Effect of HPC (Hyper-coal) on Strength of Ferro-coke during Caking Temperature

Ataru UCHIDA,¹⁾ Yoshiaki YAMAZAKI,¹⁾ Shohei MATSUO,¹⁾ Yasuhiro SAITO,^{1)*} Yohsuke MATSUSHITA,¹⁾ Hideyuki AOKI¹⁾ and Maki HAMAGUCHI²⁾

1) Department of Chemical Engineering, Graduate School of Engineering, Tohoku University 6-6-07 Aoba, Aramaki, Aoba-ku, Sendai, Miyagi, 980-8579 Japan. 2) Kobe Steel, LTD., 2-3-1, Shinhama, Arima-cho, Takasago, Hyogo, 676-8670 Japan.

(Received on March 9, 2017; accepted on April 27, 2017)

The effect of HPC (Hyper-coal), which was affected by the iron oxide, on coal particle adhesion during carbonization was investigated. X-ray diffraction analyses were carried out to obtain changes of iron oxide crystal structure on HPC with iron oxide addition during caking temperature. The promoted weight loss of HPC by the iron oxide during caking temperature was calculated from the weight losses by thermogravimetric analyses and gas concentrations by a gas chromatograph and a Karl Fischer titrator. Furthermore, to reveal the effect of iron oxide on coal particle adhesion at resolidification temperature, the yields of semi-coke with and without HPC/High Fluidity-HPC (HF-HPC)/Fe₂O₃/Fe₃O₄ were measured, the strength of the semi-coke samples was evaluated using diametral compression tests, and the adhesion of coal particles was evaluated using microstructure analyses. As a result, the promoted weight loss of HPC was increased by the catalysis of Fe₂O₃, and was decreased, when the Fe₂O₃ was reduced to Fe₃O₄, due to hydrogen atoms in the thermoplastic components of HPC. Thus, the strength of semi-coke with HPC increased. Furthermore, although the iron oxide affected the HPC, the adhesiveness of coal particles, which was an index of ferro-coke strength, was enhanced by HPC, and the adhesiveness of HF-HPC was higher than that of HPC. Therefore, the HPC decreased the chemical effect of iron oxide, and improved the adhesiveness.

KEY WORDS: ironmaking; ferro-coke; hyper-coal; coke strength.

1. Introduction

Coke plays a role as a reducing agent of iron ore, a heat source, and a spacer in blast furnace operations.^{1,2)} Coke strength and its reactivity are important factors to improve efficiency of blast furnace operations.^{3,4)} Ferro-coke is known as coke with high reactivity, which is produced by adding iron ore to coal in coke-making processes.^{5,6)} Ferro-coke has been investigated for its strength and reactivity. For example, Nomura *et al.* showed that iron ore decreased expansibility of coal particles though ferro-coke has high reactivity.⁷⁾ Yamazaki *et al.* reported that a decrease in expansibility of coal particles caused a decrease in their adhesiveness, and coke strength decreased.⁸⁾ Therefore, it is necessary to enhance strength of ferro-coke by improvement of adhesiveness of coal particles.

To improve strength of ferro-coke, blending HPC (Hyper-coal) into coal particles in coke-making processes has been investigated.⁹⁾ Okuyama *et al.* showed that HPC softened in low temperature and had high fluidity, and demonstrated that blending HPC into low-quality coal contributed the improvement of coke strength.¹⁰⁾ Koyano *et al.* reported that a binder including polycyclic aromatic

hydrocarbons which had an affinity for thermoplastic components of coal, improved adhesiveness of coal particles and increased coke strength.¹¹⁾ Moreover, Uchida *et al.* indicated that blending HPC into coal particles enhanced adhesiveness of coal particles and strength of coke while strength of coke decreased because adhesiveness of coal particles decreased due to the existence of metallic iron around coal particles in microscopic structure of ferro-coke.¹²⁾ These studies evaluated coke samples after carbonization and focused on the relationships between only two components, coal and iron or HPC. To investigate ferro-coke utilized in industrial processes, the evaluation of three components, coal, iron ore, and HPC is required.

Although coke quality after coal carbonization has been evaluated, carbonization process itself is regarded to be important because it is found that iron oxide causes reduction reaction during coal carbonization processes and it affects fluidity of HPC.¹³⁾ Uchida *et al.* reported that iron oxide was reduced by hydrogen atoms in HPC and thermoplastic components of coal in thermoplastic temperature, and promoted carbonization of HPC.¹³⁾ Byambasjav *et al.* showed that asphaltene was cracked by hematite (Fe₂O₃) as catalyst at 300°C, and was decomposed into low molecular compounds.¹⁴⁾ This fact suggested that hematite cut C–C bond off. However, the effect of reduction reaction and catalysis of iron oxide on coke-making processes has been

* Corresponding author: E-mail: saito@tohoku.ac.jp
DOI: <http://dx.doi.org/10.2355/isijinternational.ISIJINT-2017-130>

rarely investigated, and in particular, the dominant factors which affect strength of ferro-coke have not been well discussed.

In the present study, the effect of HPC on strength of ferro-coke during caking temperature was investigated. X-ray diffraction analyses for a sample with HPC and iron oxide was performed, and crystal structure changes of iron oxide with reduction reaction were evaluated. To investigate the effect of reduction reaction of iron oxide on weight loss ratio of HPC, weight loss of coal matrix and gas analyses during carbonization were conducted using a thermo gravimeter, a gas chromatograph, and a Karl Fischer titrator. The weight losses of HPC promoted by the iron oxide during caking temperature were estimated from measured and theoretical calculated values. Furthermore, samples with HPC, catalysts, and/or High Fluidity-HPC were employed. Yield ratios of semi-coke samples of ferro-coke were obtained, and the influence of the blending ratio of HPC, kind of catalysts, and fluidity of HPC on their yield ratios was discussed. Moreover, the strength of semi-coke samples of ferro-coke and the adhesiveness of coal particles were evaluated, and dominant factors of ferro-coke strength were discussed.

2. Experimental

2.1. Samples

Non- or slightly- caking coal was used as a sample, and Hyper-coal (HPC) and High Fluidity-HPC (HF-HPC) were employed as a binder, which are different in fluidity. HF-HPC is derived in higher temperature than HPC, and includes low molecular weight components. Proximate and ultimate analyses of coal, HPC, and HF-HPC used in this experiment are indicated in **Table 1**. The initial thermoplastic temperature, maximum fluidity, and resolidification temperature of HPC employed in the experiment are summarized in **Table 2**. HF-HPC shows wide-range thermoplastic temperature, and has higher fluidity than HPC. Hematite (Fe_2O_3 , Wako 95%) and magnetite (Fe_3O_4 , Wako 95%) were chosen as a catalyst. The diameter and blending ratio of samples are listed in **Tables 3** and **4**, respectively. Here, in the samples with hematite (*i.e.*, Samples HP00-H, HP05-H, HP10-H, HP15-H, and HfHP05-H) and samples with magnetite (*i.e.*, Samples HP00-M, HP05-M, and HfHP05-M), the amount of hematite and magnetite was determined so as to be equal that of metal iron. The amount of metal iron in samples with 30 wt% of hematite and 29 wt% of magnetite was calculated by following equation:

(Weight of metal iron in sample) =

$$\frac{2M_{\text{Fe}}}{M_{\text{Fe}_2\text{O}_3}} \times 0.30 = \frac{3M_{\text{Fe}}}{M_{\text{Fe}_3\text{O}_4}} \times 0.29 = 0.210, \quad (1)$$

where M is atomic or molecular weight. The difference in weight (*i.e.*, 1 wt%) corresponds to oxygen atoms when all the hematite is reduced to magnetite, and is defined as 'Blank' as shown in Table 4. The samples were shaped into tablets by packing and compressing coal in the mold with diameter of 25 mm. Samples HPC100, HPC70-HEM30, and HEM100 were compressed and shaped with pressure of 98 MPa in room temperature. Samples HP00-H,

HP05-H, HP10-H, HP15-H, HP00-M, HP05-M, HfHP05-H, and HfHP05-M were with 294 MPa. And then, the tablets of the samples (Samples HP00-H, HP05-H, HP10-H, HP15-H, HP00-M, HP05-M, HfHP05-H, and HfHP05-M) were heated up to 500°C with heating rate of 5°C/min, and quenched quickly in nitrogen atmosphere. To investigate behaviors of samples during caking temperature, the tablets

Table 1. Characterization of coals.

	Moisture	Ash	VM	C	H	N	S	O _{diff}	H/C
	[wt%]	[daf wt%]	[daf wt%]						[–]
Coal	3.4	7.6	40.2	80.4	5.6	1.8	0.7	11.5	0.84
HPC	0.3	0.1	41.2	86.6	5.4	1.9	0.6	5.5	0.75
HF-HPC	1.97	0.07	49.44	87.5	6.3	1.9	0.6	3.7	0.86

where HPC is hyper-coal, HF-HPC represents high fluidity hyper-coal, and VM is volatile matter.

Table 2. Data of Gieseler plastometry.

	Initial softening temperature [°C]	Maximum fluidity temperature [°C]	Resolidification temperature [°C]	log (MF/ddpm)
Coal	408	430–436	451	0.78
HPC	242	351–426	476	>4.8
HF-HPC	177	277–448	481	>4/8

where HPC is hyper-coal, HF-HPC represents high fluidity hyper-coal, and MF is maximum fluidity.

Table 3. Particle size of raw materials.

	Diameter
Coal	<1.0 mm
HPC (hyper-coal)	<150 μm
HF-HPC (high fluidity hyper-coal)	<150 μm
Fe_2O_3 (hematite)	<150 μm
Fe_3O_4 (magnetite)	<150 μm

Table 4. Blending ratio of each sample [wt%].

Sample	Coal	HPC	HF-HPC	Fe_2O_3	Fe_3O_4	Blank
HPC100	0	100	0	0	0	0
HPC70-HEM30	0	70	0	30	0	0
HEM100	0	0	0	100	0	0
HP00-H	70	0	0	30	0	0
HP05-H	65	5	0	30	0	0
HP10-H	60	10	0	30	0	0
HP15-H	55	15	0	30	0	0
HP00-M	70	0	0	0	29	1
HP05-M	65	5	0	0	29	1
HfHP05-H	65	0	5	30	0	0
HfHP05-M	65	0	5	0	29	1

where HPC is hyper-coal, and HF-HPC represents high fluidity hyper-coal. Fe_2O_3 and Fe_3O_4 mean hematite and magnetite, respectively.

at carbonization temperature of 500°C were employed for the evaluation of yield, diametral-compression tests, and microscopic structure analyses. Because the resolidification temperatures of coal, HPC, and HF-HPC are less than 500°C, the state of the tablets at carbonization temperature of 500°C is just the beginning of resolidification.

2.2. XRD Analysis

To investigate crystal structure change of iron oxide with reduction reaction during carbonization process, the structure of iron oxide in the Sample HPC70-HEM30 was analyzed at carbonization temperatures of 300, 400, 500, 600, 700, and 1 000°C by using X-ray diffractometer, XRD (RINT1500, Rigaku Corp.).

2.3. Thermogravimetric Analysis

To investigate the effect of reduction reaction of iron oxide on weight loss of coal matrix during carbonization, weight loss of samples was measured using a thermo gravimeter (TG/DTA 220, Seiko Instruments, Inc.). The Samples HPC100, HPC70-HEM30, and HEM100 of about 1 mg were heated up to 1 000°C with heating rate of 5°C/min under nitrogen atmosphere. The Sample HPC70-HEM30 is mixture of 70 wt% of HPC and 30 wt% of hematite, and if the reduction reaction of iron oxide does not affect coal matrix, weight loss of the mixture can be theoretically represented as following equation:

$$W_{\text{calc}} = 0.7 \times W_{\text{HPC100}} + 0.3 \times W_{\text{HEM100}}. \dots\dots\dots (2)$$

2.4. Gas Analysis

Light gas concentrations (H_2 , CH_4 , H_2O , CO , and CO_2) released from the tablets of the Samples HPC100 and HPC70-HEM30 (about 1 mg) during carbonization were measured to investigate the components of weight loss ratio of the samples. Crystal water released from pure iron oxide was measured by the weight loss of samples. Gas concentration of H_2 , CH_4 , CO , and CO_2 were measured by 490-GC (Varian), and that of H_2O by Karl Fischer titrator (Mitsubishi Chemical Analytech Co. Ltd.), respectively.

2.5. Evaluation of Yield

Yield ratios were evaluated from difference in weight of samples before and after carbonization, and calculated by Eq. (3):

$$(\text{Yield ratio}) = \frac{Y}{Y_0 + Y_{\text{blank}}} \times 100, \dots\dots\dots (3)$$

where Y_0 and Y are weight of the samples before and after carbonization. Y_{blank} is difference in weight of hematite and magnetite added to the samples, and in the case of Samples HP00-H, HP05-H, HP10-H, HP15-H, and HfHP05-H, the value is zero.

2.6. Diametral-compression Test

Diametral-compression tests were performed for coke samples using a universal tester (Shimadzu Corp., Autograph AG-150kN). Load was put on a sample with loading rate of 2 mm/min. The number of tests for each sample was from seven to eight times. Scale parameter was calculated using the Weibull plot in the same way of Sakai *et al.*¹⁵⁾ The

calculation method was the same method as that employed by Kanai *et al.*¹⁶⁾ Here, the scale parameter means tensile strength, and can evaluate strength of semi-coke sample.

2.7. Microscopic Structure Analysis

Epoxy resin was embedded in the Samples HP00-H, HP05-H, HP10-H, HP15-H, HP00-M, HP05-M, HfHP05-H, and HfHP05-M with vacuum impregnation equipment, and the samples were polished. Digital images of polished surface were obtained by using optical microscope (LV-100-POL, Nikon) for the above samples. The image size was 3.11 mm $\times$ 2.33 mm, and the display resolution was 1 280 pixel $\times$ 960 pixel. Thirty images were taken for each sample, and were combined and trimmed to obtain the combined image with size of 10 mm $\times$ 10 mm and display resolution of 4 116 pixels $\times$ 4 116 pixels. Pores were extracted by setting threshold for brightness of pixel in digital microscopic image and binarizing the image with discriminant analysis method using image analysis software (WinROOF ver. 6.1, Mitani Corp.). Roundness of pores was obtained by analyzing combined binary image with the image analysis software. Roundness is a shape parameter, and is defined as follows:

$$(\text{Roundness}) = \frac{4\pi S}{L^2}, \dots\dots\dots (4)$$

where L and S are perimeter and area of pore, respectively.

3. Results and Discussion

3.1. Changes of Crystal Structure of Iron Oxide

To investigate changes of crystal structure of iron oxide in carbonization process, the crystal structure was analyzed using XRD. The measured results in the Sample HPC70-HEM30 at carbonization temperatures from 300 to 1 000°C are shown in Fig. 1. Iron oxide was reduced from hematite to magnetite with an increase in temperature at 300–500°C. Hematite seems to be reduced to magnetite by hydrogen atom in softened HPC at 300–500°C in terms of the previous study.¹³⁾ Fraction of magnetite increased at 500–600°C, and magnetite was reduced to wustite (FeO) or metal iron (Fe) over 700°C. The above results mean that the crystal structure of iron oxide changed with reduction reaction of iron oxide in carbonization process. The effect

Fig. 1. Iron oxide transitions of Sample HPC70-HEM30.

of iron oxide on thermoplastic components of HPC would change with changes in crystal structure of iron oxide because reduction reaction of iron oxide was promoted by hydrogen in softened components of HPC in thermoplastic state.¹³⁾ From the above results, weight loss ratio of thermoplastic components of HPC would change and weight of HPC contributing adhesiveness of coal particles would also change because reduction reaction of iron oxide from hematite to magnetite is promoted in 300–500°C.

3.2. Effect of Reduction of Iron Oxide on Weight Loss Ratio of HPC

Thermogravimetric analyses were carried out to investigate weight loss ratio of HPC promoted with change in crystal structure of iron oxide in carbonization process. The results of thermogravimetric analyses are shown in Fig. 2. The solid line is the measured value of Sample HPC70-HEM30, and dashed line is theoretically calculated one from the measured values of Samples HPC100 and HEM100 as the ratio of 7:3 as shown in Eq. (2). The measured value of Sample HPC70-HEM30 (*i.e.*, with interaction) involves weight loss ratio of HPC promoted by reduction reaction of iron oxide, that of oxygen atoms abstracted from iron oxide reagent with reduction reaction of iron oxide, and crystal water originally in iron oxide reagent. On the other hand, the calculated one (*i.e.*, without interaction) does not involve weight loss ratio of HPC promoted by reduction reaction of iron oxide and that of oxygen atoms abstracted from iron oxide reagent with reduction reaction of iron oxide. In the present study, weight loss ratio of HPC promoted by reduction reaction of iron oxide in the Sample HPC70-HEM30 was estimated by following method.

Figure 3 shows weight loss ratios of Sample HPC70-HEM30 and those calculated by weight loss ratio of Samples HPC100 and HEM100, which were measured individually. Here, the weight loss ratios, W were normalized based on the initial weight of each chemical species. The difference of $W_{\text{HPC70-HEM30}}$ (Fig. 3(a)) and W_{calc} (Fig. 3(b)) is regarded as weight loss ratio of sample, which is promoted by reduction reaction of iron oxide as follows:

$$\Delta W_{\text{promoted, total}} = W_{\text{HPC70-HEM30}} - W_{\text{calc}} \quad \dots\dots (5)$$

Fig. 2. Weight loss of sample (HPC: Fe_2O_3 = 70: 30). “With interaction” indicates the measured value of Sample HPC70-HEM30, and “Without interaction” indicates theoretically calculated one from the measured values of Samples HPC100 and HEM100.

Furthermore, in the present experimental condition, the experiments were performed in nitrogen atmosphere, and the measured value of Sample HPC70-HEM30 and the calculated one from the measured values of Sample HPC100 and HEM100 were compared. Thus, we can evaluate the interaction of HPC and oxygen atoms abstracted from iron oxide reagent with reduction reaction of iron oxide. The weight loss ratio of HPC caused by reduction reaction of iron oxide, $\Delta W_{\text{promoted, HPC}}$ is obtained by subtracting from $\Delta W_{\text{promoted, total}}$ to $\Delta W_{\text{promoted, O}}$ as following equation:

$$\Delta W_{\text{promoted, total}} = \Delta W_{\text{promoted, HPC}} + \Delta W_{\text{promoted, O}} \quad \dots\dots (6)$$

where $\Delta W_{\text{promoted, O}}$ is weight loss ratio of oxygen atoms, and involves weight loss ratio of gases with oxygen atom (CO , CO_2 , and H_2O). Figure 4 shows the weight loss ratios of all the released gas components measured by the gas chromatograph and Karl Fischer titrator. In the present study, those gas components were divided into light gas components (H_2 , CH_4 , H_2O , CO , and CO_2) and the other, and the low molecular weight gases were classified into each atom, such as C, H, and O shown in Fig. 4(b). The weight loss ratios of $\Delta W_{\text{promoted, O}}$ and $\Delta W_{\text{promoted, total}}$ were obtained. Here, $\Delta W_{\text{promoted, O}}$ was calculated from Eq. (7):

$$\Delta W_{\text{promoted, O}} = \frac{M_{\text{O}}}{M_{\text{CO}}} \Delta W_{\text{promoted, CO}} + \frac{2M_{\text{O}}}{M_{\text{CO}_2}} \Delta W_{\text{promoted, CO}_2} + \frac{M_{\text{O}}}{M_{\text{H}_2\text{O}}} \Delta W_{\text{promoted, H}_2\text{O}} \quad \dots\dots (7)$$

(a) Measured value of Sample HPC70-HEM30

(b) Calculated value from the measured values of Samples HPC100 and HEM100

Fig. 3. Relative weight loss ratio of sample (HPC: Fe_2O_3 = 70: 30).

where M is atomic or molecular weight. Therefore, the weight loss ratio of HPC, $\Delta W_{\text{promoted,HPC}}$ which is caused by reduction reaction of iron oxide can be estimated by subtracting that of $\Delta W_{\text{promoted,O}}$ from $\Delta W_{\text{promoted,total}}$, and Fig. 5 was derived from Figs. 3 and 4. For example, at temperature of 500°C, the weight loss ratios were $\Delta W_{\text{promoted,CO}} = -0.0525$ wt%, $\Delta W_{\text{promoted,CO}_2} = 0.287$ wt%, $\Delta W_{\text{promoted,H}_2\text{O}} = 1.194$ wt%, and $\Delta W_{\text{promoted,total}} = -0.0590$ wt%. Thus, because $\Delta W_{\text{promoted,O}} = 1.241$ wt%, $\Delta W_{\text{promoted,HPC}} = -1.30$ wt%.

(a) All the released gas components in Sample HPC70-HEM30

(b) Classified low molecular weight gases

Fig. 4. Relative weight loss of gas components in Sample HPC70-HME30 (HPC: $\text{Fe}_2\text{O}_3 = 70:30$).

Fig. 5. Promoted relative weight loss of HPC by reduction reaction of iron oxide (HPC: $\text{Fe}_2\text{O}_3 = 70:30$).

Figure 5 shows $\Delta W_{\text{promoted,HPC}}$ which is promoted by reduction reaction of iron oxide. The amount of weight loss of thermoplastic components of HPC ($\Delta W_{\text{promoted,HPC}}$) increased at 300–450°C. This is because hematite is thought to cut C–C bond of hydrocarbon in thermoplastic HPC and to contribute to release of thermoplastic components.¹⁴⁾ Weight loss ratio of thermoplastic components in HPC decreased at 460–630°C. In other words, carbonization of HPC was promoted in this temperature range, and the release of thermoplastic components was inhibited. From the fact that the release of hydrogen was promoted, this is caused by the reduction of hematite with hydrogen in thermoplastic HPC because the hydrogen reduction of iron oxide occurred. Furthermore, dehydrogenation of thermoplastic components of HPC occurred because the release of gases with carbon atoms and the other gases was inhibited, and the carbonization of HPC would be promoted.

3.3. Effect of Blending Ratio of HPC, Kind of Catalysts, and Fluidity of HPC on Yield Ratio

Yield ratio of semi-coke samples at temperature of 500°C is obtained to investigate the effect of blending ratio of HPC, catalyst, and fluidity of HPC on yield ratio of semi-coke in thermoplastic temperature. Yield ratios of the Samples HP00-H, HP05-H, HP10-H, HP15-H, HP00-M, HP05-M, HfHP05-H, and HfHP05-M are shown in Fig. 6. Here, the yield ratios were calculated from Eq. (3). Focusing on the Sample HP00-H ((i) in Fig. 6), HP05-H ((ii) in Fig. 6), HP10-H ((iii) in Fig. 6), and HP15-H ((iv) in Fig. 6), the yield ratio increased with an increase in blending ratio of HPC. This would be because weight loss with reduction reaction of iron oxide at 500°C was suspended, and carbonization of HPC was promoted. Moreover, comparing yield ratios of samples with hematite (*i.e.*, Samples HP00-H ((i) in Fig. 6) and HP05-H ((ii) in Fig. 6)) and ones with magnetite (*i.e.*, Samples HP00-M ((v) in Fig. 6) and HP05-M ((vi) in Fig. 6)), yield ratio was lower in the samples with magnetite than in those with hematite. This is because although reduction reaction from hematite to magnetite occurred at 500°C as shown in Fig. 1, the reaction from magnetite to hematite did not occur, and carbonization of thermoplastic

Fig. 6. Difference of yield ratio of each sample at carbonization temperature of 500°C: (i) Sample HP00-H; (ii) Sample HP05-H; (iii) Sample HP10-H; (iv) Sample HP15-H; (v) Sample HP00-M; (vi) Sample HP05-M; (vii) Sample HfHP05-H; (viii) Sample HfHP05-M.

components in coal and HPC was not promoted. In addition, large difference did not appear in yield ratio when the same kind of iron oxide was used, in other words, when the Sample HP05-H ((ii) in Fig. 6) is compared with the Sample HfHP05-H ((vii) in Fig. 6), and the Sample HP05-M ((vi) in Fig. 6) with the Sample HfHP05-M ((viii) in Fig. 6). Therefore, HPC increased yield ratio independent of its fluidity. Moreover, when HF-HPC was employed as a binder instead of HPC, yield ratio of the Sample HfHP05-H ((vii) in Fig. 6) was higher than that of the Sample HfHP05-M ((viii) in Fig. 6) as is the case with HPC. It is shown that carbonization of HPC is promoted by reduction reaction of hematite independent of its fluidity.

3.4. Adhesiveness of Coal Particles in Semi-coke

According to above results, yield ratio of ferro-coke with HPC is found to increase in thermoplastic temperature because reduction reaction from hematite to magnetite by hydrogen atoms of HPC is promoted. It seems that HPC increases thermoplastic components of HPC and coal which contribute to adhesiveness of coal particles. Therefore, adhesiveness of coal particles, which is dominant factor of strength of ferro-coke seems to be formed with being influenced by iron oxide. Hence, strength of semi-coke and adhesiveness of coal particles in resolidification temperature after thermoplastic temperature are investigated.

Weibull plots of the Samples HP00-H, HP05-H, HP10-H, HP15-H, HP00-M, HP05-M, HfHP05-H, and HfHP05-M obtained by diametral compression tests, and the scale parameters calculated from the Weibull plots are shown in Fig. 7. Furthermore, Fig. 8 shows existence ratio of roundness of pores in the Sample HP00-H, HP05-H, HP00-M, HP05-M, HfHP05-H, and HfHP05-M. Comparing samples with coal and hematite and those with coal and magnetite, the scale parameter of Sample HP00-H ((i) in Fig. 7) is smaller than that of Sample HP00-M ((v) in Fig. 7). This would indicate that thermoplastic components of coal were decomposed due to catalysis of hematite, and the adhesiveness of coal particles decreased. In the previous study, Uchida *et al.*¹²⁾ defined pores with roundness of less than 0.05 as non-adhesion pores with iron particles between coal particles in experiments with ferro-coke combined with HPC, and reported that adhesiveness of coal particles can be evaluated by finding the pores with roundness of less than 0.05. In the present study, the existence ratio of pores with roundness of less than 0.05 was used as index of the adhesiveness.

Focusing on Samples HP00-H ((i) in Fig. 7), HP05-H ((ii) in Fig. 7), HP10-H ((iii) in Fig. 7), and HP15-H ((iv) in Fig. 7), the scale parameter increased with the addition of HPC. Therefore, adhesiveness of coal particles would be enhanced with the addition of HPC. This is derived from the fact that the existence ratio of pores with low roundness of less than 0.05 in the Sample HP05-H ((ii) in Fig. 8) was lower than that in the Sample HP00-H ((i) in Fig. 8). Furthermore, comparing sample with coal, HPC, and hematite (*i.e.*, Sample HP05-H) and the one with coal, HPC, and magnetite (*i.e.*, Sample HP05-M), scale parameter of Sample HP05-M ((vi) in Fig. 7) is larger than that of Sample HP05-H ((ii) in Fig. 7). It is shown that adhesiveness of coal particles increased due to the addition of HPC because the

(a) Weibull plot for each sample

(b) Relationship between material and scale parameter

Fig. 7. Coke strength for each sample at carbonization temperature of 500°C: (i) Sample HP00-H; (ii) Sample HP05-H; (iii) Sample HP10-H; (iv) Sample HP15-H; (v) Sample HP00-M; (vi) Sample HP05-M; (vii) Sample HfHP05-H; (viii) Sample HfHP05-M.

Fig. 8. Distributions of pore roundness of each sample at carbonization temperature of 500°C: (i) Sample HP00-H; (ii) Sample HP05-H; (v) Sample HP00-M; (vi) Sample HP05-M; (vii) Sample HfHP05-H; (viii) Sample HfHP05-M.

existence ratio of pores with low roundness of less than 0.05 in Sample HP05-M ((vi) in Fig. 8) was lower than that in Sample HP05-H ((ii) in Fig. 8).

The Samples HP05-H, HP05-M, HfHP05-H, and HfHP05-M are compared to investigate effect of difference in fluidity of HPC in thermoplastic temperature on adhesiveness of coal particles. For the same catalyst, the

scale parameters of the Samples HfHP05-H ((vii) in Fig. 7) and HfHP05-M ((viii) in Fig. 7) indicate lower in strength than those of Samples HP05-H ((ii) in Fig. 7) and HP05-M ((vi) in Fig. 7). Yamamoto *et al.* reported that strength of ferro-coke carbonized in high temperature was increased by increasing blending ratio of a binder and enhancing fluidity of blended sample.¹⁷⁾ The samples with HF-HPC did not carbonize at 500°C more than that with HPC because resolidification temperature of HF-HPC is higher than that of HPC. Therefore, the strength of the Samples HP05-H ((ii) in Fig. 7) and HP05-M ((vi) in Fig. 7) was higher than that of the Samples HfHP05-H ((vii) in Fig. 7) and HfHP05-M ((viii) in Fig. 7) because the samples with HPC were resolidified at lower temperature than those with HF-HPC, and the carbonization of the samples with HPC progressed more than those with HF-HPC. Adhesiveness of the samples with HF-HPC seems to be higher than that with HPC because the existence ratio of pores with roundness of less than 0.05 in the Sample HfHP05-H ((vii) in Fig. 8) was less than that in the Sample HP05-H ((ii) in Fig. 8). In the semi-coke samples, HF-HPC flows into space between coal particles and enhances adhesiveness of coal particles in thermoplastic temperature because HF-HPC has higher fluidity than HPC. Therefore, HF-HPC has possibility to improve coke strength compared with HPC if carbonization of the sample with HF-HPC can progress.

From above results, HPC influenced by iron oxide in thermoplastic temperature softens and flows into space between coal particles, and enhances adhesiveness of coal particles. Consequently, dominant factors of ferro-coke strength are found to be formed by thermoplastic components of coal and HPC.

4. Conclusions

In the present study, to investigate Hyper-coal (HPC) influenced by iron oxide in thermoplastic process on microscopic structure of ferro-coke, HPC and hematite (Fe_3O_4) as well as High Fluidity-HPC (HF-HPC) and magnetite (Fe_2O_3) were employed, and thermogravimetry, X-ray diffraction (XRD) analyses, diametral compression tests, and structure analyses with microscopic image were performed. This study can be summarized as follows:

(1) Hematite was reduced to magnetite by hydrogen atoms of thermoplastic components of coal or HPC at 300–500°C. The reduction reaction from hematite to magnetite promoted carbonization of HPC, and yield ratio of HPC at resolidification increased.

(2) Thermoplastic components of coal were decomposed by catalysis of hematite at 300–450°C.

(3) An addition of HPC increased yield ratio of samples, and enhanced adhesiveness of coal particles at resolidification. HF-HPC would improve adhesiveness of semi-coke more than HPC.

Above the results, it is necessary to improve adhesiveness of coal particles with HPC which is rich in hydrogen and

softens at low temperature to enhance strength of ferro-coke.

Acknowledgements

We would like to express our sincere appreciation to the authors for their permission to use some of the results found in “Elucidation of the Mechanism for Developing Strength of New Binders.” This study was carried out on consignment from Kobe Steel, Ltd. as a part of “Project to Develop Technology for an innovative Iron-making Process for Efficient Use of Resources,” which was funded by the New Energy and Industrial Technology Development Organization (NEDO).

Nomenclature

L :	perimeter of pore	[m]
M :	atomic or molecular weight	[g/mol]
S :	area of pore	[m ²]
W :	weight loss ratio	[wt%]
ΔW :	weight loss ratio	[wt%]
Y :	weight of sample	[g]

Subscripts

blank:	difference in weight of hematite and magnetite
HPC:	HPC
calc:	theoretical calculated
O:	oxygen
promoted:	promoted
HPC100:	Sample HPC100
HPC70-HEM30:	Sample HPC70-HEM30
HEM100:	Sample HEM100
total:	total
0:	initial

REFERENCES

- 1) I. Shimoyama: *Tetsu-to-Hagané*, **96** (2010), 209.
- 2) M. Shimizu and M. Naito: *Tetsu-to-Hagané*, **92** (2006), 694.
- 3) M. Naito, A. Okamoto, K. Yamaguchi, T. Yamaguchi and Y. Inoue: *Tetsu-to-Hagané*, **87** (2001), 357.
- 4) K. Higuchi, S. Nomura, K. Kunitomo, H. Yokoyama and M. Naito: *Tetsu-to-Hagané*, **98** (2012), 517.
- 5) M. Naito, S. Nomura and K. Kato: *Tetsu-to-Hagané*, **96** (2010), 201.
- 6) T. Yamamoto, T. Sato, H. Fujimoto, T. Anyashiki, K. Fukuda, M. Sato, K. Takeda and T. Ariyama: *Tetsu-to-Hagané*, **97** (2011), 501.
- 7) S. Nomura, H. Terashima, E. Sato and M. Naito: *Tetsu-to-Hagané*, **92** (2006), 849.
- 8) Y. Yamazaki, H. Hayashizaki, K. Ueoka, K. Hiraki, Y. Matsushita, H. Aoki and T. Miura: *Tetsu-to-Hagané*, **96** (2010), 536.
- 9) T. Takanohashi, T. Shishido, H. Kawashima and I. Sato: *Fuel*, **87** (2008), 592.
- 10) N. Okuyama, T. Shigehisa, Y. Nishibata, K. Matsudaira and M. Nishimura: *Tetsu-to-Hagané*, **92** (2006), 213.
- 11) K. Koyano, K. Ueoka, T. Takanohashi, K. Fukuda and K. Ota: *ISIJ Int.*, **51** (2011), 1044.
- 12) A. Uchida, T. Kanai, Y. Yamazaki, K. Hiraki, Y. Saito, H. Aoki, N. Komatsu, N. Okuyama and M. Hamaguchi: *ISIJ Int.*, **53** (2013), 403.
- 13) A. Uchida, Y. Yamazaki, S. Matsuo, Y. Saito, H. Aoki and M. Hamaguchi: *ISIJ Int.*, **56** (2016), 2132.
- 14) E. Byambajav and Y. Ohtsuka: *Appl. Catal. A: Gen.*, **252** (2003), 193.
- 15) M. Sakai, R. Nishimura, M. Nishimura and K. Fukuda: *Tetsu-to-Hagané*, **92** (2006), 164.
- 16) T. Kanai, Y. Yamazaki, X. Zhang, A. Uchida, Y. Saito, M. Shoji, H. Aoki, S. Nomura, Y. Kubota, H. Hayashizaki and S. Miyashita: *J. Therm. Sci. Technol.*, **7** (2012), 351.
- 17) T. Yamamoto, K. Sato, H. Fujimoto, T. Anyashiki, M. Sato and K. Takeda: *Tetsu-to-Hagané*, **96** (2010), 683.