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 methods to contribute to the decrease in the carbon dioxide emissions. Such composites are used in commercial blast furnaces, which are prepared by using steel dusts. 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. Therefore, catalytic effect of metallic iron can accelerate the carbothermic reduction in the composite.

Reduction of iron oxide is a step reaction of $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4 \rightarrow \text{FeO} \rightarrow \text{Fe}$. Several steps are required to obtain metallic iron from $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$. It means that utilization of catalytic effect of metallic iron, Fe, at lower temperature is difficult. If $\text{FeO}$ is used as a primary iron source, $\text{Fe}$ will be formed much lower temperature. However, $\text{FeO}$ is not a stoichiometric compound and is not available as a natural mineral since it is unstable below 840 K. In order to use $\text{FeO}$ 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 $\text{Fe}_2\text{O}_3$ and $\text{Fe}_3\text{O}_4$ to $\text{FeO}$ 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 $\text{FeO}$ as an iron source of the ironmaking process. 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 $\text{FeO}$ 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% CO$_2$ 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.
prepared FeO, and carbonaceous materials were crushed, and the particle sizes were controlled under 45 μm 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 ± 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. The composite was placed in an Al₂O₃ 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%N₂ gas was introduced to the chamber at a rate of 8.33 × 10⁻⁶ Nm³/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 CO₂ 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 CO₂ 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., Fe₂O₃. 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 CO₂), 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 Fe₃O₄. Above 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 CO₂), 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 Fe₃O₄. Above 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 CO₂), 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 Fe₃O₄. Above 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 CO₂), 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 Fe₃O₄. Above 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 CO₂), 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 Fe₃O₄. Above 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 CO₂), 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 Fe₃O₄. Above 750°C, reduction degree starts to increase rapidly, and reduction reaction completes at approximately 1 050°C.
Therefore, 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. 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. 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, and it affects to the reduction of iron oxide as shown in the following equation.

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

Change in the generation rates of H\textsubscript{2}, H\textsubscript{2}O, CO and CO\textsubscript{2} gases from the composite using pre-reduced ore and coke with temperature is shown in **Fig. 5**. The generation rates of H\textsubscript{2} and H\textsubscript{2}O are small, which is less than one-tenth of CO and CO\textsubscript{2} gas generation rates. Effect of hydrogen on the reduction is very small because its contribution is only approximately 1% of the total reduction from the calculation using these gas generation behavior. In the case using biomass char, the effect of hydrogen seems to be similar to the coke case, because volatile matter in biomass char was small. Accordingly, hydrogen reduction is not a major effect of the difference of reduction behavior between the composites using graphite and others.

Na and K in ash in carbonaceous materials give catalytic effects to the gasification reaction of carbon. On the other hand, ash concentrates on the surface of carbonaceous material due to the gasification of carbon, and it may suppress the gasification rate. **Figure 6** 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\textsubscript{2}S, COS, and SO\textsubscript{2} gases by heating. Such sulfur compounds lead to decreasing reduction rate of iron oxide and deactivation of catalytic effect of metallic iron 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.

Figures 8 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 condition, because sulfur content in biomass char is much lower than that in 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 1 050°C. However, the reduction rate for the former case is significantly greater 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. 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. It 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)$_y$(SiO$_2$)$_z$ was calculated using FACTSAGE for the cases of Ca/S = 131 and 234 as shown in Fig. 16. Compositions of FeO, CaO, and SiO$_2$ 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+SiO$_2$ to FeO on T$_{95}$. The value of (CaO+SiO$_2$)/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.

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