Reduction and Melting Behaviors of Carbon – Iron Oxide Composite Using Iron Carbides and Free Carbon Obtained by Vapor Deposition

R. Higashi[1], *D. Maruoka*[2], *Y. Iwami*[3] *and T. Murakami*[4]

1.Graduate Student, Graduate School of Environmental Studies, Tohoku University, Sendai, Japan, 980-8579. Email: ryota.higashi.r3@dc.tohoku.ac.jp
2.Assistant Professor, Graduate School of Environmental Studies, Tohoku University, Sendai, Japan, 980-8579. Email: daisuke.maruoka.e6@tohoku.ac.jp
3.Senior Researcher, JFE Steel Corporation, Fukuyama, Japan, 721-8510. Email: yu-iwami@jfe-steel.co.jp
4.Professor, Graduate School of Environmental Studies, Tohoku University, Sendai, Japan, 980-8579. Email: taichi@material.tohoku.ac.jp

Keywords: Carbon-iron ore composite, Carburization, Iron carbide, Carbon neutrality, Carbon recycling

ABSTRACT

The iron making industry consumes a large amount of fossil fuel derived carbon as heat source, reducing agent of iron ores and carburizing agent of reduced iron. Although the demand for drastic decrease of carbon dioxide emission, carbon is an essential element for smelting process of molten iron. The carbon recycling ironmaking process by circulating CO has been already proposed to achieve carbon neutrality. However, the production of molten hot metal is not considered in this process because sufficient amount of carbon does not dissolve in reduced iron by CO. Therefore, our group has suggested a new carbon recycling iron making process which can produce hot metal. In this process, free carbon and iron carbides produced by carbon deposition reaction using metallic iron as a catalyst are used. It is known that only Fe_3C is obtained as iron carbide by using CO gas, however, Fe_5C_2 is also produced by adding H_2 gas. The composite agglomerated with these carbonaceous materials and fine iron ore (Deposited Carbon-Iron oxide Composite: DCIC) is reduced and melted in a furnace. It is reported that Fe_3C in DCIC accelerates the reduction reaction and melting of the composite. In this study, the effects of iron carbides and free carbon on the melting behavior of DCIC are investigated.

Fe_3C, Fe_5C_2 and free carbon were produced by vapor deposition using porous iron whiskers and CO-CO_2-H_2 gas. These were agglomerated with hematite reagent at a certain ratio to prepare DCIC samples with and without Fe_5C_2. The samples were heated up to 1300°C in inert atmosphere. The DCIC containing Fe_5C_2 completely melted and iron nuggets were obtained after the experiment. This behavior was not observed in the composite without Fe_5C_2. This indicates that using Fe_5C_2 is more preferable than Fe_3C for molten iron production using DCIC.

INTRODUCTION

The blast furnace ironmaking process has been adopted as the main process at integrated steel mills because of its high efficiency. However, it needs a large amount of fossil fuel derived carbon for its heat source, reducing agent of iron ores and carburizing agent of reduced iron. Thus, it is essential to develop a new process to achieve carbon-neutral steelmaking. Currently, research and development for the commercialization of hydrogen reduction ironmaking with shaft furnace have been conducted around the world. However, ironmaking processes based on DRI production such as MIDREX process, are largely limited by the grade of the iron ore. This is because the gangue in the DRI obstructs the conduction of heat to the metallic iron. Another matter is the increase in the amount of molten slag in the melting process of DRI with EAF. To improve this problem, it is effective to produce hot metal separated from molten slag before the refining process. Nonetheless, carbon must be added to reduced iron for the production of the hot metal. Therefore, attempts using biomass char as a carburizing agent have been made to produce hot metal carbon-neutrally (Robinson *et al*, 2022; Norgate *et al*, 2012). Practical application, however, is difficult in countries with large crude steel production such as China and Japan. This is because of difficulty to supply the required amount of carbon with biomass. As long as the amount of available biomass char is limited, the application of Carbon Capture and Utilization (CCU) is inevitable to achieve carbon neutrality in ironmaking process.

Examples of CCU application in steel mills include iACRES (Kato, 2010) and carbon recycling blast furnace (Kawashiri, Nouchi and Kashihara, 2022). iACRES is designed to recycle CO reformed by high-temperature electrolysis of CO_2 and the reverse water gas shift reaction as shown in Eq. (1) and Eq (2), respectively. CH_4 produced by the methanation reaction described as Eq. (3), on the other hand, is reused in the carbon recycling blast furnace. In both cases, the carbon cycle is achieved by reforming and reusing the CO_2 recovered from the exhaust gas, but its scope is limited to the reduction process. To extend the scope to oxidation refining, a carburizing agent for hot metal production should be reused.

$$2CO_2 = 2CO + O_2 \qquad (1)$$
$$CO_2 + H = CO + H_2O \qquad (2)$$
$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \qquad (3)$$

There are mainly two routes for carburization of iron. One is direct carburization by solid carbon and another is indirect one by CO gas. The reaction equations are described as Eq. (4) and Eqs. (5)-(6), respectively.

$$\mathrm{Fe(s) + C(s) = Fe(s) + \underline{C}} \qquad (4)$$

$$\mathrm{CO(g) = C^{*} + O^{*}} \qquad (5)$$

$$\mathrm{CO(g) + O^{*} = CO_2(g)} \qquad (6)$$

$$\mathrm{C^{*} = \underline{C}} \qquad (7)$$

(*) and (_) mean the atom absorbing on and dissolving in Fe, respectively. Murakami and Nagata (2003) compared the melting rate of metallic iron plate by direct carburization with a graphite piece and gas carburization with CO at 1250°C and reported that the melting proceeded more than 1000 times faster with direct contact carburization than with gas carburization. This is because the mass transfer of carbon to molten iron at the boundary between the carburizing agent and solid iron is the rate-limiting factor for iron melting. Indirect carburization, which requires the desorption process of gas molecules, supplies carbon to molten iron slower than direct one. Therefore, considering hot metal production in carbon recycling ironmaking, it is desirable to reform the CO_2 in the exhaust gas to solid carbon. However, the solid carbon is recovered in a fine powder state, which causes handling problems.

Therefore, the authors propose the following new ironmaking process named Carbon Recycling Ironmaking Process using DCIC (CRIP-D), which extends the scope of carbon recycling to steel production without fossil fuel derived carbon. Hydrogen and energy are added to the gas generated from iron ore reduction process and hot metal refining process. The gas is reformed to CO-rich gas through reverse water gas shift reaction catalyzed by porous iron. Regarding the production of the porous iron, it has been reported that metallic iron whiskers were produced by reducing carbon-iron ore composite prepared using charcoal (Murakami *et al*, 2017). Due to intertwining the fibrous structure, the porous iron showed about 95 % of porosity. This porous iron is also used as a substrate for carbon deposition reaction using reformed CO-rich gas. The carbon in the gas, therefore, can be recovered as not only free carbon but also iron carbide. Furthermore, the reaction rate can be improved by increasing the catalytically active area, and the handling of carbon powder can be more easily by incorporating the deposited carbon into the pores. Nishihiro *et al* (2019) conducted carbon deposition reaction catalyzed by metallic iron particles. They reported that a larger amount of carbon was deposited by using CO-H_2 mixed gas than pure CO gas. Sawai, Iguchi and Hayashi (1999a; 1999b) also reported that cementite (Fe_3C) was produced by using CO-CO_2 mixed gas for carbonizing metallic iron particles, while not only cementite but also Hägg iron carbide (Fe_5C_2) were produced by using CO-CO_2-H_2 mixed gas. Regarding the utilization of iron carbides, Sato *et al* (2011) conducted melting experiment under elevated temperature using tablets made of metallic iron powder with cementite or graphite powder. The melting rate of the tablet with cementite was higher than that with graphite. This indicates iron carbides are suitable for a carburizing agent. Murakami *et al* (2017) also conducted elevated temperature test on the carbon-iron ore composite using coal and graphite. The reduction and carburization reactions were reported to be accelerated by dividing the function of carbonaceous materials as reducing and carburizing agents. Thus, Deposited Carbon-Iron Ore composite (DCIC) with high reactivity may be prepared by using the free carbon and iron carbides recovered in the proposed process as reducing and carburizing agents, respectively. Hot metal can be produced with DCIC in rotary hearth furnaces and shaft furnaces (Hasanbeigi, Arens and Price, 2017). By replacing some of the raw materials in the blast furnace with DCIC, it is expected to reduce CO_2 emissions while using the facilities in the proven integrated steelmaking technology (Yokoyama *et al*, 2014). The gas after the carbon deposition reaction is introduced in to hot metal production process as a reducing agent and heat source since the gas contains certain amount of CO and H_2. Carbon recycling is achieved by reforming the gases emitted in the reducing, hot metal production and refining process.

In this study, the porous iron whiskers with high porosity are focused on, as a substrate for carbon deposition reaction. Furthermore, the reduction and melting behaviors of carbon-iron oxide composite prepared using recovered deposited carbon are investigated to examine the fundamental possibility of CRIP-D.

EXPERIMENTAL

Sample preparation

Hematite reagent (1 μm size, purity 99.9 %) and biomass char (53-150 μm size) were well mixed to have the molar ratio of fixed carbon in the char to oxygen in the hematite, C/O ratio, was 0.75. The biomass char contained 95.2 mass% of the fixed carbon. The porous iron was prepared by carbothermal reduction of the mixture in the crucible with 26 mm diameter at 1000°C in an inert atmosphere. The reduced iron showed high porosity of 94.6 % due to its fibrous structure. The sample for carbon deposition experiment was prepared by cutting the porous iron with 5 mm in thick, and was set in an experiment apparatus shown in Fig. 1. The sample holder has meshed bottom woven by Pt wire with 0.5 mm in diameter. The wire was coated with ceramic to avoid the carbon deposition reaction on the wire. The sample holder was prepared by sandwiching the porous iron sample between the ring with preheater zone and another mullite ring. The gap between the sample side and the ring was filled with inorganic adhesive. In addition, the surface of the adhesive was coated with ceramic wool to protect the reaction tube. Curing of the inorganic adhesive and pre-reduction were conducted in Ar-10%H_2 atmosphere at 250°C and 800°C, respectively. The carbon deposition reaction proceeded for 120 min in two conditions. One is used pure CO at 800°C. The other is used CO-CO_2-H_2 gas mixture at 600°C. The gas flow rate was set as 500 mL/min. After the carbon deposition reaction, the samples were pulverized. The sample labelled “a” is obtained from the carbon deposition experiment using CO gas. Whereas, the sample obtained using the gas mixture had grey and black layers, which were separated into two samples.

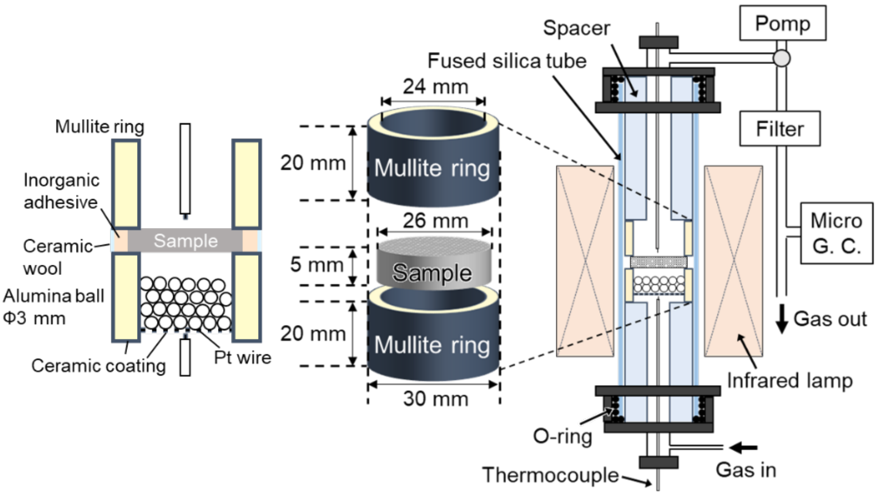

FIG 1 – Schematic diagram of an apparatus for carbon deposition using an image furnace.

Each layer was also pulverized separately into samples b and c. Figure 2 shows XRD profiles obtained for each deposited carbon sample using a sealed X-ray tube with a Fe anode (tube voltage 40 kV, tube current 30 mA) as an X-ray source. Some noises are appeared in sample c. Fe_3C is the only iron carbide phase in sample a. Fe_5C_2, on the other hand, exists in samples b and c. A broad graphite peak is observed in sample c, suggesting free carbon deposition. The carbon contents analyzed by infrared absorption method after combustion are 14.3 %, 6.62 % and 48.5 % in samples a, b and c, respectively.

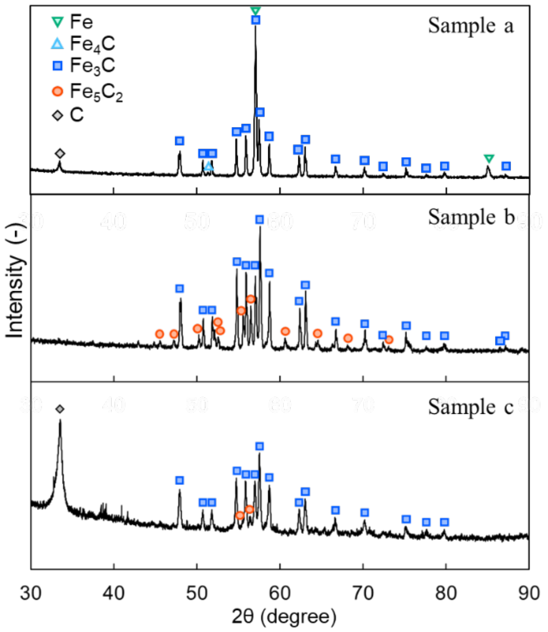

FIG 2 – XRD profiles of samples with deposited carbon obtained by using CO gas and CO-CO_2-H_2 gas mixture.

In situ XRD Measurement

Decomposition behavior of different types of iron carbides was investigated *in situ* using XRD at elevated temperatures. X-ray enters the chamber through a window made of beryllium. The chamber can be sealed, allowing control of the internal atmosphere. Sample b was filled in a black quartz glass sample holder and heated by an infrared heating equipment attached to the chamber. The sample temperature was monitored using a thermocouple with a sheath inserted into the sample holder. The sample temperature elevated by 10°C/min to 700°C under N_2 atmosphere. The gas flow rate was set as 200 mL/min. XRD measurement were repeatedly conducted in the range of 2θ=55°~58°.

Reduction experiment using deposited carbon-iron oxide composite

The deposited carbon-iron oxide composite was prepared by press-shaping of the mixture of the hematite reagent (1 μm size, purity 99.9 %) and deposited carbon samples sieved under 106 μm into a cylindrical composite. Fe_2O_3-θ was the composite sample using sample "a" so that C/O ratio was 1.0. The C/Fe ratio of Fe_2O_3-θ was 0.52. Fe_2O_3-χ was also prepared by mixing samples b and c with hematite so that C/O = 1.0 and C/Fe = 0.52. The composite sample was set in the experimental apparatus as shown in Fig. 3. After evacuating air in the chamber, Ar-5 %N_2 gas was introduced at the rate of 500 mL/min under atmospheric pressure. Then, the sample was heated up to 1300°C at a heating rate of 10°C/min using an infrared image furnace, and cooled down by turning off the power. The temperature at 1 mm upper the surface of the sample was monitored using an R-type thermocouple. The concentrations of CO, CO_2 and N_2 of the outlet gas were measured during the experiment at 90 s intervals by a gas chromatography. N_2 gas was used as a tracer to estimate the amount of gas generated from the sample. Reduction degree (RD) of the sample was calculated by Eq. (8) using the amounts of generated gas.

$$\boldsymbol{RD} = \frac{\boldsymbol{M}_{\mathbf{CO}} + \mathbf{2}\boldsymbol{M}_{\mathbf{CO_2}}}{\boldsymbol{M}_{\mathbf{total\ O}}} \tag{8}$$

M_{CO} and $M_{\mathrm{CO_2}}$ are the molar amounts of CO and CO_2 gases detected by the gas chromatography, respectively. $M_{\mathrm{total\ O}}$ is the molar amount of monatomic oxygen in the Fe_2O_3 reagent.

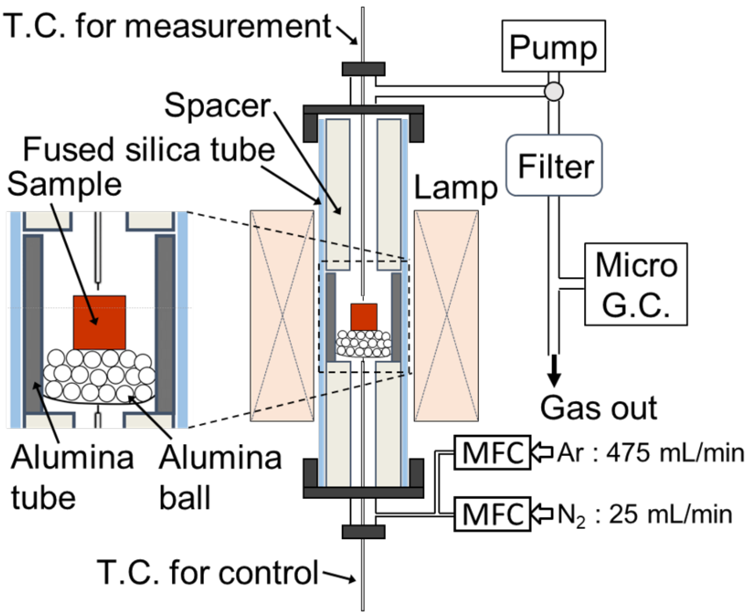

FIG 3 – Schematic diagram of an experimental apparatus for reduction experiment.

RESULTS AND DISCUSSION

In situ XRD Measurement

Figure 4 shows changes in XRD profiles obtained for sample b with temperature. The peaks of Fe_3C, Fe_5C_2 and Fe are detected at room temperature before heating up. However, the peaks of Fe_5C_2 are decreasing from 620°C and disappeared at 660°C. The peaks of Fe_3C, on the other hand, remains after heating up to 700°C. This indicates that the two different iron carbides obtained by carbon deposition reaction are expected to show different reactivity as a reducing and carburizing agent. Fe_5C_2 is more easily decomposed than Fe_3C.

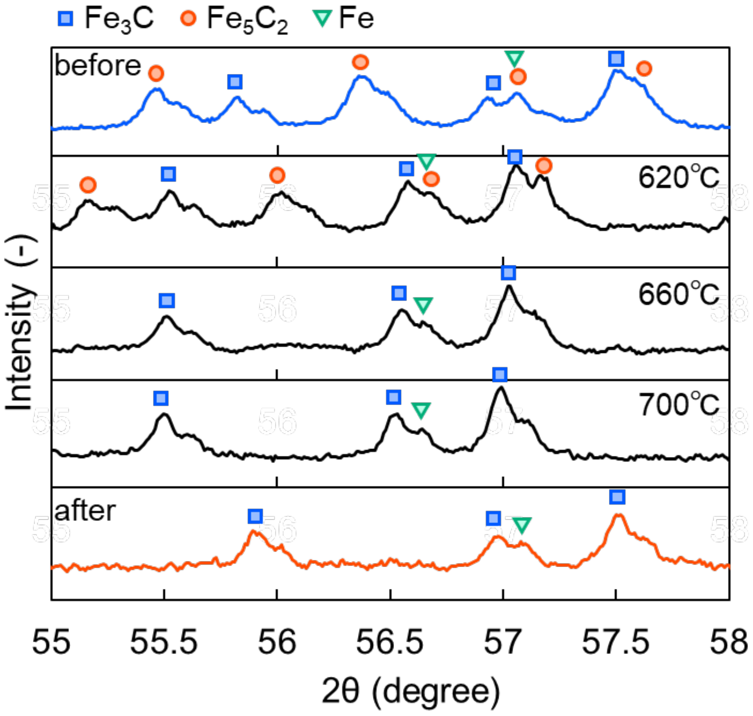

FIG 4 – XRD profiles of sample b heated up to 700°C and at room temperature before and after heating.

Reduction experiment using deposited carbon-iron oxide composite

The appearance of Fe_2O_3-θ and Fe_2O_3-χ after the reduction experiment are shown in Fig. 5. Each sample shows metallic luster. Fe_2O_3-θ keeps cylindrical shape, while Fe_2O_3-χ becomes an iron nugget. This indicates the reactivity of iron carbide affects the melting behavior of carbon-iron oxide composite.

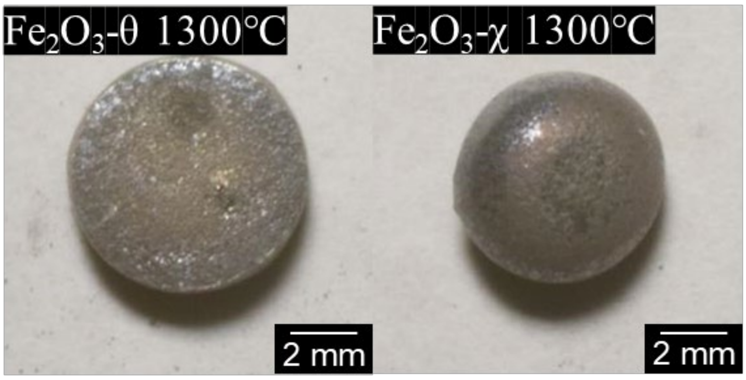

FIG 5 – Appearances of Fe_2O_3-θ and Fe_2O_3-χ after reduction heated up to 1300°C.

Figure 6 shows the changes in the partial pressure ratio of CO to $CO+CO_2$ gas (CO gas ratio) generated from the composite, and the reduction degree of iron oxide with temperature, drawn on the Fe-O phase diagram. The equilibrium line of the Boudouard reaction ($C + CO_2 = 2CO$) is represented as dashed line in the diagram. The CO gas ratio obtained for Fe_2O_3-θ starts to be increase along with the equilibrium line of the Boudouard reaction. Then, the ratio reaches the Fe_3O_4/FeO equilibrium at 650°C and FeO/Fe equilibrium at 800°C. The ratio obtained for Fe_2O_3-χ, on the other hand, starts to increase above the equilibrium line of Boudouard reaction at 620°C, which corresponds to the decomposition of Fe_5C_2. This suggests the possibility of improving the reducibility of the carbon-iron oxide composite since the carbon generated by the decomposition of Fe_5C_2 is easily gasified. The ratio then directly reaches the FeO/Fe equilibrium at 720°C. The reduction degrees are drastically increased soon after the gas ratio moves to Fe-single phase region in both composites. The metallic iron has a catalytic effect for gasification of carbon, and accelerates the reduction reaction of iron oxides (Higashi *et al*, 2023). Therefore, almost all of the iron oxides in the composites are reduced to metallic iron by heating up to 1300°C.

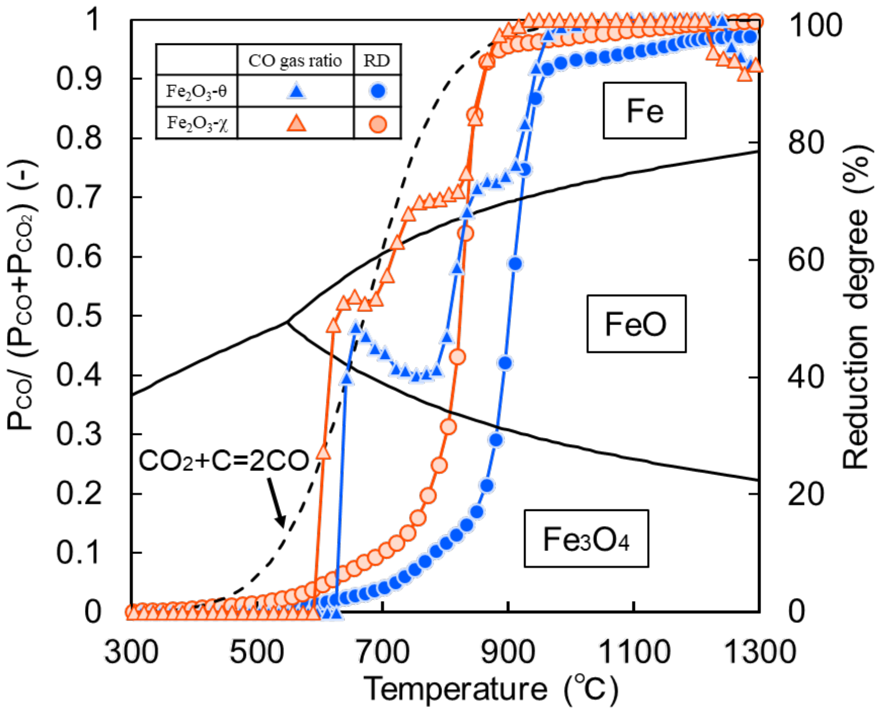

FIG 6 – Changes with temperature in the ratio of CO to CO+CO$_2$ for the Fe$_2$O$_3$-θ and Fe$_2$O$_3$-χ and in the reduction degree, plotted on the phase diagram of the Fe-O system.

CONCLUSIONS

In this study, the porous iron whiskers with high porosity were focused on, as a substrate for carbon deposition reaction. Furthermore, the reduction and melting behaviors of carbon-iron oxide composite prepared using recovered deposited carbon were investigated. The following results were obtained.

- Fe_3C is obtained as iron carbides by using CO gas for carburizing the porous iron. Fe_5C_2 is also produced by using CO-CO_2-H_2 gas mixture.
- Fe_5C_2 is more easily decomposed than Fe_3C.
- Carbon-Iron oxide composite containing not only Fe_3C but also Fe_5C_2 shows rapid reduction reaction at lower temperature and complete melting of metallic iron at 1300°C.

ACKNOWLEDGEMENT

This work was supported by JSPS Grant-in-Aid for JSPS Fellows Grant Number 22KJ0282, Steel Foundation for Environmental Protection Technology and JFE 21st Century Foundation.

REFERENCES

Hasanbeigi, A, Arens, M and Price, L, 2014. Alternative emerging ironmaking technologies for energy-efficiency and carbon dioxide emissions reduction: A technical review, *Renew Sust Energ Rev,* 33:645-658.

Higashi, R, Maruoka, D, Kasai, E and Murakami, T, 2023. Low Temperature Reduction Mechanism of Carbon-Iron Ore Composite Using Woody Biomass, *ISIJ Int,* 63(12):1972-1978.

Kato, Y, 2010. Carbon Recycling for Reduction of Carbon Dioxide Emission from Iron-making Process, *ISIJ Int,* 50(1):181-185.

Kawashiri, Y, Nouchi, T and Kashihara, Y, 2022. Reduction of CO_2 Emissions from Blast Furnace with Carbon Recycling Methane, *JFE TECHNICAL REPORT,* 28:9-15.

Murakami, T and Nagata, K, 2003. NEW IRONMAKING PROCESS FROM THE VIEWPOINT OF CARBURIZATION AND IRON MELTING AT LOW TEMPERATURE, *Extr Metall Rev,* 24:253-267.

Murakami, T, Ohno, M, Suzuki, K, Owaki, K and Kasai, E, 2017. Acceleration of Carburization and Melting of Reduced Iron in Iron Ore–Carbon Composite Using Different Types of Carbonaceous Materials, *ISIJ Int,* 57(11):1928-1936.

Murakami, T, Takahashi, T, Fuji, S, Maruoka, D and Kasai, E, 2017. Development of Manufacturing Principle of Porous Iron by Carbothermic Reduction of Composite of Hematite and Biomass Char, *Material Transactions,* 58(12):1742-1748.

Norgate, T, Haque, N, Somerville, M and Jahanshahi, S, 2012. Biomass as a Source of Renewable Carbon for Iron and Steelmaking, *ISIJ Int,* 52(8):1472-1481.

Robinson, R, Brabie, L, Pettersson, M, Amovic, M and Ljunggren, R, 2022. An Empirical Comparative Study of Renewable Biochar and Fossil Carbon as Carburizer in Steelmaking, *ISIJ Int,* 62(12):2522-2528.

Sato, K, Noguchi, T, Miki, T, Sasaki, Y and Hino, M, 2011. Effect of Fe_3C on Carburization and Smelting Behavior of Reduced Iron in Blast Furnace, *ISIJ Int,* 51(8):1269-1273.

Sawai, S, Iguchi, Y and Hayashi, S, 1999a. Carbidization Rate of Reduced Iron with CO-CO_2 Gas Mixture, *Tetsu-to-Hagané,* 85(1):6-13. (in Japanese)

Sawai, S, Iguchi, Y and Hayashi, S, 1999b. Carbidization Rate of Reduced Iron Ore in H_2-CO-CO_2 Gas Mixture, *Tetsu-to-Hagané,* 85(1):20-26. (in Japanese)

Yokoyama, H, Higuchi, K, Ito, T and Oshio, A, 2014. Decrease in the Carbon Consumption of a Commercial Blast Furnace by Using Carbon Composite Iron Ore, *Tetsu-to-Hagané,* 100(5):601-609. (in Japanese)