Acceleration of Carburization and Melting of Reduced Iron in Iron Ore–Carbon Composite Using Different Types of Carbonaceous Materials

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In the ironmaking process, not only faster reduction of iron ore but also the acceleration of carburizing and melting of reduced iron is very important to save energy. In this study, the use of different types of carbonaceous materials having the superior functions for reducing and carburizing is suggested for the acceleration of carburization and melting of reduced iron in a iron ore–carbon composite.

A tablet sample made of mixed powder of iron ore and carbonaceous materials such as coal, charcoal, coke, and graphite was heated up to 1 573 K, and its reduction, carburization, and melting behaviors were evaluated. It was found that coal and charcoal, which generate reducing gases at lower temperature, are suitable for the reducing agents. On the other hand, graphite and coke should be used as carburizing agents because of their lower reactivity with CO2. Using coal and graphite for the reducing and carburizing agents, respectively, accelerates the carburization and melting of reduced iron in the composite unlike when only coal is used. The effect of the particle size of graphite on the carburization is strong. Carbon concentration in the reduced iron in the composite held at 1 573 K for 1.8 ks increases with increasing particle size of graphite. Reduction of iron ore is accelerated by mix-grinding of the ore and reducing agent. The carburization is accelerated using charcoal as the reducing agent, whereas agglomeration of melted iron in the mixed grinding sample is inhibited when the reducing agent comprises coal and graphite.

KEY WORDS: iron oxide–carbon composite; carburizing agent; reducing agent; melting of iron; mix-grinding.

1. Introduction

In the iron- and steel-making industry, fossil fuel energy saving is required against a background of a rapid increase in the consumptions of iron ore and energy resources and carbon dioxide emission. In particular, reducing the energy consumption of the ironmaking process is important. Lowering the thermal reserve zone temperature in a blast furnace may be one of the effective methods to accomplish this. Focus has been placed on the use of an iron ore–carbon composite which has high reactivity as is well known. One of the most important factors for the stable operation of a blast furnace is the permeability. A decrease in the pressure drop of the region from the cohesive zone to the dropping zone is effective for decreasing the reduction agent ratio (RAR). To achieve such decrease, decreasing the thickness of the cohesive zone and accelerating the melt formation of reduced iron and separation of iron and slag are important.

In this study, the focus is placed on the acceleration of iron melt formation by carburization using the composite burden. Furthermore, this behavior is also important for direct reduction ironmaking process, such as FASTMET and ITmkIII. A number of studies have been conducted on the carburization and melting behavior of iron by carbon. One of the authors reported that carburization by solid carbon is superior to that by CO gas for melt formation by in-situ observation. Chapman et al. reported that carbon dissolution to molten iron was prevented by mineral matter composed of SiO2 and Al2O3 that originate from ash in coke. However, Ohno et al. suggested a mechanism of iron carburization during smelting reduction, which made carburization possible without direct contact between the reduced iron and carbonaceous material. For this mechanism, when iron oxide containing slag contacts carbon, it is reduced and iron particles carburized by carbon are immediately formed.

CO gas bubbles are generated at the interface between the carbon and slag. The molten particles are carried from the slag–carbon interface to the slag–iron interface by the Marangoni effect. Then, molten particles are spread on the solid iron surface. However, reduced bulk solid iron cannot melt by this carbon at lower temperature because the amount of carbon carried with molten iron is limited. Nagata et al. suggested that the slag with low FeO content in the iron ore–carbon composite suppresses both the carburization and melting of iron because of fayalite slag formation.

In the iron ore–carbon composite, the gasification reaction...
of carbonaceous materials proceeds simultaneously with reduction, and then, ash components concentrate on the surface of carbonaceous materials. Therefore, it is difficult to achieve direct contact between the carbon and reduced iron. Thus, carbonaceous materials without covering ash should remain after reduction.

In this study, the authors suggest that the function of carbon is divided into reducing and carburizing agents. To prevent the concentration of the ash component on the surface of the carbonaceous material until the beginning of carburization, two types of carbonaceous materials are used as the reducing agent with lower gasification temperature and carburizing agent with higher gasification temperature. The possibility of acceleration of carburization and melting of reduced iron in the composite under elevated temperature was discussed. Furthermore, the effects of the particle size of the carburizing agent and mixed-grinding treatment of carbonaceous materials and iron ore on the carburizing behavior were examined.

2. Experimental

Australian Pisolitic ore with the size under 45 μm, whose chemical composition was shown in Table 1, was chosen as the iron source. The amount of combined water in the ore, LOI, is 10.1 mass%. Thus, most of iron component in the ore exists as the form of FeOOH. The carbonaceous materials used in this study are coal, charcoal, coke, and graphite reagent. Table 2 shows the amount of fixed carbon, volatile matter, and ash as well as the particle size of the carbonaceous materials. Charcoal was prepared by carbonizing treatment of cedar for 3.6 ks at 723 K, which was determined to obtain large amount of volatile matter in charcoal. The mixing ratio, C/O, which was defined as the molar ratio of fixed carbon in the coal to oxygen in the iron oxide, was 1.0. C/O for reducing and carburizing agents are 0.8 and 0.2, respectively. The powders of the ore and carbonaceous materials were well mixed without reducing the particle size. Furthermore, the carbonaceous materials of coal, charcoal, and graphite for the reducing agent (C/O = 0.8) were mixed-grinded with ore using a planetary ball mill. The rotation speed and grinding time were 700 rpm and 0.9 ks, respectively. This process was performed 4 times with a cooling time of longer than 2.7 ks between cycles. After the mix-grinding, the powder was mixed with graphite (C/O=0.2) as the carburizing agent, and a sample powder was obtained. Table 3 lists the mixture ratio and particle size of the prepared samples. Samples using coal and graphite as the reducing and carburizing agents, respectively, were also prepared by mixed-grinding with ore (M2 in Table 3). Then, the mixed powder was press-shaped under a pressure of 9.8 × 10⁷ Pa, and a composite sample with a 10 mm in diameter and 10 mm in height was obtained.

The composite sample was set into the reaction chamber, as shown in Fig. 1. After evacuating air from the chamber using a vacuum pump, Ar–5%N₂ gas was introduced at a rate of 8.33 × 10⁻⁶ Nm³/s. The chamber was then heated up to 1 573 K at a heating rate of 0.33 K/s using an infrared

### Table 1. Chemical composition of iron ore used in this study.

<table>
<thead>
<tr>
<th></th>
<th>T–Fe</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>LOI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rove River</td>
<td>57.16</td>
<td>5.51</td>
<td>2.54</td>
<td>0.01</td>
<td>0.09</td>
<td>10.13</td>
</tr>
</tbody>
</table>

### Table 2. The amount of fixed carbon, volatile matter, and ash in carbonaceous materials and their particle size.

<table>
<thead>
<tr>
<th></th>
<th>Fixed carbon (mass%)</th>
<th>Volatile matter (mass%)</th>
<th>Ash (mass%)</th>
<th>Particle size (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal</td>
<td>55.5</td>
<td>36.1</td>
<td>8.4</td>
<td>53–150</td>
</tr>
<tr>
<td>Charcoal</td>
<td>62.4</td>
<td>35.6</td>
<td>2.0</td>
<td>53–150</td>
</tr>
<tr>
<td>Coke</td>
<td>86.0</td>
<td>0.9</td>
<td>11.1</td>
<td>53–150</td>
</tr>
<tr>
<td>Graphite</td>
<td>98.0</td>
<td>–</td>
<td>2.0</td>
<td>ave. 20, 53–150, 150–250, 250–500</td>
</tr>
</tbody>
</table>

### Table 3. Preparation conditions of composite samples.

<table>
<thead>
<tr>
<th>Reducing agent</th>
<th>C/O</th>
<th>Mixed grinding</th>
<th>Carburizing agent</th>
<th>C/O</th>
<th>Mixed grinding</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1 Coal</td>
<td>1.0</td>
<td>×</td>
<td>–</td>
<td>–</td>
<td>×</td>
</tr>
<tr>
<td>S2 Charcoal</td>
<td>1.0</td>
<td>×</td>
<td>–</td>
<td>–</td>
<td>×</td>
</tr>
<tr>
<td>S3 Graphite</td>
<td>1.0</td>
<td>×</td>
<td>–</td>
<td>–</td>
<td>×</td>
</tr>
<tr>
<td>S4 Coke</td>
<td>1.0</td>
<td>×</td>
<td>–</td>
<td>–</td>
<td>×</td>
</tr>
<tr>
<td>T1 Coal</td>
<td>0.8</td>
<td>×</td>
<td>Graphite (20 μm)</td>
<td>0.2</td>
<td>×</td>
</tr>
<tr>
<td>T2 Coal</td>
<td>0.8</td>
<td>×</td>
<td>Graphite (53–150 μm)</td>
<td>0.2</td>
<td>×</td>
</tr>
<tr>
<td>T3 Coal</td>
<td>0.8</td>
<td>×</td>
<td>Graphite (150–250 μm)</td>
<td>0.2</td>
<td>×</td>
</tr>
<tr>
<td>T4 Coal</td>
<td>0.8</td>
<td>×</td>
<td>Graphite (250–500 μm)</td>
<td>0.2</td>
<td>×</td>
</tr>
<tr>
<td>M1 Coal</td>
<td>0.8</td>
<td>○</td>
<td>Graphite (150–250 μm)</td>
<td>0.2</td>
<td>○</td>
</tr>
<tr>
<td>M2 Coal</td>
<td>0.8</td>
<td>○</td>
<td>Graphite (150–250 μm)</td>
<td>0.2</td>
<td>○</td>
</tr>
<tr>
<td>M3 Charcoal</td>
<td>0.8</td>
<td>○</td>
<td>Graphite (150–250 μm)</td>
<td>0.2</td>
<td>×</td>
</tr>
<tr>
<td>M4 Graphite</td>
<td>0.8</td>
<td>○</td>
<td>Graphite (150–250 μm)</td>
<td>0.2</td>
<td>×</td>
</tr>
</tbody>
</table>

Fig. 1. Schematic diagram of experimental apparatus for reduction of composite.
image furnace. After holding the sample for 0 and 1.8 ks, it was cooled. The cooling rate from 1 573 K to 1 273 K is approximately 10 K/s. The temperature was measured at a height of 1 mm from the composite sample using a Pt/Pt–13%Rh thermocouple. The concentrations of CO, CO₂, H₂, H₂O, CH₄, C₂H₄, C₂H₆, and N₂ gases were also measured by gas chromatography. Using the concentration of these gases, reduction degree, R.D. was calculated applying the following equation.

\[
R.D. = \frac{M_{\text{CO}} + 2M_{\text{CO}_2} + M_{\text{H}_2\text{O}} - M_{\text{vol}}}{M_{\text{total}} \cdot O} \quad \ldots \ldots (1)
\]

Here, \(M_{\text{CO}}\), \(M_{\text{CO}_2}\), and \(M_{\text{H}_2\text{O}}\) are the molar amounts of oxygen atom in the CO, CO₂, and H₂O gases, respectively, generated from the ore-coal composite. \(M_{\text{vol}}\) is the molar amount generated from volatile matter in the coal. \(M_{\text{total}} \cdot O\) is the molar amount originally contained in the iron oxide in the ore.

Gasification degree from coal, G.D. was also calculated using the following equation:

\[
G.D. = \frac{N_{\text{CO}} + N_{\text{CO}_2} + N_{\text{C}_{\text{total}}}}{N_{\text{total}} \cdot C} \quad \ldots \ldots (2)
\]

where \(N_{\text{CO}}, N_{\text{CO}_2},\) and \(N_{\text{C}_{\text{total}}}\) are the molar amounts of carbon atom in the CO, CO₂, and \(C_{\text{total}} (C_{\text{total}}=\text{CH}_4, \text{C}_2\text{H}_4, \text{C}_2\text{H}_6)\), respectively. \(N_{\text{total}} \cdot C\) represents the amount of carbon atom in the coal. In this study, this “gasification degree” includes not only solution loss reaction but also gasification of hydrocarbon.

The appearances and microstructures of the composite samples were observed after the experiment using an optical microscope.

The composite sample heated up to 1 573 K was pulverized using an alumina mortar after cooling in liquid nitrogen. The pulverized powder was added to distilled water, and any remaining carbon was purged. After drying, the sample was added to ethanol, and then, any fine particles that floated under ultrasonic waves were purged. A metallic iron sample was obtained after repeating this treatment several times. The sample was confirmed to be the single phase of metallic iron by XRD, and then, the carbon concentration in the metallic iron was measured by the infrared absorption method.

3. Results and Discussion

3.1. Reduction Behavior of Composite Using a Single Carbonaceous Material

Figure 2 shows the change in the gas generation rate from the coal composite (S1) with temperature. The vertical axis on the right-hand side represents the generation rate of CO and H₂O gas because the amount of these generated gases was higher than that of the other gases. H₂O gas resulting from combined water in the ore starts to generate at approximately 600 K. Above 700 K, CH₄ gas starts to generated from coal because it contains volatile matter, and the generation rate of CH₄ gas is the maximum at approximately 800 K. The value decreases with increasing temperature and is below the detection limit at approximately 1 100 K. H₂ gas also starts to generate at approximately 700 K, and the generation rate of H₂ gas shows the peak value at approximately 1 050 K. However, that of CO gas shows two peaks at 1 150 and 1 320 K. These behaviors correspond to the previous report⁷ based on C/O of 0.8.

Figure 3 shows the changes in reduction and gasification degrees of the composite using different carbonaceous materials with temperature. Reduction degree of the S1 composite using coal starts to increase at approximately 600 K. Gasification degree of this composite also slightly starts to increase at the same temperature because of the gas

![Fig. 2. Changes in the generation rates of gases from coal composite (S1) with temperature.](image)

![Fig. 3. Changes in reduction and gasification degrees of the composite using coal (S1), charcoal (S2), graphite (S3), and coke (S4) with temperature.](image)
generation caused by the volatile matter in coal, as observed in Fig. 2. The increase in reduction degree once stops when reduction degree reaches 11% because the reduction of hematite to magnetite is completed. These degrees increase rapidly at approximately 1 050 K, and the increase rate of these degrees decreases above approximately 1 350 K. Finally, reduction and gasification degrees were 82.3% and 73.5%, respectively, at 1 573 K.

When using charcoal (S2), gasification and reduction reactions start at approximately 1 000 K while gasification caused by volatile matter slightly proceeds below this temperature. Reduction reaction is slower than that of S1 because of the reactivity difference of carbonaceous materials. The final values of reduction and gasification degrees at 1 573 K are 85.9% and 75.2%, respectively. These values are the highest using one type of carbonaceous material.

When using graphite (S3), these reactions start at approximately 1 250 K. The increase rates of these degrees decreases above approximately 1 450 K. These values are 76.1% and 71.7%, respectively, at 1 573 K. When using coke (S4), the starting temperature of these reactions is the highest. Slow increases in these degrees is also observed. At 1 573 K, therefore, these degrees are 63.5% and 61.4%, respectively, which are the lowest values in this study. Accordingly, reduction reaction in the composite using coal and charcoal proceeds at lower temperature because the gasification temperature of the composite is lower. However, graphite and coke are suitable as carburizing agents because the gasification temperature of the composite using graphite and coke is higher.

Figure 4 shows the appearance of the composite using coal, graphite, and coke after the experiment at 1 573 K. No obvious shape change is observed for the composite using coal and charcoal before and after the experiment, and the cylindrical shape is maintained while the composite shrinks and cracks are observed. When using graphite and coke, on the other hand, the sample shape was obviously changed and contacted the Al2O3 balls. The surface of the coke composite (S4) shows the area of black parts and metallic luster. The microstructures of the composites are shown in Fig. 5. The white and gray particles are metallic iron and carbonaceous materials, respectively, and the black part is resin. Reduction degree of the coal and charcoal composites reaches a higher value than 80%, which indicates that most of the iron oxide was reduced to metallic iron. The reduced iron observed in the microstructure consists of small particles with sizes of less than 10 μm, and agglomerated or melted iron is not observed. For graphite and coke, on the other
hand, large agglomerated iron is observed. Furthermore, a dendrite morphology and pearlite structure are observed, which indicates that the reduced iron was carburized and melted in the composite. However, reduction degree of these composites was much lower than that using coal and charcoal. Therefore, a high amount of FeO remained in the composite. In case of S3, reduction degree was approximately 50% at 1 430 K. The composition of remained oxide was 86%FeO-10%Al2O3-4%SiO2 and the melt of oxide formed at this temperature. Reduction degree increases from this temperature. Therefore, it can be concluded that smelting reduction and carburization through the slag with high FeO content may proceed.

3.2. Reaction Behavior of Composite Using Different Types of Carbonaceous Materials

3.2.1. Advantage of Utilization of Different Carbonaceous Materials

The change in the partial pressure of oxygen calculated from the generation behavior of CO and CO2 gas from the composite (T1) using coal as the reducing agent and graphite as the carburizing agent with temperature is shown in Fig. 6 in the phase diagram of the Fe–C–O system. For comparison, the results using only coal or graphite are also shown in this figure. The thin dashed lines are the co-activity lines of carbon in iron. These values are 0.5, 0.3, 0.1, and 0.05. The oxygen partial pressure of the graphite composite (S3) appears very high below 1 000 K because the reaction did not start, as observed in Fig. 3. After starting the reaction, the oxygen partial pressure decreases, and it falls below the equilibrium line of Fe3O4 and FeO at 1 250 K. It reaches to the stable area of metallic iron at 1 370 K. Above 1 500 K, the carbon activity of the gas is almost 0.1, which indicates that the reduced iron of the composite cannot melt by CO gas carburization, whereas carburization into solid Fe can proceed. However, the oxygen partial pressure of the coal composite (S1) is lower below 1 000 K because CO and CO2 gases are generated at lower temperature because of the volatile matter in coal. The oxygen partial pressure passes through the equilibrium line of FeO and metallic Fe at 1 050 K and increases with increasing temperature. The behavior of the change in the oxygen partial pressure of the composite using coal and graphite (T1) is almost the same as that of S3 composite. Therefore, it is concluded that the melt formation of reduced iron cannot proceed by CO gas.

Figure 7 shows the microstructure and appearance of the composite (T1) using two types of carbonaceous materials of coal for the reducing agent and graphite for the carburizing agent heated up to 1 573 K. Figures 7(a) and 7(b) show the surface and center of the composite, respectively. Densification of the composite by functional separation of carbonaceous material proceeds compared with the results using only coal as shown in Fig. 4. Furthermore, agglomerated iron particles (the white arrows in figure) are observed in contrast to the microstructure of the coal composite (S1), and coal particles remain. It means that functional separation of the carbonaceous material may accelerate the carburization and melting by direct contact with graphite particles and reduced iron because of the similar oxygen partial pressure between the composite (T1) and (S1). In fact, the carbon concentrations in the reduced iron of the coal composite (S1) and coal + graphite composite (T1) were 0.5 mass% and 0.8 mass%, respectively.

3.2.2. Effect of Particle Size of Carburizing Agent on the Carburizing and Melting Behaviors

Figure 8 shows the change in the partial pressure of oxy-
gen in the gas generated from the composite using graphite as the carburizing agent with different particle sizes. The behaviors of the changes in the oxygen partial pressure in all composites are almost the same. Namely, this behavior indicates that the reduced iron in all the composites cannot melt by CO gas carburization. Table 4 lists the reduction and gasification degrees of the composite heated up to 1 573 K. Except for the results of the T1 composite which has a smaller particle size of graphite, these degrees are approximately 80%. In the T1 composite, there is the possibility that graphite also reacts with CO2 gas, and the generated CO gas contributes to the reduction. The microstructures of the T1–T4 composites heated up to 1 573 K are shown in Fig. 9. In all the composites, agglomerated and melted iron particles are observed. In these particles, the black phase is graphite, which forms during solidification of the melted iron. It indicates that a high carbon concentration is present in these particles.

Obtaining a contact point between solid iron and carbon is most important for the carburization and melting of iron by direct contact with each other. When the amount of reducing agent is the same, decreasing the particle size of the carburizing agent enables a contact point to be made. However, the decrease in the size also leads to activating the gasification reaction of the carburizing agent. Therefore, the amount of remained carburizing agents after gasification decreases if the size of the agents decreases. When agent particles with small size contact the large solid iron particle, reacted iron partly melt and quickly re-solidifies because the total carbon content is not sufficient to maintain the liquid phase and because diffusion of carbon in solid iron is fast. In fact, the amount of remained graphite in the T1 composite using graphite with a particle size of 20 μm is small. Figure 10 shows the carbon concentration in the composite heated up to 1 573 K without holding temperature. The dashed lines are the liquidus and solidus. In the T1 composite, the carbon concentration is below the solidus line, which indicates that total carbon concentration is low, while reduced iron locally melted. The carbon concentration in the reduced iron increases with increasing the particle size of graphite from 20 μm to 53–150 μm. In this case, the carbon concentration is also above the solidus line. However, further increasing the particle size of graphite leads to decreasing the carbon concentration. For the T4 composite with the size of 250–500 μm, the carbon concentration is below the solidus line, which indicates that the number of contacting points between graphite and iron decreases.

In the composite, many graphite particles remained after heating up to 1 573 K. Therefore, an experiment in which the composite was held for 1.8 ks at 1 573 K was carried out. Figure 11 shows the microstructures of the composite. In all the composites, the size of the agglomerated iron particles increased by maintaining the temperature, which indicates that carburizing time is required. In Fig. 10, the carbon concentration of the iron in the composite after holding for 1.8 ks is also shown. The carbon concentration increases with increasing the particle size of graphite, which

Table 4. Reduction and gasification degrees obtained for T1, T2, T3, and T4 composites prepared using different particles size of graphite.

<table>
<thead>
<tr>
<th>Particle size (μm)</th>
<th>T1</th>
<th>T2</th>
<th>T3</th>
<th>T4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reduction degree (%)</td>
<td>85.0</td>
<td>79.9</td>
<td>78.3</td>
<td>80.5</td>
</tr>
<tr>
<td>Gasification degree (%)</td>
<td>84.9</td>
<td>77.9</td>
<td>77.6</td>
<td>79.6</td>
</tr>
</tbody>
</table>

However, the decrease in the size also leads to activating the gasification reaction of the carburizing agent. Therefore, the amount of remained carburizing agents after gasification decreases if the size of the agents decreases. When agent particles with small size contact the large solid iron particle, reacted iron partly melt and quickly re-solidifies because the total carbon content is not sufficient to maintain the liquid phase and because diffusion of carbon in solid iron is fast. In fact, the amount of remained graphite in the T1 composite using graphite with a particle size of 20 μm is small. Figure 10 shows the carbon concentration in the composite heated up to 1 573 K without holding temperature. The dashed lines are the liquidus and solidus. In the T1 composite, the carbon concentration is below the solidus line, which indicates that total carbon concentration is low, while reduced iron locally melted. The carbon concentration in the reduced iron increases with increasing the particle size of graphite from 20 μm to 53–150 μm. In this case, the carbon concentration is also above the solidus line. However, further increasing the particle size of graphite leads to decreasing the carbon concentration. For the T4 composite with the size of 250–500 μm, the carbon concentration is below the solidus line, which indicates that the number of contacting points between graphite and iron decreases.

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agrees with the microstructural observation. The behavior difference with and without holding indicates that there is not enough time for carburization in latter case.

3.2.3. Effect of Mix-grinding on the Carburizing Behavior

Figure 12 shows the change in the partial pressure of oxygen calculated from the concentration of CO and CO$_2$ gas generated from the mix-grinded composite (M1 and M2) using two types of carbonaceous materials of coal and graphite together with that of the simple mix composite (T3). Similar behaviors of the change in oxygen partial pressure are observed by 1 250 K, except for the temperature passing through the equilibrium line of Fe and FeO. These results may be due to the effect of mix-grinding of graphite. Above this temperature, the oxygen partial pressure of the M1 and M2 composite is lower than that of the T3 composite. The carbon activity of the M1 composite increases with increasing temperature and reaches 0.5 at 1 370 K. A further increase in temperature leads to decreasing carbon activity, and the carbon activity is 0.06 at 1 573 K. That of the M2 composite is lower than that of the M1 composite above 1 423 K, which is the eutectic temperature of the Fe–C system. This finding indicates that the melt formation in the mix-grinded composite cannot proceed by CO gas while there is a possibility to accelerate the carburization.

Appearance of the T3, M1, and M2 composites using two types of carbonaceous materials heated up to 1 573 K for 1.8 ks are shown in Fig. 13. In the T3 composite, metallic luster is observed even though there are numerous
cracks on the surface of the composite. In the M1 composite mix-grinded with ore and coal, on the other hand, the surface color is black. The composite was very brittle and scarcely maintainable. Therefore, black powder is observed. The M2 composite was also very brittle. SEM images of the M1 and M2 composites using two types of carbonaceous materials are presented in Fig. 14. The fracture surface of the composite was observed. In both composites, numerous spherical particles with the sizes of a few micrometers are observed. However, these particles are not agglomerated. The reason may be that the ash components in coal and gangue in ore are dispersed into the iron ore by the mix-grinding treatment.

Carbon particles are also observed in the M1 composite and represent the graphite added to the composite as the carburizing agent. Reduction degree of the M1 and M2 composites after heating up to 1 573 K are 87.5% and 89.4%, respectively. These values are higher than that of the T3 composite as shown in Table 4. Generally, it is well known that the reduction reaction is accelerated because of strong contact between iron ore and carbonaceous material by mix-grinding, which corresponds well with this result.

Figure 15 shows the change in the partial pressure of oxygen calculated from the concentration of CO and CO$_2$ gas generated from the M1, M3, and M4 composites. Coal, charcoal, and graphite were used for the reducing agent in these composites. The oxygen partial pressure of the M1 and M3 composites reaches the stable region of $\gamma$-Fe at 1 085 K and 1 160 K, respectively, which is a relatively lower temperature. However, that of the M4 composite using graphite as the reducing agent exceeds the equilibrium line of Fe and FeO at 1 250 K, which indicates that metallic iron forms at this temperature. Above 1 423 K, the oxygen partial pressures of all the composites are in the stable region of $\gamma$-Fe, which indicates that the melt formation of iron cannot be realized by CO gas carburization. In terms of the appearance and microstructure of the M3 and M4 composites heated up to 1 573 K for 1.8 ks as shown in Fig. 16, the M4 composite is not columnar such as the shape before the experiment; however, many small spherical and porous iron particles are observed. The cross-section shows the solidification microstructure of the Fe–C binary system. Reduced iron can melt by carburization attributable to graphite when the reduction temperature is high. On the other hand, the shape of the M3...
composite is columnar. On the surface of the composite, numerous pores and metallic luster can be observed. In addition, the same solidification microstructure is obtained as that of the M3 composite. It is different from that of the M1 composite, which may be caused by the difference in the ash composition in the reducing agent.

Based on these results, it can be concluded that the carburization and melt formation of reduced iron can be accelerated by the existence of carbonaceous material, which can directly contact with the reduced iron.

4. Conclusions

The possibility to accelerate carburizing and melting of reduced iron in the iron ore and carbon composite was examined using different types of carbonaceous materials as the reducing and carburizing agents. The following results were obtained:

(1) Carbonaceous material that generates reducing gases at lower temperature, such as coal and charcoal, is suitable as a reducing agent. On the other hand, carbonaceous material for utilization as the carburizing agent should exhibit lower reactivity with CO2, such as graphite.

(2) The utilization of two types of carbonaceous materials for the reducing and carburizing agents can accelerate the carburization into reduced iron in the composite and the melt formation.

(3) The particle size of the carburizing agent strongly affects the carburization and melting of iron. The decrease in this size cannot accelerate the melting because the carburizing agent is preliminarily consumed by the gasification reaction with CO2, and the formed molten iron rapidly re-solidifies. The optimum size of the carburizing agent is 150–250 μm for graphite.

(4) Reduction reaction of the composite can be accelerated by mix-grinding treatment of the reducing agent and iron ore. However, the type of reducing agent has a strong effect on the carburization of reduced iron by graphite. When coal and graphite are used for the reducing agent, the agglomeration of melted iron particles is suppressed. Using charcoal as reducing agent, on the other hand, enables acceleration of not only the reduction reaction but also the carburization and melt formation.

REFERENCES