₂O₃ and Fe₃O₄ to FeO is relatively easier because the equilibrium oxygen partial pressure is not very low. It means that the gas with higher oxygen partial pressure such as outlet gas of the blast furnace can be utilized. Further, if carbon neutral resources such as biomass char are used, carbon dioxide emission originated to fossil fuels will be decreased. But, there has been only few reports on the utilization of FeO as an iron source of the ironmaking process.⁴)

Iron ores and coals/cokes contain gangues and ashes as impurities, respectively, and limestone is generally used as a fluxing materials to control slag basicity in the ironmaking process. Coals/cokes also contain sulfur, which is a surface-active element and tends to act as an inhibitor of a catalyst. In this study, therefore, reduction behaviors of the composites prepared by the pre-reduced FeO and carbonaceous materials are examined to clarify the effects of kinds of carbon sources containing different sulfur levels and CaO addition to the composite.

2. Experimental Procedure

2.1. Sample Preparation

Tables 1 and 2 list chemical composition of iron ore and the results of the proximate and ultimate analyses of carbonaceous materials used in this study. Ash content in coke and de-ashed one was measured according to JIS M8812. Hematite reagent (99.9%) was also used. Iron ore and hematite were reduced to FeO under the condition of 40%CO–60%CO₂ gas flow at 1 100°C for 14.4 ks. After reduction, it was checked by XRD that the oxide sample was FeO single phase. Coke sample was soaked in mixed acid of hydrochloric and hydrofluoric acids for 432 ks. After that, it was washed by distilled water, and then dried. Iron ore,
prepared FeO, and carbonaceous materials were crushed, and the particle sizes were controlled under 45 \( \mu \)m by sieve.

Iron oxide and carbonaceous materials were mixed with the molar ratio of carbon in carbonaceous materials to oxygen in iron oxide (C/O) of 0.8. The mixed powder was ground using a planetary ball mill under 700 rpm for 0.9 ks, which was repeated 4 times. After every grinding cycles, the grinding was stopped for more than 150 s to cool down the sample. The ground sample was press-shaped into a columnar tablet with a diameter of 10 mm and a height of 7 \( \pm \) 0.5 mm. For comparison, the samples with sulfur and CaO addition were prepared. 0.68% addition of sulfur reagent (98%) for graphite to the sample after ball milling was carried out, which is same value in coke. CaO was added to the sample before ball milling. In case of Ca/S = 131, the addition ratio of CaO for coke and biomass char was 0.656 and 0.273 g/g-carbonaceous materials, respectively.

2.2. Reduction Experiment

Figure 1 shows a schematic diagram of the experimental apparatus for the reduction of the composite.\(^4\) The composite was placed in an Al\(_2\)O\(_3\) holder, and it was set in the reaction chamber. Sample temperature was measured at 1 mm over the top surface of the composite sample using a Pt/Pt-13%Rh thermocouple. Ar-5%N\(_2\) gas was introduced to the chamber at a rate of 8.33 \( \times 10^{-6}\) Nm\(^3\)/s after evacuating the air in the chamber. The sample was heated up to 1 200°C with a heating rate of 0.33 K/s, and then permitted to cool. The concentrations of CO and CO\(_2\) in the outlet gas were continuously measured by infrared gas analysis and periodically (every 90 s) by gas chromatography.

2.3. Analysis of Samples

The value of reduction degree was calculated by estimating the amount of CO and CO\(_2\) generated from the composite. In this study, reduction degree "0" is defined as the point at which all iron in the oxide shows ferric form, i.e., Fe\(_2\)O\(_3\). Before and after reduction experiment, specific surface area of the sample was measured by BET using nitrogen gas.

3. Results and Discussion

3.1. Reaction Behavior of FeO-graphite Composite

Figure 2 shows change in reduction degree of the composite using pre-reduced ore (FeO) and graphite, together with that using conventional iron ore and graphite. Reduction degree of the composite using iron ore starts to increase at approximately 500°C, and its increase retardates at 800°C. Above 900°C, reduction degree rapidly increases again. Reduction reaction almost completes at approximately 1 100°C. On the other hand, initial reduction degree of the composite using pre-reduced ore is 27% because iron oxide is FeO. At approximately 750°C, reduction degree starts to increase rapidly, and reduction reaction completes at approximately 1 050°C. It can be concluded that the reduction completed temperature of FeO composite is lower than that of iron ore complete. Figure 3 shows the gas ratio of P\(_{CO}^{}\)/\((P_{CO}^{}+P_{CO}_2^{})\), hereafter “CO gas ratio”, generated from the composite with temperature on the phase diagram of the Fe–C–O system. Below 600°C, CO gas ratio move on the equilibrium line between Fe and Fe\(_2\)O\(_3\). Above that, CO gas ratio increases gradually with increasing temperature, and approaches to the equilibrium line of the carbon gasification reaction. It seems that the gasification reaction of graphite activates at this temperature range. It is well known that gasification rate of graphite is small below 1 000°C.\(^5\)

Table 1. Chemical composition of iron ore (mass%).

<table>
<thead>
<tr>
<th></th>
<th>T–Fe</th>
<th>CaO</th>
<th>SiO(_2)</th>
<th>Al(_2)O(_3)</th>
<th>LOI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ore</td>
<td>56.6</td>
<td>0.15</td>
<td>4.94</td>
<td>2.90</td>
<td>10.8</td>
</tr>
<tr>
<td>Pre-reduced ore</td>
<td>69.8</td>
<td>0.17</td>
<td>5.58</td>
<td>3.30</td>
<td>–</td>
</tr>
</tbody>
</table>

Table 2. Results of the proximate and ultimate analyses of carbonaceous materials.

<table>
<thead>
<tr>
<th></th>
<th>Proximate analysis (mass%)</th>
<th>Ultimate analysis (mass%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fixed carbon</td>
<td>Volatile matter</td>
</tr>
<tr>
<td>Graphite</td>
<td>98.0</td>
<td>–</td>
</tr>
<tr>
<td>Coke</td>
<td>87.5</td>
<td>1.00</td>
</tr>
<tr>
<td>De-ashed coke</td>
<td>97.6</td>
<td>1.11</td>
</tr>
<tr>
<td>Biomass char</td>
<td>87.9</td>
<td>2.83</td>
</tr>
</tbody>
</table>

Fig. 1. Schematic diagram of the experimental apparatus for the reduction of the composite.\(^6\)

Fig. 2. Change in reduction degree of the composite using pre-reduced ore and graphite with temperature, together with that using iron ore and graphite.
There is a possibility that metallic iron acts as a catalyst of the gasification reaction because metallic iron already forms at this temperature. Furthermore, CO gas ratio is slightly larger than that of the equilibrium line of carbon gasification. The reason may be that direct reduction reaction as Eq. (1) proceed easier because the sample was mix-grinded.

\[
\text{FeO} + \text{C} = \text{Fe} + \text{CO} \quad \text{.............. (1)}
\]

3.2. Effect of Carbonaceous Materials Type on Reduction Behavior

Figure 4 compares the reduction behaviors of the composites using iron ore and pre-reduced ore. Three types of carbonaceous materials (graphite, coke and biomass char) were used. In the case using iron ore, reduction of the composite prepared by biomass char proceeds at lowest temperature, and that by graphite does at highest one. This result is well agreement with the previous study.\(^6\) In the case using pre-reduced ore, on the other hand, reduction of the composite using graphite starts at lowest temperature and it is different result from that using iron ore. To discuss the reason why graphite composite shows lower reduction temperature than coke and biomass char composites, the difference of these properties of carbonaceous materials was evaluated.

Carbonaceous materials used in this study have different crystallinity, and hydrogen, ash and sulfur contents. It is well known that crystallinity of graphite is much higher than that of coke and biomass char and a decrease in the crystallinity makes the gasification reaction of carbon active.\(^7\) It means that reduction reaction in the composite proceeds at lower temperature when the crystallinity of carbon is low. Therefore, the difference of carbon crystallinity is not the reason that the graphite composite shows lower reduction temperature.

Coke and biomass char contains some amounts of hydrogen as listed in Table 2 while hydrogen concentration in graphite is very low. Hydrogen is discharged from carbonaceous materials as hydrogen, water vapor, and hydrocarbon gases,\(^8\) and it affects to the reduction of iron oxide as shown in the following equation.

\[
\text{FeO}_x + \text{H}_2 \rightarrow \text{FeO}_{x-1} + \text{H}_2\text{O} \quad \text{.............. (2)}
\]

3.3. Effect of Sulfur Addition on Reduction Behavior

Figure 5 shows change in reduction degree of the composite using de-ashed coke with temperature. Reduction reaction of the composite using de-ashed coke proceeds at higher temperature than that using original coke. It means that the catalytic effect of ash disappeared by the de-ash treatment. Therefore, it can be concluded that the effect of ash is not a major reason.

Sulfur component in carbonaceous materials is emitted as H\(_2\)S, COS, and SO\(_2\) gases by heating.\(^9\) Such sulfur compounds lead to decreasing reduction rate of iron oxide\(^10\) and deactivation of catalytic effect of metallic iron\(^11\) because sulfur tends to adsorb on the surface of iron oxide and metallic iron. To evaluate the effect of sulfur, changes in reduction degree of the composite with and without the sulfur addition are shown in Fig. 7. In this study, elemental sulfur was used to add to the composite using graphite and FeO prepared from hematite reagent while generally major sulfur states in carbonaceous materials are organic one. The additive amount of sulfur was controlled as the same level to coke. Most of added sulfur is expected to be evaporated above 445°C which is boiling point of elemental sulfur. Part of sulfur adsorbs to the surface of iron oxide, and it may affect to the reduction behavior. Reduction degree of the composite without the sulfur addition starts to increase at approximately 700°C, and reduction reaction completes at 850°C. On the other hand, an increase in
reduction degree of the composite with the sulfur addition is very little below approximately 850°C, and reduction degree rapidly increases above 900°C. Change in reduction degree becomes small at 1 000°C, and reduction reaction finishes at 1 100°C. It means that the sulfur addition leads to marked prevention of reduction reaction at lower temperature. Figure 8 shows the change in CO gas ratio of these composites with temperature on the phase diagram of Fe–C–O system. Below 600°C, the behavior of CO gas ratio of these composites is similar. Above this temperature, however, CO gas ratio of the composite with the sulfur addition decreases with temperature while that without the sulfur addition increases. Decrease in CO gas ratio reflects that the rate of indirect reduction reaction as shown in Eq. (3) becomes larger than that of gasification reaction as shown in Eq. (4) or the latter becomes smaller than the former.

\[
\text{FeO} + \text{CO} \rightarrow \text{Fe} + \text{CO}_2 \quad \ldots (3)
\]
\[
\text{C} + \text{CO}_2 \rightarrow 2\text{CO} \quad \ldots (4)
\]

Sulfur makes reduction rate small by its adsorption on FeO surface.\(^{11,13}\) Furthermore, sulfur in reducing gas reacts with the surface of metallic iron as a form of FeS. It deactivates the catalytic effect of metallic iron on the gasification.\(^{12}\) This is the reason that the addition of sulfur to the composite leads to increasing reduction temperature. Namely, the reason why reduction of per-reduced ore-graphite composite proceeded at lower temperature is that those effect of sulfur can be neglected because of low sulfur content. In case of iron ore-graphite composite, on the other hand, the rate of indirect reduction such as hematite to magnetite and magnetite to wustite is very low because the gasification rate of graphite is very low at lower temperature. Therefore, reduction temperature of wustite to metallic iron is highest in these three composites using iron ore.

3.3. Effect of CaO Addition on the Reduction Behavior of Pre-reduced Ore Composite

It is known that CaO tends to react with sulfur gas such as H\(_2\)S, and CaS in a reducing atmosphere.\(^{14}\) Therefore, it is expected that CaO addition to the composite with sulfur makes the inhibition effect of sulfur small. Figures 9 and 10 show the changes in reduction degree of pre-reduced ore–biomass char and pre-reduced ore–coke composites, respectively with different Ca/S values. The absolute additive amount of CaO in the composite using biomass char is smaller than that using coke in the case of same Ca/S values. The absolute additive amount of CaO in the composite using biomass char is smaller than that using coke. Different reduction behaviors were obtained for these composites when different Ca/S was applied. The temperatures at which reduction degree start to increase rapidly and it reaches to 95% are defined as \(T_{\text{start}}\) and \(T_{95}\), respectively. Figures 11 and 12 show the effect...
of Ca/S in the composite using biomass and coke on $T_{\text{start}}$ and $T_{95}$, respectively. $T_{\text{start}}$ of both composite using biomass and coke decreases with increasing Ca/S. $T_{\text{start}}$ of former composite is lower than that of latter composite when Ca/S is small, and the difference becomes small with increasing Ca/S. These results indicate that the addition of CaO leads to a decrease in the effect of sulfur on the reduction. For the case of biomass composite, effect of Ca/S on $T_{95}$ is similar to that on $T_{\text{start}}$. For the case of coke composite, however, $T_{95}$ increases with increasing the value of Ca/S at greater than 131, while $T_{95}$ decreases when it is less than that value. Figure 13 shows the changes in reduction rate of pre-reduced-coke composites with the different values of Ca/S, 131 and 234. Reduction rate is slightly smaller for the case of Ca/S = 131 than that of Ca/S = 234 below 800°C and above 1050°C. However, the reduction rate for the former case is significantly larger between these temperatures. It means that total reduction rate of the composite for the case of Ca/S = 131 is larger than that of 234. Change in CO gas ratio are plotted on the phase diagram of Fe–C–O system as shown in Fig. 14. At the temperature range from approximately 850°C to 910°C, CO gas ratio for the case of Ca/S = 234 significantly increases with increasing temperature. It may due to either the increase in the gasification rate or the decrease in that of reduction rate. While if CO gas ratio increases by an increase in the rate of gasification reaction, reduction rate will also increase. However, the reduction rate of the composite with Ca/S = 234 was similar to that with Ca/S = 134 in this temperature range. Consequently, it can be concluded that the increase in CO gas ratio is caused by a decrease in the reduction rate. In the system of Fe–S–O, melt can form at lower temperature such as 910°C, and the addition of CaO makes the melting point lower. It is known that the formation of melt leads to the coarsening of grains by liquid sintering. Ii appears that the reduction rate decreases by decreasing the reactive surface area due to local melt formation. Change in specific surface area of the composite with different Ca/S with temperature is shown in Fig. 15. The value
at 0°C corresponds to that before heating. Specific surface areas of both composites decrease with increasing temperature due to agglomeration of iron ore particles. Both values are similar below 800°C. However, it becomes smaller for the case of Ca/S = 234 than that of Ca/S = 131 at 900°C by about 22%. Here, shrinkage ratio of composite was defined as the following equation,

\[
\text{Shrinkage ratio(%)} = \frac{V_{\text{before}} - V_{\text{after}}}{V_{\text{before}}} \times 100 \quad \ldots (5)
\]

where \(V_{\text{before}}\) and \(V_{\text{after}}\) are the volume of composite before and after heating. Shrinkage ratios of these two composites of Ca/S = 131 and 234 are 24% and 34%, respectively at 1000°C. The latter is larger shrinkage ratio than the former.

Pseudo-binary phase diagram of S-(FeO)x(CaO)y(SiO2)z was calculated using FACTSAGE for the cases of Ca/S = 131 and 234 as shown in Fig. 16. Compositions of FeO, CaO, and SiO2 were estimated as the values at 900°C, because the reduction rates were different above this temperature. Although sulfur content of the composite is not clear, it seems to be less than the initial value of 0.1 mass%. There is no stable sulfide phase and liquid phase forms above approximately 870°C. Effect of sulfur content on the phase diagram is not large at the level less than 0.1 mass%. The amount of formed liquid per 1 g of iron was calculated at 900°C assuming sulfur content was 0.1 mass%. These values were 0.0079 and 0.0084 g/g-Fe for the cases of Ca/S = 131 and 234, respectively, and such difference was caused by the difference of CaO content. It supports the estimation that the greater decrease in the reduction rate for the case of Ca/S = 234 is led by larger amount of slag formation due to the higher sulfur content.

Figure 17 shows the effect of the weight ratio of CaO+SiO2 to FeO on T95. The value of (CaO+SiO2)/FeO is different even if the Ca/S values are same, since sulfur content of the carbonaceous materials used in this study is different (see Table 2). Effect of the amount of slag formed
in the composite prepared by biomass char on the decrease in the reduction rate is smaller than the composite prepared by coke. It is because the amount of CaO addition is smaller. In this case, $T_{95}$ significantly decreases with increase in $(\text{CaO} + \text{SiO}_2)/\text{FeO}$. On the other hand, the effect of slag formation is larger for the composite prepared by coke and $T_{95}$ increases with increase in $(\text{CaO} + \text{SiO}_2)/\text{FeO}$ when CaO addition is larger than a certain value.

4. Conclusions

A series of the carbothermic reduction experiments were performed using the composite prepared by the pre-reduced iron oxide (FeO) and different types of carbonaceous materials. Based on the experimental results, effects of type of the carbonaceous materials and CaO addition on the reduction behavior of the composites were evaluated. The results are summarized as follows:

- Composite prepared by the iron ore pre-reduced to FeO shows the significantly lower reduction temperature than that by the original ore because the catalytic effect of metallic iron on the gasification reaction can act at lower temperature.

- Reduction temperature of the composites prepared by coke and biomass char are higher than that by graphite. It appears to be due to an inhibition effect of sulfur contained in coke and biomass char on the catalytic function of metallic iron promoting the gasification reaction, through its vaporization and adsorption on the iron oxide surface in high temperatures.

- This effect of sulfur can be suppressed by the addition of CaO. However, excess addition of CaO leads to an increase in the temperature where reduction degree reaches 95%. It may be caused by a decrease in the specific surface area due to the slag melt formation leading to a decrease in reduction rate.

REFERENCES