Development of Manufacturing Principle of Porous Iron by Carbothermic Reduction of Composite of Hematite and Biomass Char

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Iron-based porous metals have several advantages such as high strength and low cost compared with aluminum alloy foams. In recent years, a number of manufacturing technologies for iron-based porous metals have been proposed. However, a practical process could not be developed because of lower porosity, higher cost of raw materials, and so on. In this study, a new manufacturing principle of porous iron was proposed by applying carbothermic reduction using a composite of hematite and carbonaceous material. In the reduction experiment, graphite, coal, and three different charcoals were used as reductants. Based on the results, the characteristics and mechanism of the volume change of the composite were investigated under different pressures.

Reduction behavior significantly varied among the different types of reductants. The composites containing graphite and coal shrank during the reduction process when heated up to 1373 K. However, swelling behavior was observed for the composite prepared using charcoal containing some amounts of sodium and sulfur as ash components. When this composite was heated up to 1273 K at a rate of 0.167 K s^{-1} at 0.3 MPa, porous iron with a maximum porosity of 97.7% was successfully obtained. The bulk density of the composite changed during the reduction of wustite to metallic iron and formed iron whiskers. The formation of the whiskered iron texture led to a considerable swelling of the composite. On the other hand, the composite prepared using charcoal with low sodium and sulfur concentrations in the ash did not swell after the formation of metallic iron. Furthermore, when such elements in the charcoal were preliminarily removed, the composite did not swell.

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1. Introduction

Porous metals have a high potential to be used in a wide variety of applications such as ultra-lightweight structural components, heat insulation, and energy absorption¹⁾, because these materials have unique physical and chemical properties. Porous aluminum is one of the well-known foamed metals with porosity greater than 90%²⁾. However, porous iron and steel are superior to porous aluminum because of low cost, high strength, better weldability, etc.

Several methods to produce porous iron have been described³⁾. Park *et al.* reported a production method of porous iron using the powders of cast iron (Fe- 2.5 mass% C) and a foaming agent of MgCO_3 and SrCO_3 ⁴⁾. The porosity of their porous iron was less than 60%. Furthermore, one of the authors reported the method using the powders of iron, graphite, and iron oxide⁵⁾. In this case, the foaming gas was generated by the reduction reaction of iron oxide with graphite. However, its porosity was also less than 70%. Lotus-type porous iron, in which the pores are formed by the gas generated owing to the difference in the gas solubility between the liquid and solid aligned in one direction by unidirectional solidification, was reported¹⁾. It had higher strength than the conventional porous metals. However, the maximum porosity of the obtained porous irons was approximately 60%.

A production method to obtain porous iron with porosity higher than 90% was reported using SUS powder, hexane as the foaming agent, a surface-active agent, and polyvinyl alcohol⁶⁾. The maximum porosity obtained using this method was 98% with a pore size of 0.4–0.9 mm. Furthermore, it is reported that the additive manufacturing method can pro-

duce porous stainless steel⁷⁾. However, the cost of the raw materials for these processes is extremely high. Therefore, a production method with not only high porosity but also low cost is required. In light of the above-mentioned observations, the authors suggest a new method for producing iron foam using the well-mixed powders of iron oxide and carbonaceous material. During the heating of these powders, reduction of iron oxide by solid carbonaceous material starts, and CO_2 gas is generated, as described in eq. (1). The generated CO_2 gas reacts with solid carbonaceous material and CO gas is generated, as described in eq. (2). CO gas then reduces iron oxide as shown in eqs. (3)–(5). These reactions occur as chain reactions, and this process is known as carbothermic reduction. The microstructure of the formed metallic iron in the reduced composite is porous⁸⁾.

When certain types of iron ore pellets were reduced by a CO-containing gas at approximately 1173 K, the pellets swelled fourfold compared with their initial volume⁹⁾. The formed metallic iron was whisker-shaped. This swelling of the pellets caused a serious problem in the operation of the blast furnace for iron making. Therefore, many studies have investigated methods to prevent this phenomenon. At the temperature range of 1173–1273 K, the abnormal swelling proceeds by CO gas reduction; however, H_2 gas reduction did not lead to this swelling¹⁰⁾. However, there is no report

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on the production of porous iron based on the swelling phenomenon of the iron ore pellet. In this study, a possible production principle of porous iron combined with this abnormal swelling and carbothermic reduction of the composite was studied.

2. Experimental

2.1 Sample preparation

Hematite (average particle size: 0.5 μm , purity: 99.9%) was used in this study. Three types of biomass chars (Charcoal A, B, and C), coal, and graphite (average size: 20 μm) were used as reductants. Biomass char and coal were pulverized and sieved to obtain a controlled particle size of 53–150 μm . The results of proximate analysis, which indicate the amount of fixed carbon, volatile matter, and ash in these carbonaceous materials, are shown in Table 1. The composition of the ash in charcoal and coal is also shown in Table 2. CA-800, shown in this table, is a sample of charcoal A heat-treated under an inert gas atmosphere at 1073 K for 3.6 ks. Charcoal A was deashed by washing with hydrochloric and hydrofluoric acid solutions, and CA' was obtained. Furthermore, CA'-Na was also prepared by mixing CA' with aqueous sodium hydroxide to control the concentration of Na with the same as ash in CA, followed by drying at 378 K. The gasification test of carbonaceous materials was carried out by thermogravimetric analysis under a CO_2 gas flow of $3.33 \times 10^{-6} \text{ Nm}^3\text{s}^{-1}$ at a heating rate of 0.167 K s^{-1} .

Hematite and carbonaceous materials were mixed well in a molar ratio of fixed carbon in coal to oxygen in iron oxide, C/O, of 0.8. The mixed powder was press-shaped to obtain a columnar composite sample of 10 mm height. The diameter of the composite obtained using charcoal was 18 mm, and that of the graphite and coal composite was 10 mm. The density of the composites was different for each of the samples. For example, that of CA was 1.5 g cm^{-3} .

2.2 Reduction and foaming experiment

A composite sample was heated to the target temperature

under an Ar-5% N_2 gas flow and at different total pressures (0.1–1.0 MPa) at a heating rate of 0.167 K s^{-1} , followed by cooling. In this study, different experimental apparatuses detailed in previous reports^{11,12)} were used to conduct the experiments under high and atmospheric pressures. In both experiments, the experimental conditions were the same, except for the gas flow rate. The gas flow rate for the experiment conducted under the high pressure was $3.3 \times 10^{-5} \text{ Nm}^3\text{s}^{-1}$ ¹¹⁾, while that for the experiment conducted at the atmospheric pressure was $8.33 \times 10^{-6} \text{ Nm}^3\text{s}^{-1}$ ¹²⁾. The concentration of CO , CO_2 , H_2 , H_2O , CH_4 , and N_2 in the outlet gas was measured every 90 s by a gas chromatography. Using the amount of the generated gas, reduction degree of the composite sample could be calculated from the following equation.

$$RD(T) = \frac{\int_{T_0}^T n_{\text{comp}} dT - \int_{T_0}^T n_{\text{ore}} dT - \int_{T_0}^T n_{\text{coal}} dT}{n_{\text{oxide}}} \times 100 \quad (6)$$

Here, n_{comp} and n_{coal} are the molar amounts of oxygen atom in the CO , CO_2 and H_2O gases generated from the composite and that from coal, respectively, n_{ore} and n_{oxide} are that of oxygen atom in H_2O generated from the ore and that originally contained in iron oxide in the composite, respectively. T_0 is the initial experimental temperature. Density of the obtained sample before and after heating was measured by Archimedes' method. The appearance and the cross section of the samples were observed. The specific surface area of the obtained sample was measured by the BET method.

3. Results and Discussion

3.1 Gasification behavior of carbonaceous materials

Figure 1 shows the weight loss fraction of carbonaceous materials heated to 1473 K at a heating rate of 0.167 K s^{-1} under a CO_2 atmosphere. The rate of this fraction can also be seen in this figure. The weight loss fraction was defined using the following equation,

$$(\text{Weight loss fraction}) = \frac{W_{\text{after}} - W_{\text{before}}}{F.C. + V.M. + \text{Oxygen}} \times 100 \quad (7)$$

where W_{before} and W_{after} are the weight of sample before and after experiment, respectively. *F.C.* and *V.M.* are the amount of fixed carbon and volatile matter, respectively in carbonaceous materials. "*Oxygen*" is the oxygen amount originated from iron oxide. The weight loss occurs because of the decomposition of the volatile matter and the gasification reaction of the carbonaceous materials with the CO_2 gas, as described in eq. (2). Except for graphite, the weight loss occurs at temperatures as low as 373 K. This weight loss can be ascribed to the vaporization of free water presented in the ma-

Table 1 Proximate analysis of carbonaceous materials. (mass%)

	F.C.	V.M.	Ash
Graphite	98.0	-	2.0
Coal	55.5	36.1	8.4
Charcoal A [CA]	62.4	35.6	2.0
Charcoal A [CA-800]	85.3	8.4	6.3
Charcoal A' [CA']	62.3	37.7	0.0
Charcoal B [CB]	91.7	7.3	1.0
Charcoal C [CC]	72.3	15.7	12.0

Table 2 Composition of ash in charcoal and coal samples. (mass%)

	CaO	Al_2O_3	SiO_2	MgO	Fe_2O_3	P	Na	K	S
Charcoal A [CA]	62.26	-	-	8.62	-	1.1	1.6	3.5	2.1
Charcoal B [CB]	68.27	4.16	2.78	13.26	-	1.6	0.4	2.6	0.6
Charcoal C [CC]	20.57	5.67	29.74	3.65	22.73	1.3	0.9	4.4	0.7
Coal	3.30	23.43	35.63	0.55	3.60	0.49	0.34	3.25	0.31

terial. In addition, this fraction decreases above approximately 673 K because of the decomposition of the volatile matter. In contrast, no weight loss is observed for graphite below 1073 K because of the small amount of volatile matter presented in graphite. Above 1073 K, CA and CB show similar gasification behavior and low gasification temperature. CC has a slightly higher gasification temperature than both CA and CB.

3.2 Reduction behavior of composite

Figure 2 shows the change in reduction degree, under atmospheric pressure, of the composite samples containing CA, graphite, and coal with temperature. Reduction degree of the composite sample containing graphite starts to increase at approximately 1000 K. This increase plateaus at approximately 1150 K. At this temperature, reduction degree is 11.1%. It is indicative of the complete reduction of Fe_2O_3 to Fe_3O_4 , assuming that the reaction in the sample is uniform. This temperature is lower than that for the gasification of graphite. This is because the direct reduction reaction described in eq. (1) proceeds in the composite sample at 1150 K¹³. At 1223 K, the reduction degree increases again and the reduction reaction is completed at approximately 1350 K. In contrast, the reduction degree of the composite containing coal and charcoal starts to increase at approximately 920 K, and it increases with increasing temperature. This is the effect of the volatile matter because hydrogen and hydrocarbon gases are generated from the carbonaceous materials, which are the reducing agents¹². At 1373 K, the reduction degree of all samples reaches over 90%.

3.3 Effect of carbonaceous materials on swelling under atmospheric pressure

Figure 3 shows the appearances of the composite sample containing graphite, coal, and charcoal A (CA) before and after heating to 1373 K under atmospheric pressure. Reduction degree and density of the composite are also listed in this figure. The composite containing graphite and coal constricts after the experiment and the density increases. This may be because the reduced iron was sintered when heated since reduction degree is 90%. In contrast, the density of the sample containing CA decreases. The porosity

of the heated composite is calculated as 92.2% assuming that reduction reaction completes and the carbonaceous material is gasified completely. The abnormal swelling occurs when the reduction reaction of the iron oxide proceeds at the temperature range of 1173–1373 K, as described above¹⁰. Furthermore, CA composite expands in a vertical direction which is same as press-shaped direction. However, it is difficult to make clear this reason because many reactions proceeds in the composite and complex microstructure change occurs. For the graphite composite, the reduction reaction proceeds above 1373 K as shown in Fig. 2. Reduction degree of the coal composite at 1373 K is approximately 50%, which is much lower than that of the CA composite. It means that most of the metallic iron in the coal composite forms above 1373 K and explains why the composite sample does not swell.

The change in the density of the CA composite with temperature is shown in Fig. 4. The density of the CA composite heated under atmospheric pressure of 0.1 MPa at 1223 K is higher than that of CA before the experiment. It indicates that the effect of sintering the particles in the composite is stronger than the total effects of the decomposition of the volatile matter, the gasification of the fixed carbon, and the reduction of the iron oxide, resulting in an increasing den-

Fig. 2 Changes in reduction degree of samples observed using graphite, coal, and charcoal with temperature.

Fig. 1 Changes in (a) weigh loss fraction and (b) its rate obtained for carbonaceous materials heated up to 1473 K with the heating rate of 0.167 K s^{-1} under CO_2 gas atmosphere.

10 mm	Graphite	Coal	CA
Before
Density (gcm^{-3})	2.74	2.42	1.38
After
Reduction degree (%)	90	90	97
Density (gcm^{-3})	3.45	4.40	0.61

Fig. 3 Sample appearances and values of reduction degree and density observed for composites using graphite, coal, and charcoal (CA) before and after heating up to 1373 K under atmospheric pressure.

Fig. 4 Changes in density of CA composite with temperature under different total pressure.

Fig. 5 Changes in weight loss fraction of CA composite with temperature under different pressures.

sity. On the other hand, the density rapidly decreases when the temperature is increased above 1223 K. Assuming that carbon and oxygen in the composite react and gasify, and the volume of the composite does not change during the experiment, the density of the composite after the experiment is calculated as 0.87 gcm^{-3} . However, at 1373 K the density is 0.6 gcm^{-3} , which is lower than the calculated value. It shows that this density change is caused by not only the effect of the chemical reaction but also by other reasons such as the abnormal swelling described above.

3.4 Effect of pressure on reaction and density of composite

Figure 5 shows the weight loss fraction of CA composite with temperature under different pressures. Here, the weight loss fraction is regarded as 100% when the decomposition of the volatile matter, the reduction of the iron oxide, and the gasification of the fixed carbon in the charcoal are com-

pleted. Under all conditions, the weight loss fraction increases with increasing temperature. At 1073 K, the weight loss fraction of the composite under all conditions is almost 40%. However, the temperature at which the weight loss fraction starts to increase under higher pressure is lower than that under atmospheric pressure. This behavior is caused by the acceleration of the reduction reaction¹²⁾. An increasing trend in the weight loss fraction is observed with increasing total pressure.

The changes in the density of the composite with temperature under high pressures are also shown in Fig. 4. The change in the density of the composite under high pressure is similar to the trend observed under atmospheric pressure. However, the initial temperature of this change is lower. Furthermore, the density increases after showing a minimum value. In this study, the minimum density was obtained at 1273 K under 0.3 MPa, and the weight loss fraction, porosity, and volume change ratio were 98.1%, 97.7%, and 507%,

respectively. The volume change ratio was calculated from the following equation,

(Volume change ratio) = $\frac{V_2}{V_1} \times 100$ (8)

where V1 and V2 are the volume of composite sample before and after experiment, respectively. The fractured surface of the CA composite heated to 1273 K under 0.3 MPa, which shows the minimum density, is shown in Fig. 6. After the experiment, the CA composite samples could be easily cut by a wooden toothpick. Many iron whiskers with a diameter of approximately 1 μm and a large aspect ratio are observed. Large pores with the size of approximately 100 μm are observed from Fig. 12(a). These pores were originated from the space of charcoal, and charcoal disappeared by the gasification reaction. Figure 7 shows the microstructure of the CA composite heated to 1251 K under atmospheric pressure with a weight loss fraction of 65.0%, and the microstructure of the CA composite heated to 1223 K under 1.0 MPa with a weight loss fraction of 74.7%. The grey and white areas observed are FeO and metallic iron, respectively. The thin rod with dark grey indicated by the arrow is charcoal that remained after the completion of the reaction. FeO is several dozen micrometers in size, while the initial size of the hematite is 0.5 μm. This indicates that the particles of the raw materials are sintered during the reduction reaction. Under both high and atmospheric pressures, the whisker formation of the metallic iron on the FeO particle is observed. Then, this iron whisker formation leads to the expansion of the composite.

3.5 Effect of charcoal characteristics on swelling of composite

Using charcoal A, the swelling behavior of the composite was observed. On the contrary, the composite containing coal and graphite shrunk after the experiment, as described above in Fig. 3. In order to discuss the reason of the difference between CA and coal, other types of charcoal, namely CB and CC, were investigated. The appearance of the composites after being heated up to 1273 K under 0.3 MPa is shown in Fig. 8. The composites obtained by using the three types of charcoal have different appearances. Table 3 lists the volume change ratio and the weight loss fraction of the composites. Maximum volume change ratio was observed for the CA composite. On the other hand, the CB composites shrink. The volume change ratio of the CB composite shows the minimum value. The difference of shape change of the composites is the same as the difference between the amounts of the volatile matter in charcoals. The weight loss

Fig. 8 Appearances of composite samples using CA, CB, and CC of charcoal, heated up to 1273 K under 0.3 MPa.

Fig. 6 SEM images of CA composites heated up to 1273 K under 0.3 MPa. (a) low, (b) middle, and (c) high magnifications.

Fig. 7 Microstructures of CA composites heated up to (a) 1251 K under 0.1 MPa and (b) 1223 K under atmospheric pressure.

fraction of the CA and CB composites after heating up to 1273 K are above 90%, indicating that the reduction reaction is almost completed. However, that of the CC composite is 67% showing that the metallization degree of CC is less than 50%. SEM images of the fracture surface of CB and CC composites are shown in Fig. 9. The observed phase of the CB composite is metallic iron because the reduction reaction is almost complete; however, it is not whisker but plate-like in structure. In the case of the CC composite, the dark grey area on the left side of the photo is FeO. The shape of the formed metallic iron is midway between a whisker and plate. These charcoals have different volatile matter contents and ash compositions.

Figure 10 shows the appearance of the CA and CA-800 composites heated to 1123 K under 0.3 MPa. The volume change ratio and weight loss fraction of these composites are listed in Table 3. CA-800 has different volatile matter content from CA because an additional pre-heat treatment at 1073 K was carried out. The ash composition and the amount of the volatile matter in the CA-800 are similar to that of CB. However, the volume change ratio of the CA-800 composite is 225%, which is much higher than that of the CB composite, even though the temperature is 50 K lower. However, it shows a similar volume change ratio to that of the CA composite at the same temperature. Hence, it can be concluded that the amount of the volatile matter has a lesser effect on abnormal swelling.

The ash in charcoal is composed of various elements as shown in Table 2. CA has a high concentration of Na and S, whereas CB has a high Mg concentration. To negate the effect of ash, a deashing treatment of CA was carried out, and the resulting ash was described as CA'. NaOH was added to CA', and the obtained ash was described as CA'-Na. Figure 11 shows the appearance of the CA' and CA'-Na composites heated to 1273 K under 0.3 MPa. The volume change ratios and weight loss fractions of these composites are listed in Table 3. The weight loss fraction of the CA'

composite is higher than 90%. It indicates that the reduction reaction is almost complete. The volume change ratio is less than 100%, while that of the CA composite is higher than 500%. The microstructures of these composites are shown in Fig. 12. The formed metallic iron is not whisker-shaped and is similar to that of the CC composite. These results indicate that some elements in ash affect the swelling behavior. The addition of Na to the CA' composite slightly increased the volume change ratio of the CA'-Na compared to that of the

Fig. 10 Appearances of (a) CA and (b) CA-800 composites heated up to 1223 K under 0.3 MPa.

Fig. 11 Appearances of the composite samples using CA' and CA'-Na at 1273 K under 0.3 MPa.

Table 3 Volume change ratio and weight loss fraction of composite obtained using various charcoal.

Charcoal	CA	CB	CC	CA	CA-800	CA'	CA'-Na
Temperature (K)		1273		1223			1273
Volume change ratio (%)	507	54.5	230	282	225	71.0	102
Weight loss fraction (%)	98.1	91.2	67.0	77.3	89.1	93.9	95.7

Fig. 9 SEM images of (a) CB and (b) CC composites heated up to 1373 K under 0.3 MPa.

Fig. 12 SEM images of CA' and CA'-Na composites heated up to 1273 K under 0.3 MPa.

CA' composite, while both weight loss fractions were higher than 90%. The shape of the formed metallic iron of the CA'-Na composite looks like whiskers, while the aspect ratio is much smaller than that of the CA composite shown in Fig. 6. It means that Na affects the formation of iron whiskers. However, its mechanism has not been clearly understood yet. The observed aspect ratio was smaller and abnormal swelling did not occur. It indicates that not only Na but also other elements such as K and S are needed to be considered to discuss its mechanism. Furthermore, macro-pores are also observed in these samples as is the case with the CA composite.

4. Conclusions

A new production principle of porous iron is proposed by applying the carbothermic reduction reactions with the swelling behavior of composite consisted of a mixed powder of iron oxide and carbonaceous material. The following results are obtained.

- (1) The swelling behavior of the composite strongly depends on the type of carbonaceous materials. The composite shrinks during reduction when graphite and coal are used. In contrast, the composite containing charcoal with a higher amount of Na and S in the ash shows abnormal swelling, and the formed metallic iron is whisker-shaped with a diameter of approximately 1 μm when heated up to 1373 K under 0.3 MPa. The aspect ratio of this whisker is significantly large. The maximum porosity of the obtained composite is 97.7%.
- (2) The total pressure affects the swelling behavior because the reduction temperature decreases with increasing pressure. It indicates that this swelling is closely related

to the reduction reaction. Furthermore, sintering of the formed metallic iron occurs during reduction. Therefore, the balance between the swelling and sintering leads to the resultant porosity.

- (3) When using deashed charcoal, the swelling by the formation of whisker-shaped iron in the composite was not observed. In the composite obtained by the adding Na to the deashing charcoal, however, whisker-shaped iron formed, but significant swelling did not occur. Therefore, it can be concluded that the components of ash are important factors to control the swelling behaviors.

REFERENCES

- 1) H. Nakajima: *Ferrum* **16** (2011) 599–606.
- 2) J. Banhart: *Prog. Mater. Sci.* **46** (2001) 559–632.
- 3) T. Murakami and E. Kasai: *Bulletin of the Advanced Materials Processing Building* **62** (2007) 37–45.
- 4) C. Park and S.R. Nutt: *Mater. Sci. Eng. A* **288** (2000) 111–118.
- 5) T. Murakami, K. Ohara, T. Narushima and C. Ouchi: *Mater. Trans.* **11** (2007) 2937–2944.
- 6) T. Shimizu and K. Matsuzaki, *Proc. Int. Conf. on Porous metals and Metal Foaming Technology*, ed. by H. Nakajima and N. Kanetake (The Japan Inst. Metals, 2005) pp. 191–194.
- 7) S. Ghouse, S. Babu, R.J. Van Arkel, K. Nai, P.A. Hooper and J.R.T. Feffers: *Mater. Des.* **131** (2017) 498–508.
- 8) T. Matsumura, Y. Takenaka and M. Shimizu: *Tetsu-to-Hagané* **85** (1999) 652–657.
- 9) S. Watanabe and M. Yoshinaga: *Sumitomo metals*, **17**, (1965) 323–327.
- 10) Y. Fuwa and S. Banya: *Tetsu-to-Hagané* **52** (1966) 231–233.
- 11) Z. Qi, T. Murakami and E. Kasai: *ISIJ Int.* **52** (2012) 1777–1783.
- 12) T. Murakami, T. Nishimura and E. Kasai: *ISIJ Int.* **49** (2009) 1686–1693.
- 13) T. Murakami, T. Nishimura, N. Tsuda and E. Kasai: *ISIJ Int.* **53** (2013) 1763–1769.