Decomposition Behavior of Fe₃C under Ar Atmosphere

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Suppression of CO₂ discharged from iron and steelmaking companies is an example of the biggest issues for the protection of global environment and sustainable growth of steelmaking industry. One of the efforts made to decrease the emission of CO₂ in ironmaking process is blowing of hydrogen gas into blast furnace. Hydrogen gas can reduce iron oxide and form harmless H₂O. Cementite (Fe₃C) may be formed by introduction of hydrogen into blast furnace and play an important role on carburization and smelting behavior of reduced iron.

In the present work, Fe₃C sample was held at 800–1100 K under Ar atmosphere to clarify the stability and the behavior of Fe₃C phase. It was confirmed that metastable Fe₃C phase will decompose under Ar atmosphere at 800 K and rapidly decompose at temperature over 900 K. Also, it was found that composite of nano-size C and Fe will form when Fe₃C decompose.

KEY WORDS: cementite; decomposition; nano-size; carburization; smelting.

1. Introduction

Suppression of CO₂ discharged from iron- and steel-making companies is an example of the biggest issues for the protection of global environment and sustainable growth of steelmaking industry. Efforts are made to solve this issue and one of the examples is Japanese national project COURSE50.¹ In this project, hydrogen-rich reformed coke oven gas will be introduced into blast furnace. In conventional ironmaking processes, CO₂ gas is generated when iron ore is reduced with CO gas. On the other hand, H₂O gas is generated instead of CO₂ in hydrogen reduction, and therefore this method can be regarded as an environmentally friendly ironmaking process. By increase of H₂ partial pressure in blast furnace, Fe₃C may form in this process. Many studies have been carried out for the Fe₃C formation.²⁻¹⁷) It is reported by Satoh et al.²,³) and Gudenau et al.¹⁸) that Fe₃C may enhance carburization and smelting of reduced iron. However, Fe₃C is a metastable phase and it may decompose into Fe and C in blast furnace. In the present work, Fe₃C sample was held at 800–1100 K under Ar atmosphere to clarify the stability and the behavior of Fe₃C phase. Sample after heating was further investigated by “in-situ” observation using a confocal laser-scanning microscope combined with an infrared image-heating furnace.

2. Experimental

Powder of Fe₃C was produced by the following procedure. Reagent grade Fe₂O₃ was sieved using a filter with 75 μm, and 0.7 g of the sieved sample was placed on Al₂O₃ boat. Sample was placed in a horizontal silica tube (O.D. 25 mm, I.D. 21 mm, L. 900 mm) inside an electric resistance furnace. The sample temperature was heated to 800 K under purified Ar flow of 0.05 L/min. After the sample temperature reached 800 K, gas was switched to 10 vol%CO₂–H₂ mixed gas with flow rate of 0.2 L/min and held for 80 min. Then gas was switched to purified Ar and the sample was quenched by pulling out the horizontal silica tube from the furnace. The sample was analyzed by XRD to confirm the presence of Fe₃C phase.

Weighed 0.2 g of produced Fe₃C was placed on Al₂O₃ boat. Sample was placed in a same horizontal silica tube inside an electric resistance furnace as explained above. The sample temperature was heated at 800, 900, 1000 and 1100 K under purified Ar flow of 0.05 L/min for 10, 30 and 60 min. Then the sample was quenched by pulling out the horizontal silica tube from the furnace. The sample was analyzed by XRD, SEM and TEM and carbon concentration of the sample was determined by infrared adsorption technique.

A confocal laser-scanning microscope combined with an infrared image-heating furnace¹⁹) was used in the present work to make microscopic “in-situ” observation during heating of samples. Weighed 0.1 g of sample obtained after heating Fe₃C under Ar was pressed into tablet shape (φ5 mm × 3 mm) and was placed in Al₂O₃ crucible (O.D. 10 mm, I.D. 8.8 mm, H. 3.3 mm). Also, sample made from mixed powder of Fe (–25 μm, 99.5%) and graphite (–45 μm, 99.5%) was prepared for comparison. The sample was placed in the infrared image-heating furnace and was heated at 8.33 K/s (500 K/min) in an argon atmosphere. Phenomena during heating process were observed on CRT monitor of the laser microscope and were recorded by VTR equipment.
3. Results and Discussion

Figure 1 shows the XRD pattern of Fe$_3$C produced in the present work and only Fe$_3$C phase was detected from the sample. Carbon content of produced Fe$_3$C was 6.20 mass% and it was close to the theoretical value of 6.67 mass%.

![Fig. 1. XRD pattern of produced Fe$_3$C.](image)

Hence, it was confirmed that nearly pure Fe$_3$C was produced in the present work.

Figures 2 and 3 shows the XRD result of sample collected after heating Fe$_3$C under Ar atmosphere. It can be seen that some Fe$_3$C decomposed and Fe was observed after 60 min at 800 K. At 900 K and higher temperatures, Fe$_3$C phase was not found and only Fe peaks were found by XRD analysis after 10, 30 and 60 min. Carbon peaks were not found in any samples. It was confirmed that Fe$_3$C phase will decompose under Ar atmosphere at 800 K and rapidly decompose at temperature over 900 K.

Carbon content of decomposed Fe$_3$C sample is shown in Table 1. It was found that carbon exists in the sample after decomposition. Carbon content tends to decrease with increase of experimental time and temperature. Soot was observed at the downstream of sample inside the silica tube after the experiment. It is considered that Fe$_3$C decomposed into Fe and C, and some C were taken away from the sample by Ar flow.

TEM images of Fe$_3$C sample decomposed at 900 K for 60 min are shown in Figs. 4 and 5. Existence of Bcc–Fe was

![Fig. 2. XRD pattern of decomposed Fe$_3$C at 800 K for 60 min.](image)

![Fig. 3. XRD pattern of decomposed Fe$_3$C at 900 K for 10 min.](image)

![Fig. 4. TEM image of decomposed cementite at 900 K for 60 min and observed pattern of bcc-Fe (111).](image)

![Fig. 5. Bright field TEM image of decomposed Fe$_3$C sample at 900 K for 60 min.](image)

<table>
<thead>
<tr>
<th>mass%C</th>
<th>T/K</th>
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<tr>
<td></td>
<td>800</td>
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<td>10</td>
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<td>t/min</td>
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confirmed by TEM. However, C could not be confirmed by TEM. Recalling that carbon was not detected by XRD, it is likely to be amorphous. Also, phase having size of approximately 2 nm was found in Fe. This nm sized phase consists from element lighter than Fe, which is most likely to be C from the result shown in Table 1. The size of nano-size C was independent with decomposition temperature and time. It was found that composite of nano-size C and Fe will form when Fe3C decompose. Existence of Fe3C will enhance carburization and smelting of reduced iron. However, even if Fe3C is decomposed, Fe–C composite containing nano size C may have positive effect on enhancing carburization and smelting of reduced iron.

Samples obtained by decomposition of Fe3C at 800, 900, 1000 and 1100 K for 60 min was pressed into tablet shape and the temperature when this sample completely meltdown was measured by confocal laser-scanning microscope combined with an infrared image-heating furnace. Also, mixed Fe, C powders having the same C content was also used for experiment as comparison. The experimental result is shown in Fig. 6 using Fe–C phase diagram. It is clear that samples obtained by Fe3C decomposition completely melted at temperature 71–130 K lower than mixed Fe, C powder sample having the same C content. This is obviously due to the difference of interfacial area between Fe and C. When C exist as nano size particles, C will rapidly dissolve into Fe and reach liquidus. The reason why samples obtained by Fe3C decomposition completely melted below liquidus is not clear, but the reason might be that some solid particles existed and could not be observed during experiment. It was made clear that presence of Fe3C and also decomposed Fe3C will enhance carburization and smelting of reduced iron. This could be utilized to lower the average temperature of blast furnace and reduce energy consumption and CO2 emission during ironmaking process.

4. Conclusion

Behavior of Fe3C phase at 800–1000 K under Ar atmosphere was investigated. It was confirmed that metastable Fe3C phase will decompose under Ar atmosphere at 800 K and rapidly decompose at temperature over 900 K. Also, it was found that composite of nano-size C and Fe will form when Fe3C decompose. Fe–C composite obtained by Fe3C was heated in confocal laser-scanning microscope combined with an infrared image-heating furnace. It was found that Fe–C composite completely melted at temperature 71–130 K lower than mixed Fe, C powder sample having the same C content due to the difference of interfacial area between Fe and C. Presence of decomposed Fe3C will enhance carburization and smelting of reduced iron.

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REFERENCES