Effect of Temperature and CO₂ Concentration on Gasification Behavior of Carbon Fiber Containing Fine Iron Particles

Kazuto NISHIHIRO,1)* Takayuki MAEDA,2) Ko-ichiro OHNO2) and Kazuya KUNITOMO2)

1) Department of Materials Process Engineering, Graduate School of Engineering, Kyushu University, 744 Motooka, Nishi-Ku, Fukuoka-ken, 819-0395 Japan.
2) Department of Materials Science and Engineering, Faculty of Engineering, Kyushu University, 744 Motooka, Nishi-Ku, Fukuoka-ken, 819-0395 Japan.

(Received on April 12, 2019; accepted on June 11, 2019)

In direct reduced iron (DRI) process, CO–H₂ gas mixture is used as a reducing agent, which may make the operation unstable owing to a carbon deposition reaction and metal dusting reaction through Fe₃C. The Fe₃C decomposition reaction forms iron particles which acts as a catalyst for a carbon fiber deposition reaction at around 600°C. Such a carbon fiber deposition not only causes the loss of the carbon but also decreases the reducibility of the gas. On the other hand, the carbon fiber is likely gasified by CO–CO₂ gas mixture at around 1000°C. In the present study, the carbon fiber gasification was quantitative analyzed using thermobalance to clarify the mechanism of the carbon fiber gasification reaction. To prepare a carbon fiber sample, the carbon was deposited with a reduced iron catalyst at 600°C in 50vol%CO-50vol%H₂. Carbon fiber containing fine iron particles was gasified with various compositions of CO–CO₂ gas mixture at 1000°C. Further, the effect of temperature of the gasified reaction was also investigated at 800°C, 900°C and 1000°C in 100vol%CO₂. According to XRD analysis of the sample after gasification, Fe₃C in the sample before gasification decomposed to iron and a portion of iron was oxidized to Fe₂O₃ and FeO when gasification ratio was high. The transition of carbon fiber shape was confirmed by SEM observation. Fine iron particles located on the tip of carbon fiber were sintered during gasification of carbon fiber. The mechanism of carbon fiber gasification was evaluated considering crystalline size, such as Lₐ and Lₖ that show (002) and (110) determined by XRD analysis, respectively. It was found that the Lₐ decreased with gasification ratio at all temperatures. In addition, Lₖ decreased after gasification at 1000°C.

KEY WORDS: carbon metal dusting; Fe₃C; gasification; CO–CO₂ gas mixture; carbon fiber deposition.

1. Introduction

Natural gas is utilized as a reductant in a direct reduced iron (DRI) process to produce iron, while the main reductant of a blast furnace process is coke. Natural gas is utilized as a reductant in a direct reduced iron (DRI) process to produce iron, while the main reductant of a blast furnace process is coke. DRI is predominantly charged into an electric arc furnace process as virgin metal to attenuate tramp elements such as Ni, Cr, Mo, Cu and Sn in steel. DRI production has been increased from 0.79 Mt/year in 1970 to 68.4 Mt/year in 2008 significantly.

The DRI process has the strong advantage points, such as low investment cost and high flexibility of production. Then, the DRI process would be one of the promising iron making process. Recently, a shaft furnace process using natural gas as a reducing agent is the predominantly process to produce DRI. In the shaft furnace process, the reducing gas, CO and H₂, is produced by the reforming reaction of CH₄ and CO₂ reforming. The reducing gas is heated up to around 1000°C and blown into the reaction furnace. Simultaneously, carbon deposition reaction by CO–H₂ gas mixture may occur around 600°C in the reduction process according to following reactions catalyzed by iron which is produced by reduction reaction;

\[
\text{CO}(g) + \text{H}_2(g) = \text{H}_2\text{O}(g) + \text{C}(s)
\]

\[
\Delta G = -127800 + 19T\log T + 78.4T \quad (J/mol)^{33}
\]

\[
2\text{CO}(g) = \text{CO}_2(g) + \text{C}(s)
\]

\[
\Delta G = -160210 + 168T \quad (J/mol)^{33}
\]

Carbon deposition reaction have bad influence on stable operation owing to sooting on gas path and also the deterioration in gas permeability by the formation of ferrous dusts. Carbon deposition reaction catalyzed by iron would cause complicated reactions with metal dusting and carbon fiber deposition. These reactions deteriorate the permeability of the furnace and waste the reducing gas; however, the carbon fiber can also convert to CO as reduction gas at around 1000°C in the furnace by the reaction with CO₂. Hence, investigating the mechanism of carbon fiber gasification would be beneficial to stable operation. In addition, the fine iron particles on the tips of the carbon fibers act as a catalyst for gasification reaction as report by Marsh et al. Therefore, it could be said that the conversion of the carbon
fiber to CO gas is promoted by fine iron particle catalyst. The purpose of this work is to investigate the gasification behavior of carbon fiber containing fine iron particles and the gasification reactivity in pure CO₂ and CO–CO₂ gas mixture.

2. Experimental Procedure

2.1. Carbon Fiber Sample Preparation and Experimental Apparatus

20 g reagent of Fe₂O₃ powder (−1 μm, purity of 98.5%), the chemical composition is shown in Table 1, was pressed into a tablet shape (30 mm diameter, 15 mm high), then sintered at 1400°C for 3600 s under the air atmosphere. The sintered Fe₂O₃ tablet was granulated to −45 μm particle size using a mortar. In order to obtain reduced iron sample, the prepared fine Fe₂O₃ was reduced by 100 vol% H₂ for 30 minutes at 800°C in an horizontal electric furnace. Formation of reduced iron was confirmed by both XRD analysis and weight change of the sample after reduction. In order to obtain carbon fiber sample, 0.04 g iron sample was settled up in the gas atmosphere of 50 vol% CO–50 vol% H₂ for 60 minutes at 600°C in electric horizontal furnace. The mass of obtained carbon fiber sample was 25 times larger than the mass of the iron sample. The schematic setup of the carbon gasification experiment is shown in Fig. 1. The total gas flow rate of mixture gas of CO and CO₂ into the reaction tube (Inner diameter: 35 mm) was 3.33 × 10⁻⁵ Nm³/s (2NL/min). Nitrogen gas was introduced 8.33 × 10⁻⁶ Nm³/s (0.5NL/min) from the top of the furnace during experiment in order to protect thermobalance. The sample was placed into a SiO₂ basket (20 mm inner diameter, 16 mm height) with ceramic fiber, as shown in Fig. 2. The SiO₂ basket was hung in a thermobalance by Pt wire. The initial weight of the carbon fiber sample was fixed as 0.15 g.

The sample was heated in 100 vol% N₂ up to experimental temperature, 800°C, 900°C and 1000°C in 10 minutes and then it was reacted by pure CO₂ and CO–CO₂ gas mixture for 30 minutes. The composition of the reaction gas was 100 vol% CO₂, 89 vol% CO₂–11 vol% CO₂, 83 vol% CO₂–17 vol% CO, 35 vol% CO₂–65 vol% CO and 29 vol% CO₂–71 vol% CO. The experiment at 800°C and 900°C was carried out in 100 vol% CO₂. The weight change of the sample was measured continuously using thermobalance during carbon gasification. Finally, the sample was cooled to room temperature in 100 vol% N₂ in 30 min. Microstructure of the deposited carbon was observed by SEM (SU3500) and mineral phase was analyzed by SEM-EDX (SU3500) and XRD (Smart Lab, Rigaku).

2.2. Carbon Fiber Sample Characterization

A number of studies about carbon deposition reaction has been investigated. Y. Kashiwaya and coworkers studied the morphology of the deposited carbon. According to their research, fine iron particle is contained in carbon fiber. In addition, the diffraction peaks of Fe–C was observed from the fine iron particles by TEM observation. J. Zhang et al. detected the diffraction peaks of Fe₃C and Fe₂C in deposited carbon by XRD analysis. From their researches, fine iron particles would be produced as Fe–C, after that Fe–C would be converted into Fe₃C or Fe₂C because of instability of Fe–C. Therefore, in order to make the component of sample clear, SEM observation was carried out. Figure 3 shows the surface observation and the cross section observation of the carbon fiber sample. From this figure, the sample was composed of the carbon fibers and the fine iron particles on the tips of the carbon fibers. From the cross section observation, reduced iron sample was not remained in the sample. It could be presumed that the most reduced iron sample was decomposed to fine iron particles. Figure 4 provides the results obtained from XRD analysis of the sample. As shown in Fig. 4, the diffraction peaks of Fe₃C was obtained as same as other researchers. These results suggest that the component of iron in the sample would be fine iron particles and fine iron particles would be Fe₃C before gasification experiment. Therefore, the experiment sample of this study was defined as the mixture of fine Fe₃C particles and carbon fiber.

Table 1. Chemical composition of Fe₂O₃ reagent (mass%).

| Fe₂O₃ | MnO | SiO₂ |
|------|-----|------|
| 98.5 | 0.3 | 0.06 |

3. Results and Discussion

3.1. Effect of Temperature and Gas Composition on Carbon Deposition Reaction

Gasification ratio (Gₜ) at time “t” was calculated using
Eq. (3).

\[ G_t = \frac{\Delta W_t}{W} \times 100 \% \] ........................ (3)

Where \( \Delta W_t(g) \) is the amount of weight change during experiment. \( W(g) \) is the initial weight of the sample. Fig- 

ure 5 shows the gasification ratio of sample obtained by thermobalance during experiment. From this figure, the gasification ratio reached over 90% in all conditions. The high gasification ratio demonstrated a high reactivity of the carbon fiber sample. Furthermore, the result showed that initial gasification rate was increased with an increasing the CO\(_2\) concentration of inlet gas. It is owing to the presence of sufficient amount of CO\(_2\) for proceeding Eq. (4).

\[ \text{C(s)} + \text{CO}_2(g) \rightarrow 2\text{CO}(g) \] ........................ (4)

Figure 6 shows the effect of temperature on gasification ratio in 100vol%CO\(_2\). From this figure, initial gasification rate increased with increasing reaction temperature. Gasification ratio after 1 800 s at 900°C and 1 000°C was almost over 90%. On the other hand, the gasification ratio at 800°C was attained around 75% after reaction. To obtain higher gasification ratio, sufficient reaction temperature is needed and the maximum gasification ratio after 1 800 s is assumed to be between 800°C and 900°C.

Figure 7 shows the gasification ratio after reaction for 1 800 s in each gas composition. From this figure, the gasification ratio after 1 800 s and the concentration of CO\(_2\) in inlet gas do not have the correlation. SEM observation of the surface of sample before reaction and after reaction for 1 800 s at 1 000°C in each gas composition are shown in Fig. 8. The SEM observation clearly shows that carbon fiber layer is almost completely disappeared after reaction in each gas composition, and fine iron particles were sintering after
1 800 s gasification. EDX analysis was also conducted in all gas mixtures for 1 800 s and one example of the results is shown in Fig. 9. Sintered iron is assumed to be iron oxide because the diffraction peaks of Fe and O were detected, and same results were obtained in all gas compositions. Since, the carbon fiber sample containing fine iron particles are changed to sintered iron oxide after gasification reaction. However, the diffraction peaks of oxygen was also obtained from sintered iron in 29vol%CO₂-71vol%CO which was reducing atmosphere, and further studies would be needed in order to clear the iron oxidation mechanism.

3.2. Process of Sintering Iron Particles
Considering Figs. 5 and 6, the gasification is almost finished after around 500 s except for 100vol%CO₂ at 800°C. Sintering was assumed to be accompanied with carbon gasification reaction. In order to recognize the sintering mechanism of fine iron particles, the carbon gasification was interrupted by the condition as shown in Table 2. XRD patterns of carbon fiber samples after the gasification experiment are shown in Fig. 8. Where G is gasification ratio in each condition. From Fig. 10, the diffraction peaks of cementite and carbon were detected before gasification. The diffraction peaks of cementite were not obtained after Fig. 6. Gasification ratio curves during gasification reaction in 100vol%CO₂ at each temperature.

Fig. 7. Gasification ratio after 1 800 s reaction in each gas composition at 1 000°C.

Fig. 8. Secondary electron images of samples before gasification and after 1 800 s gasification in each gas compositions at 1 000°C.

Fig. 9. EDX spot analysis of samples after 1 800 s gasification in 100vol%CO₂ at 1 000°C.
gasification in all conditions. Consequently, cementite might be decomposed to carbon and iron in accordance with thermodynamics following reaction (5).

\[
\text{Fe}_3\text{C(s)} \rightarrow 3\text{Fe(s)} + \text{C(s)} \quad \text{............... (5)}
\]

It was found that Fe was oxidized to Fe$_3$O$_4$ and FeO with 100vol%CO$_2$ at 900°C after 300 s and 1 000°C after 220 s where the gasification ratio was relatively large. It is presumed that the oxidation of fine iron particle was suppressed by carbon fiber. In order to recognize the surface of sample during carbon gasification and oxidation of iron large gasification ratio, SEM observation of sample after 300 s gasification at 900°C was carried out and the results were shown in Fig. 11. Figure 11 indicated that fine iron particles was existed the top of carbon fiber before gasification reaction because carbon fiber deposition reaction is catalyzed by fine iron particles. The surface of sample was not transformed drastically after 150 s and 220 s gasification. However, obviously, the iron cluster was found after 300 s gasification reaction. In order to classify iron cluster and carbon, BSE observation was also carried out. From BSE observation, it was confirmed that a lot of fine iron particles are covered by carbon phase nearby the sintered iron. This

| Reaction temperature (°C) | 800 | 900 | 1 000 |
|---------------------------|-----|-----|-------|
| Reaction time (s)         | 150, 300, 450 | 150, 220, 300 | 100, 150, 220 |


![Fig. 10. XRD patterns of sample before reaction and after gasification reaction.](image)

![Fig. 11. Secondary electron and back scattering electron images of sample before reaction and after gasification at 900°C.](image)
carbon phase would be composed of a congregated carbon fiber by gasification reaction. In addition, the many fine iron particles clustered and formed sintered iron during carbon gasification.

From these results, in the present study, the carbon fiber gasification reaction containing fine iron particles is proposed as following steps shown in Fig. 12:

i. Carbon fiber is gasified by gasification reaction. The morphology of the carbon fiber was preserved in the initial stage of gasification reaction.

ii. A lot of fine iron particles aggregates in carbon phase which is composed of congregated carbon fiber.

iii. Fine iron particles sinter and grow at the surface with the small amount of carbon.

iv. Most of carbon fiber and carbon phase is gasified and iron oxide cluster is formed by iron clusters.

3.3. Crystallography of Gasification in Carbon Fiber

In order to clarify the mechanism of carbon gasification, the crystallite size of carbon was evaluated by XRD analysis before and after experiments. According to a previous report by Sherrer,\textsuperscript{18} the size of crystalline carbon (L (Å)) is defined by Eq. (6).

\[ L = \frac{A\lambda}{B\cos\theta} \]  
\( (6) \)

Where A (-) is the shape factor, \( \lambda \) (Å) is wavelength of X rays, B (degree) is peak width at half of height and \( \theta \) (degree) is diffraction angle. In the present study, the crystallite sizes of carbon was obtained by “Gakushin” method,\textsuperscript{19,20} which is proposed by the Committee of the Japan society for the promotion of sciences proposed. In order to obtain high accuracy, XRD analysis was carried out by adding 10 mass% silicon for carbon in sample. (002) and (110) in carbon, (111) and (331) in silicon was analyzed by XRD as shown in Fig. 13, respectively. Slit system shows Table 3. Slit systems for the measurement of each reflections.

| hkl reflections of carbon | 002 | 110 |
|--------------------------|-----|-----|
| Incidence slit           | 1/2°| 2/3°|
| Slit system              |     |     |
| Receiving slit 1         | 1/2°| 2/3°|
| Receiving slit 2         | 0.15 mm | 0.60 mm |
| Measuring range          | 24°–30° | 75°–80° |

Figure 14 shows the size of crystalline, such as \( L_a \) and \( L_c \) that show (002) and (110), respectively. \( L_a \) decreased after gasification reaction at all temperatures, reports by Y. Kashiwaya \textit{et al.}\textsuperscript{21} Such results indicate that the gasification reaction by CO\textsubscript{2} shows a selective crystallography in the \( L_a \) direction. On the other hand, \( L_c \) is increased at 800°C and 900°C, while it decreased at 1 000°C. Moreover, in the present study, the \( L_c \) at 800°C is larger than at 900°C whereas in the reports by Y. Kashiwaya \textit{et al.}\textsuperscript{21} Therefore, the gasification reaction containing fine iron particles seem to progress from another reaction path in this study. According to previous research by Y. Yamamoto\textsuperscript{22} \textit{et al.}, they proposed that redox reaction would occur during carbon gasification containing iron oxide catalyst. However, it is presumed that oxidation of fine iron particles would hardly occur during the initial stage of carbon gasification reaction because fine iron particles was close to carbon fiber. The morphology of carbon fiber and fine iron particles was examined in the report by Y. Kashiwaya \textit{et al.}\textsuperscript{21} According to their reports, carbon fiber has distinctive structure which composed of laminated \( L_a \) in the direction of \( L_c \) from fine iron particles. Therefore,
gasification reaction would occur easier toward $L_c$ rather than $L_a$ in case carbon fiber gasified by CO$_2$ which is supplied by fine iron particles. As one example, gasification reaction between carbon in iron and bulk CO$_2$ have been studied.\textsuperscript{22)} Figure 10 shows the diffraction peaks of iron was detected in the initial stage of gasification. Hence, there is the possibility that solid carburizing and gasification would occur in case carbon fiber and fine iron particles. $L_c$ would decrease along with gasification reaction by assuming that solid carbon carburized toward $L_c$. However, further investigation about whether solid carburizing between carbon fiber and fine iron particles occur or not is needed.

4. Conclusion

The effect of CO$_2$ concentration on the carbon gasification reaction was clarified using carbon fiber with fine iron particle samples in the either CO–CO$_2$ gas mixture or pure CO$_2$ at 800°C, 900°C, and 1 000°C. Results can be summarized as follows:

(1) In perspective of reaction temperature, the largest gasification rate at the beginning of reaction was obtained at 1 000°C. In perspective of gas composition, the largest gasification rate at the beginning of the reaction was obtained in 100vol%CO$_2$.

(2) XRD analysis of samples after carbon gasification reaction implied that Fe$_3$C which was composed by reduced iron sample and deposited carbon was decomposed to iron in CO–CO$_2$ gas mixture and pure CO$_2$. In large gasification ratio, iron was oxidized by CO$_2$ to FeO or Fe$_3$O$_4$. SEM observation implied that fine iron particles were sintered during carbon gasification reaction.

(3) The analysis in crystallographic of carbon gasification reaction evaluates the size of carbon fiber crystalline. From the analyzes of crystallographic, $L_a$ decreased with increasing gasification ratio at 800°C, 900°C and 1 000°C. $L_c$ increased after gasification at 800°C and 900°C, while $L_c$ decreased after gasification at 1 000°C.

REFERENCES

1) M. Atushi, H. Uemura and T. Sakaguchi: Kobe Steel Eng. Rep., \textbf{60} (2010), 5 (in Japanese).
2) Y. Inada: Kobe Steel Eng. Rep., \textbf{50} (2000), 86 (in Japanese).
3) N. Takamatsu, K. Yonezawa, H. Ueno, W. Tamaki and S. Hayashi: Tetsu-to-Hagané, \textbf{100} (2014), 740 (in Japanese).
4) H. Sakamoto, Y. Iguchi and S. Hayashi: Tetsu-to-Hagané, \textbf{83} (1997), 175 (in Japanese).
5) D. Kaneko, O. Davies, O. Tsuchiya and H. Sakoh: Tetsu-to-Hagané, 73 (1987), 2116 (in Japanese).
6) Y. Nishiyama, T. Doi and K. Moriguchi: J. Jpn. Inst. Met., \textbf{77} (2013), 210 (in Japanese).
7) S. Ando, N. Kurose, T. Shimoo and H. Kimura: J. Jpn. Inst. Met., \textbf{49} (1985), 737 (in Japanese).
8) S. Ando, T. Shimoo and H. Kimura: J. Jpn. Inst. Met., \textbf{49} (1985), 45 (in Japanese).
9) N. Towhidi and J. Szekely: Metall. Trans. B, \textbf{14} (1983), 359.
10) H. J. Grabke: Mater. Corros., \textbf{54} (2003), 736.
11) S. Sawai, Y. Iguchi and S. Hayashi: Tetsu-to-Hagané, \textbf{85} (1999), 20 (in Japanese).
12) E. T. Turkdogan, R. G. Olsson and J. V. Vinters: Carbon, \textbf{8} (1970), 545.
13) M. Ohzumi: Tetsu Yakin Netsurikigaku (Iron Metallurgical Thermodynamics), Nikkan Kogyo Shimbun, Tokyo, (1971), 63.
14) H. Ogi, T. Maeda, K. Ohno and K. Kunitomo: ISIJ Int., \textbf{55} (2015), 2550.
15) Y. Kashiwaya and K. Ishii: J. Jpn. Inst. Met., \textbf{52} (1988), 1103 (in Japanese).
16) J. Zhang, A. Schneider and G. Inden: Corros. Sci., \textbf{45} (2003), 281.
17) Y. Kashiwaya and K. Ishii: Tetsu-to-Hagané, \textbf{76} (1990), 1254 (in Japanese).
18) N. Iwashita: Tanso, \textbf{2006} (2006), No. 221, 48 (in Japanese).
19) The 117 Committee of the Japan Society for the Promotion of Sciences: Tanso, \textbf{2006} (2006), No. 221, 52 (in Japanese).
20) Y. Kashiwaya, S. Nakaya and K. Ishii: Tetsu-to-Hagané, \textbf{77} (1991), 759 (in Japanese).
21) Y. Yamamoto, Y. Kashiwaya, S. Miura, M. Nishimura, K. Katou, S. Nomura, M. Kubota, K. Kunitomo and M. Naito: Tetsu-to-Hagané, \textbf{96} (2010), 297 (in Japanese).