Coking Technology Using Heavy Oil Residue and Hyper Coal

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Oil sand bitumen and hypercoal are examined as a caking additives to the mixture of strongly coking coal and non-slightly coking coal. Samples were coked, then their strength, crystallinity of the carbon structure, and an anisotropic microstructure were measured. Oil sand bitumen addition enhanced strength, but 15% addition caused a strength decline because of the formation of large pores and cracks. Hypercoal addition increased strength with increased its content. Correlation was observed between increased strength and the crystallinity of a carbon structure or the anisotropic microstructure. Results suggest that mutual melting occurred between a coal blend and a caking additive. Then the caking additive took a carbon structure with high crystallinity by coking, achieved a function as a binder material that connects coal-particle interfaces, and ultimately enhanced strength.

KEY WORDS: caking additive; coking; oil sand bitumen; hypercoal.

1. Introduction

Coke plays various and different roles in the upper and lower part of a blast furnace. It generates hot gases by a combustion reaction as a heat source and produces reducing gas for iron ore reduction at the raceway in the lower furnace. It sustains and improves gas and liquid permeability as a spacer at the dripping zone in the lower furnace and the core part. Moreover, it carburizes metal for encouraging fusibility at the cohesive zone, and improves blast furnace reaction efficiency by promoting the solid–gas coupling reaction at the shaft part. Especially, it is important as a spacer in the lower part of a blast furnace, where ores and sintered ores melt, so that strong demand exists for high-strength coke. Recent global rise in steel demand as well as in China has tightened the supply and demand of coking coal. Coal as a coke material is classified as strongly coking coal, weakly coking coal, and non-slightly coking coal according to its chemical and physical properties such as calorific power, softening and melting properties, and coking properties. Generally various coals are blended into a coke material. Because coking properties contribute to strength, a certain amount of strongly coking coal is indispensable. As this pushes cost, the reduction technology of strongly coking coal that is apt to be short and slender has been demanded.

The caking additive is used for encouraging the fraction of raw materials of inferior quality as well as reducing strongly coking coal. Generally, a higher fraction of non-slightly coking coal promotes the formation of pores or cracks because of different behaviors from coking coal such as decline in softening and melting properties, expansibility and shrinkage at carbonization of the coal blend, so that its

qualities such as coke strength deteriorates. For that reason, it is necessary that a certain amount of strongly coking coal be blended for sustainment of coke strength. In addition, because the coal employed for a coal blend has various properties according to the locality, control of softening and melting properties and coke strength require sufficient understanding of chemical and physical interaction of various coals. The softening and melting properties of a coal blend and the overlap of softening and melting temperature of each coal affect the coking properties of the coal blend. The authors have reported a strong blending effect by the addition of coal solvent extract of low softening and melting temperature to a raw material with low softening and melting temperature.^{1–3)} Caking additive technique⁴⁾ is an approach for applying a caking additive to a coke material with low coking properties to improve them and produce high-strength coke. High molecular compounds of high coking properties with little ash, high softening and melting temperature, and high aromaticity such as tar pitch and asphalt thermal decomposition pitch are adopted as a caking additive. However, some problems exist such as restricted addition of petroleum-derived caking additives with much sulfur content. This study focuses on hyper-coal and oil sand bitumen as a new caking additive that might enable us to use unused carbon resources as a raw material.

Hyper-coal is obtained by solvent extraction of coal at 623–673 K and separate recovery of the solvent.^{5–7)} Coal has poor solubility into a solvent because of its structure with molecules entangled intricately. However aggregation relieved by heat improves its extractability to a solvent. Ash stays in the insoluble component as slurry in this process. It is retrieved by solid–liquid separation. Consequently, the extract contains no ash, but comprises dicyclic aromatic compounds such as naphthalene and methylnaphthalene, and has high calorific power. The dicyclic aromatic com-

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pound has a structure resembling the basic structure of coal, and has high affinity with coal. This hyper-coal has very high flowability and broad softening and melting temperature range. Reportedly, the softening and melting properties of a coal blend are greatly improved by blending this hyper-coal instead of the coking coal in a coal blend.⁷⁾ Also, indirect tensile testing to the coke produced from this coal blend reportedly indicates enhanced radial compression strength. For those reasons, it has been hypothesized that the non-aggregated structure of hyper-coal allows high molecule mobility at low temperature and therefore high softening and melting properties. Moreover, hyper-coal permeates and melts in the particle pore of the surrounding coal blend at low temperature. Then it fills and welds interparticle spacing and increases melting components. Therefore, coke production is expected to be implemented with an increased fraction of non-slightly coking coal. It is even reported that hyper-coal made of steam coal of poor softening or melting properties presents high softening and melting properties at low temperature, and that hyper-coal made of various coals demonstrates comparable strength improvement. These facts confirm that hyper-coal can be produced from lean coal such as brown coal and subbituminous coal. Therefore, hyper-coal might contribute greatly to diversification and stable supply of coking coal resources.

Oil sand is the sandstone containing bitumen, a heavy crude oil with high viscosity similar to asphalt, also referred to as tar sand. Various definitions exist for an oil sand. The law of the State of Alberta in Canada, advanced in survey and development of natural resources, defines it as the sand containing viscous hydrocarbons that is hard to recover in natural state through a well with the ordinary production procedure. The oil sand comprises sand granules, bitumen, water, and fine minerals in its physical structure. As for the oil sand of Athabasca of the State of Alberta, the physical properties of an oil reservoir with an oil content of 12 wt% (average) are as follows: apparent density, 1.79–2.09 (an average of 1.90); porosity, 34–46% (an average of 40.6%). Except the oil content, 2–3 wt% of connate water and 82 wt% of minerals (sand) are included.⁸⁾ It is supposed that bitumen exists in the space between quartz grains wet in water and fine clay minerals are unevenly distributed. The properties of bitumen are the following, although they might vary with mineral deposits: relative density is 0.98–1.02, and viscosity as high as 10 Pa s. Its elemental composition is about 83 wt% C, about 10 wt%H, containing various elements such as S, N, and O, with many heavy metal components such as V and Ni. As for distillation characteristics,

only 10–20% of light fraction equivalent to kerosene and gas oil is contained. The principal component is supposed as aromatic polycyclic compounds or polycyclic naphthene compounds. For that reason, oil sand bitumen is subjected to refining technology, such as cracking and hydrogenation for reforming and impurity elimination, and is processed as synthetic crude oil. The oil sands are economically disadvantageous under the present technology and usage, but the economic efficiency and shortage of other resources will encourage its technical development and production. Furthermore, it might be utilized as a caking additive because the principal component of its super-heavy fraction has a structure of a polycyclic naphthene ring compound, a similar structure to hyper-coal.

Little study has been performed on the change of the coke architecture by applying these as a caking additive. Therefore this study examined coked coal blends using hyper-coal and oil sand bitumen as a caking additive, and evaluated the effect of caking additives according to an analysis of strength, carbon structure, and anisotropic microstructure.

2. Experimental

2.1. Samples Used

Various cokes were produced using coal of various origins and coking properties. Raw materials employed include coal A (strongly coking coal), coal B (non-slightly coking coal), Base coal (A : B = 25 : 75), oil sand bitumen single coal (OSB 100%), hyper-coal single coal (HPC 100%), and 5–15% of coal A in Base coal replaced by OSB or HPC. Properties of used coal and other samples are summarized in **Table 1**. Coal samples were used after drying, and the particle size was < 1 mm for coal A and B, < 0.15 mm for HPC. OSB was bituminous and not can be sieved, so it was melted at higher temperature and blended with coal particles. **Table 2** shows the mixing ratio of each coal sample.

Blended coals were ground, mixed and coked by canned combustion. The raw material ground and mixed was filled in a metal tube, with a flow rate of 1 L min⁻¹ of N₂ supplied under a pressurizing condition, heated to 1 273 K at a heating rate of 3 K min⁻¹, and kept for 30 min to make coke. Then it was self-cooled under N₂ atmosphere until 673 K after completion of carbonization. A sample was collected after cooling. Each sample was prepared for four times, and these all samples were analyzed.

The average strength of the coked samples was measured with a crushing test by Kobe Steel, Ltd, using LXA-500 (Furukawa sanki systems Co. Ltd.). The coked samples

Table 1. Proximate, ultimate and maceral analyses for various samples.

Sample name	Proximate analysis		Ultimate analysis						Thermal palsticity ³⁾				Maceral analysis ⁴⁾				
	ash	VM	C	H	N	S	O _{diff.}	ST	MFT	RT	log (MFD)	Ro	Exinite	Vitrinite	Inertinite	TI	
	[wt%]db ¹⁾		[wt%] (da ²⁾)						[°C]		[ddpm]	[–]	[%]			[%]	
Coal A	10.5	21.8	89.6	4.7	1.6	0.3	3.8	432	474	505	1.82	1.29	0.0	75.0	25.0	28.8	
Coal B	10.0	28.0	87.0	4.8	2.0	0.6	5.7	414	456	478	1.20	1.00	0.4	75.2	24.4	30.8	
HPC	0.1	45.4	89.8	5.9	1.9	0.6	1.7	256	357–438	476	>4.78	1.00	0.0	100.0	0.0	0.2	
OSB	0.1	91.0	83.4	10.5	0.4	4.6	1.1					–	–	–	–	–	

1) dry basis, 2) dry and ash free basis, 3) Gieseler plastometry (JIS M8801), ST: Softening temp., MFT: Maximum fluid temp., RT: Resolidification temp., 4) JIS M8816.

were cut to about 20 mm lengths. Then the strength of each sample was measured with crushing test after computing density. The average strength of each sample was determined during 8 times of crushing tests (four samples were cut to be eight pieces) by indirect tensile test. The strength of prepared sample was calculated by the following equation; $\sigma = 2 P / \pi D L$, where σ denotes the maximum tensile, P : load weight, D : sample diameter, L : sample length.

The analysis of anisotropy, isotropy, and inertinite of the microstructure of coke was conducted by Kobe Steel, Ltd. using polarization microscopy.

Raman spectra were used for evaluation of the coke carbon structure. Raman spectroscopy measures the oscillation of polarizability variation of a molecule or a crystal. Therefore, crystal symmetry should be considered. This technique has been used for carbon materials and rubbers as analyses for crystals and solids. Raman spectroscopy is very effective for the evaluation of carbon materials. Information about their internal structure that is unobtainable by other methods can be obtained.^{9–18)} The Raman spectra of amorphous carbon appear around 1 150, 1 350, 1 500, and the 1 620 cm^{-1} , and are respectively referred to as D4, D1, D3, and D2. The D4 band is supposed to be attributed to an imperfect graphite lattice, polyene, and the impurity originated by oscillation symmetric with A1g. It is considered that the D1 band is an imperfect graphite lattice and that a graphite layer end originated by oscillation symmetric with A1g. The D3 band is believed to be the vibration of amorphous carbon origin. The D2 band is an imperfect graphite lattice and a graphite layer surface originated by oscillation symmetric with E2g. In addition, the G band of an ideal graphite lattice originated by oscillation symmetric with E2g is observed around 1 580 cm^{-1} in carbon having crystallinity to some degree. These bands of carbon with low crystallinity are generally observed overlapped in Raman spectroscopy. Therefore, they are separated into each spectrum by deconvolution. As the intensity and area value of these spectra depend on measurement points, Raman parameters, the ratios of the half band width, intensity, and area value of deconvoluted spectra are used for comparing various carbon structures. D/G, the most common parameter, is the intensity ratio of Raman spectra before deconvolution. It is reported that this param-

eter declines with an increase in the heat treatment temperature of carbon with low crystallinity. However, this parameter decreases at elevated temperature not less than 1 273 K and is not considered suitable. It is also known that the half band width of the G band generally declines with increase in the crystallinity of graphite. For that reason, some studies adopt the ratio of the half band width of the D and G bands. Moreover, there exist difference in a carbon structure and interfaces of a different carbon structure according to measurement points in carbon with low crystallinity. Therefore carbon structure evaluation by Raman mapping is also adopted, in which Raman spectra are measured at multiple points along with the X- and Y-axes. The above-mentioned Raman parameters are color-coded on a map.

As for measurement, each sample was processed into a plate and figured, and the structure distribution of carbonaceous was measured. A laser employed was a monochromatic light of an excited wavelength of 532 nm and a laser diameter of about 1 μm . Measurement was carried out along the X-axis and Y-axis direction at about 3–50 points of an interval of 2 μm for data acquisition. Each datum obtained was subjected to deconvolution for every datum point, the intensities of D1, D3, D4, and G bands were computed, and the fractions thereof were parameterized and color-coded on a figure. D1/G, the ratio of D1 to G bands was employed as a parameter.

3. Results and Discussion

3.1. Coking and Strength Test of Single Coals and Base Coal

Each single coal and Base coal was coked, its strength was computed with the crushing test, and the coking properties of each single coal were investigated. **Figure 1** shows changes after coking and crushing test of each sample. Coal A could be molded well by coking, while powdering occurred at molding of coal B. This is supposed because softening, melting, and expansion hardly took place in coal

Table 2. Compositions of samples.

Samples	Composition/%			
	A coal	B coal	OSB	HPC
A coal	100	–	–	–
B coal	–	100	–	–
OSB	–	–	100	–
HPC	–	–	–	100
Base coal	25	75	–	–
A/B/OSB (20/75/5)	20	75	5	–
A/B/OSB (15/75/10)	15	75	10	–
A/B/OSB (10/75/15)	10	75	15	–
A/B/HPC (20/75/5)	20	75	–	5
A/B/HPC (15/75/10)	15	75	–	10
A/B/HPC (10/75/15)	10	75	–	15

Fig. 1. Crush test results for A coal, B coal and base coal.

B with low coking properties, so that it could not be molded. However, in Base coal, 25% of coal A compensated softening, melting and expansion, so that the coking properties were improved. There remained almost no carbonaceous solid in the tube after coking of OSB, whereas HPC could not be molded attributable to insufficient strength. This is considered because OSB containing much H and O turned to hydrogen, water, carbon monoxide, and carbon dioxide by carbonization and was discharged out of the tube, and finally small amount of carbonaceous solids were left. Furthermore, as OSB and HPC are a polycyclic naphthene ring compound and a dicyclic aromatic compound, respectively, not having a structure with molecules entangled intricately like coal, their high softening and melting properties are suggested. Because most part of each single coal volatilized as gas or tar by carbonization, it is inferred that a small amount of carbonaceous solid with low strength was left and that it could not be molded.

Next, the average strength was computed for each single coal and Base coal with 8 crushing test iterations, as shown in **Table 3**. There remained almost no carbonaceous solid after carbonization of OSB, whereas HPC had too low strength to conduct strength test. The average strength of Coal A was as high as 1.7 MPa, whereas that of coal B was as low as 0.2 MPa. This result reflects that coking property affected strength. Base coal showed high strength of 0.6 MPa, but it only obeyed the additivity rule of strengths of coals A and B. There was no synergistic effect observed by

blending strongly coking coal A with non-slightly coking coal B for the purpose of compensating the softening and melting properties of the latter. The synergistic effect by combination of coals owes to the overlapping of softening and melting temperatures of each coal in the event of coking.⁵⁾ Therefore, it is suggested that temperature differs for coals A and B.

3.2. Carbon Structure of Each Single Coal and Base Coal, and Anisotropic Microstructure Analysis

To investigate the crystallinity of the carbon structure of each single coal and Base coal, the carbon structure was evaluated by Raman mapping. **Figure 2** indicates Raman mapping of each single coal and Base coal and the computed Raman parameter D1/G. Raman parameters D/G and D1/G are the ratios of D and D1 bands originated by the carbon structure of low crystallinity and G band originated by the carbon structure of high crystallinity, respectively. Blue region in Fig. 2, which represents small D1/G, indicates that G is more intense and has higher crystallinity compared with D1. The red region inversely indicates much D1 and weak G, and therefore low crystallinity. Raman mapping of coal A suggests the distribution of structures of high and low crystallinity, whereas no distribution by crystallinity difference was observed with coal B and Base coal. Therefore, coal A > Base coal > coal B as for Raman parameters D1/G, that is, coal B > Base coal > coal A as for crystallinity. Crystallinity is considered to be affected by intrinsic properties in coal such as the microstructure and softening and melting properties. Therefore, it is supposed to have no correlation with strength. It is assumed accordingly that strength was higher at lower crystallinity. Raman mapping evaluation was not performed for OSB and HPC because molding thereof was not completed. Instead, Raman parameter D1/G was computed by the measurement of multiple powdered samples. D1/G was great for OSB and small for HPC, *i.e.*, the crystallinity of OSB was low, but that of HPC was high, probably because volatile matter in coking inhibited the increase in crystallinity of OSB, while little volatile matter in HPC encouraged softening and melting, so that liquid-phase carburization¹⁸⁾ might enhance crystallinity.

Table 3. Average strengths, Raman parameters and fine textures of single-coked samples and base coal.

Samples	Average strength/MPa (n = 8)	Raman parameter D1/G (n = 10)	Fine texture/%		
			Anisotropic	Isotropic	Inertinite
A coal	1.68	1.3104	64.5	34.0	1.5
B coal	0.152	1.2717	33.1	66.3	0.6
OSB	–	1.3075	97.9	0.7	1.4
HPC	–	0.95554	97.3	1.8	0.9
Base coal	0.588	1.2814	39.0	60.4	0.6

Fig. 2. Raman mapping results for each sample.

Results show that OSB has low crystallinity, although HPC has high crystallinity.

Next, optical anisotropic microstructure analysis was conducted using the polarization microscope to measure enhancement in crystallinity. **Figure 3** presents results classified according to the anisotropic microstructure, isotropic microstructure, and inertinite. Inertinite hardly varies in any raw materials. Coal A had much anisotropic microstructure, although coal B had much isotropic microstructure. This result accordingly suggests that the progress of crystallinity occurs easily for coal A, but hardly for coal B by carbonization. Base coal showed anisotropic microstructure developed, but it only obeyed the additivity rule of that of coals A and B. Therefore, there was no synergistic effect by blending. OSB and HPC are mostly constituted by anisotropic microstructure. OSB and HPC are characterized by little ash because ash is removed in their production process. We reported that Si and Al, ash contained in coal, inhibit the change of a carbon structure in water gasification of coal, by carbon structure analysis with Raman mapping and elemental analysis with EDX.¹⁰⁾ Results show that the carbon structure change was not impeded by ash in OSB and HPC, but an anisotropic microstructure developed instead.

Fig. 3. Fine texture of single coked samples and base coal.

3.3. Coking and Strength Test of Sample with OSB as Caking Additive

Other samples were prepared, 5–15% of whose coal A component in the Base coal was substituted by OSB. It was coked and its strength was evaluated by the crushing test. The coking properties of each single coal were investigated. **Figure 4** shows the appearance of the sample after coking and after the crushing test. All the samples could be molded well like Base coal. Although OSB single coal had too much volatile matters to mold. This sample was molded because Base coal was readily susceptible to consolidation.

Next, each sample was subjected to eight crushing test iterations to compute average strength as shown in **Table 4**. Enhanced strength was achieved compared with Base coal by adopting OSB as a caking additive for all the samples. The overlap of softening and melting temperature ranges is important in blended coal samples. It is inferred that a temperature overlap existed between OSB and coal A or B, which brought about mutual melting. Consequently the coking properties of the whole sample improved and strength was raised. However, the sample with 15% of OSB added indicated less strength than the sample with 10% of OSB added. Kubota *et al.* reported that the coke strength is affected by the total amount and size of pores.¹⁹⁾ Much amount of gas and tar were generated on the occasion of coking of OSB. Therefore, it is assumed that pores exist in the obtained coke. Moreover, the generated amount suggests the existence of large pores. We infer that strength dropped in the sample with 15% of OSB added owing to large pores and cracks.

3.4. Carbon Structure and Anisotropic Microstructure Analysis of Sample with OSB as Caking Additive

To investigate the crystallinity of carbon structure of each sample with OSB as a caking additive, the carbon structure was evaluated with Raman mapping. **Figure 5** shows Raman mapping and computed Raman parameters D1/G of

Fig. 4. Crush test results for samples with OSB.

Table 4. Average strengths, Raman parameters and fine textures of samples with OSB.

Samples	Average strength/MPa (n = 8)	Raman parameter		Fine texture/%	
		D ₁ /G (n = 10)	Anisotropic	Isotropic	Inertinite
Base coal	0.588	1.2814	39.0	60.4	0.6
OSB	—	1.3075	97.9	0.7	1.4
A/B/OSB (20/75/5)	1.14	1.2344	39.1	60.3	0.6
A/B/OSB (15/75/10)	1.70	1.2252	43.4	54.9	1.7
A/B/OSB (10/75/15)	1.12	1.2693	45.8	53.2	1.0

Fig. 5. Raman mapping results for samples with OSB.

Fig. 6. Fine texture of samples with OSB.

each sample with OSB as a caking additive. Although Raman mapping of the sample with 5% OSB is hardly different from Base coal, distribution of carbon structure with high and low crystallinity was observed respectively in samples with 10% and 15% OSB. The similar trend for Raman parameters D1/G verified positive correlation between a carbon structure and strength. High volatile matter contents in 15%OSB blended coal might bring low crystallinity due to the inflation by gasification of volatile matter at coking of the sample.

Next, optical anisotropic microstructure analysis was carried out using the polarization microscope to evaluate crystallinity development. **Figure 6** shows the result. Anisotropic microstructure increased with increase in the addition of OSB. It is supposed that anisotropic microstructure increased because OSB had little ash (Al_2O_3 and SiO_2) and its carbon structure change was not impeded by Al_2O_3 or

Fig. 7. Crush test results for samples with HPC.

SiO_2 . Anisotropic microstructure increased also in the sample with 15% OSB of low strength and low crystallinity. It is hypothesized that anisotropic microstructure does not form a perfect graphite lattice of high crystallinity in Raman spectra. The result presented above suggests that strength was enhanced in samples with OSB as a caking additive because high softening and melting properties of OSB at low temperature implemented mutual melting, which facilitated the softening and melting of coal, which in turn facilitated crystallinity improvement, so that crystallinity was developed at coking, encouraged by an increase in addition. Carbonaceous materials with enhanced crystallinity were generated, filling the space between coal particles at softening and melting temperature. This filling material functions as a binder connecting the interface of coal particles at coking in such a state.^{20–22)} Accordingly, it was hypothesized that carbonaceous materials with high crystallinity of OSB origin functioned as a binder material by adopting OSB as a caking additive, so the strength increased.

3.5. Coking and Strength Test of Sample with HPC as Caking Additive

Other samples were prepared 5–15% of whose coal A component in the Base coal was substituted by HPC. It was coked and its strength was evaluated by the crushing test, and the coking properties of each single coal were investigated. **Figure 7** shows the sample appearance after coking and after

Table 5. Average strengths, Raman parameters, and fine textures of samples with HPC.

Samples	Average strength/MPa (n = 8)	Raman parameter		Fine texture/%	
		D ₁ /G (n = 10)	Anisotropic	Isotropic	Inertinite
Base coal	0.588	1.2814	39.0	60.4	0.6
HPC	—	0.95554	97.3	1.8	0.9
A/B/HPC (20/75/5)	1.44	1.2751	35.2	64.2	0.6
A/B/HPC (15/75/10)	2.43	1.1969	50.7	48.4	0.9
A/B/HPC (10/75/15)	2.82	1.1594	44.2	54.9	0.9

Fig. 8. Raman parameters of samples with HPC.

the crushing test. All the samples could be molded well like Base coal. HPC single coal had too much volatile material to mold, had low strength, and could not be molded because of powering. Nevertheless the present samples were molded. It is supposed because Base coal was apt to be consolidated.

Next, each sample was subjected to eight crushing test iterations to compute the average strength as shown in **Table 5**. Strength increased with increase in the addition of HPC as compared with Base coal. High softening and melting properties of HPC at a low temperature region has been reported. It is supposed that the softening and melting properties of each sample improved because the temperature region overlapped with that of coal A or coal B. The strength was enhanced according to the synergistic effect.

3.6. Carbon Structure and Anisotropic Microstructure Analysis of Samples with HPC as Caking Additive

To investigate the crystallinity of carbon structure of each sample with HPC as a caking additive, the carbon structure was evaluated with Raman mapping. **Figure 8** shows Raman mapping and computed Raman parameters D₁/G of each sample with HPC as a caking additive. Although the sample with 5% HPC is only slightly different from Base coal, the distribution of a carbon structure with high crystallinity was observed in the sample with 10 and 15% HPC. Raman parameter D₁/G behaved similarly, so that a carbon structure with high crystallinity with increase in HPC addition. Although HPC single coal had a structure with high crystallinity, the change in D/G and D₁/G was attributable

Fig. 9. Fine textures of HPC samples.

to increased carbon structure by HPC of high crystallinity. Results suggest that the carbon structure of coal A or B also takes a structure with high crystallinity by addition of HPC. Presumably, HPC enhances the softening and melting prop-

erties of each sample by mutual melting as described above. It facilitates improvement in the crystallinity of coal A or B.

Next, optical anisotropic microstructural analysis was carried out using the polarization microscope to evaluate crystallinity development. **Figure 9** shows the result. Although an anisotropic microstructure was almost equivalent to Base coal in the sample with 5% HPC, it increased in case of 10%. Then it decreased in the case of 15%. These facts suggest that the carbon structure had been altered in the coal blend before coking by addition of HPC unlike the case of OSB. Because the production method allows HPC to contain ash to only a slight degree, it is assumed that there is no obstruction of change in the carbon structure by Al_2O_3 or SiO_2 . Therefore it is considered that a carbon structure is apt to change. However, the anisotropic microstructure did not increase with increase in the addition of HPC, which implies no correlation between strength and expansion of an anisotropic microstructure. Because a carbon structure with high crystallinity was formed selectively at the interfaces of coal particles in HPC, the anisotropic microstructure was estimated as smaller because of the small anisotropic microstructure that was distributed extensively. Accordingly, it is assumed that HPC acted as a binder material that formed a carbon structure with high crystallinity connecting the interfaces of coal particles selectively by adopting HPC as a caking additive, so the strength increased.

4. Conclusion

Caking additives OSB and HPC were added as alternatives to a coal blend of strongly coking coal and non-slightly coking coal. Samples were coked, then their strength, crystallinity of the carbon structure, and an anisotropic microstructure were measured. The effects of the caking additives were investigated. OSB addition enhanced strength, but 15% addition caused a strength decline because of the formation of large pores and cracks. HPC addition increased strength with increased HPC content. Correlation was

observed between increased strength and the crystallinity of a carbon structure or the anisotropic microstructure. Results suggest that mutual melting occurred between a coal blend and a caking additive. Then the caking additive took a carbon structure with high crystallinity by coking, achieved a function as a binder material that connects coal-particle interfaces, and ultimately enhanced strength.

REFERENCES

- 1) Y. Kubota, S. Nomura, T. Arima and K. Kato: *Tetsu-to-Hagané*, **92** (2006), No. 12, 833.
- 2) M. Naito, S. Nomura and K. Kato: *Tetsu-to-Hagané*, **96** (2010), No. 5, 201.
- 3) T. Takanohashi, T. Shishido, K. Masaki, K. Fukada and A. Dobashi: *Tetsu-to-Hagané*, **92** (2006), No. 3, 132.
- 4) K. Ueoka, K. Koyano, T. Takanohashi, K. Fukada and K. Ota: *Tetsu-to-Hagané*, **96** (2010), No. 5, 218.
- 5) T. Takanohashi, T. Shishido and I. Saito: *J. Jpn. Inst. Energy*, **90** (2011), No. 9, 853.
- 6) N. Okuyama, N. Komatsu, T. Shigehisa, T. Kaneko and S. Tsuruya: *Fuel Process. Technol.*, **85** (2004), 947.
- 7) N. Okuyama, T. Shigehisa, Y. Nishibata, K. Matsudaira and M. Nishimura: *Tetsu-to-Hagané*, **92** (2006), No. 3, 213.
- 8) K. Takamura: *Can. J. Chem. Eng.*, **60** (1982), 538.
- 9) H. Nakagawa, R. Ashida, K. Kumata, K. Miura, K. Matsudaira and K. Miyagawa: *Tetsu-to-Hagané*, **92** (2006), No. 3, 145.
- 10) Y. Sekine, K. Ishikawa, E. Kikuchi, M. Matsukata and A. Akimoto: *Fuel*, **85** (2006), 122.
- 11) O. Beyssac, J. N. Rouzaud, B. Goffeé, F. Brunet and C. Chopin: *Contrib. Mineral Petrol.*, **143** (2002), 19.
- 12) C. Sheng: *Fuel*, **86** (2007), 2316.
- 13) A. Sadezky, H. Muckenhuber, H. Grothe, R. Niessner and U. Pöschl: *Carbon*, **43** (2005), 1731.
- 14) O. Beyssac, B. Goffeé, J. P. Petit, E. Froigneux, M. Moreau and J. N. Rouzaud: *Spectrochim. Acta, Part A*, **59** (2003), 2267.
- 15) S. Potgieter-Vermaak, N. Maledi, N. Wagner, J. H. P. Van Heerden, R. Van Grieken and J. H. Potgieter: *J. Raman Spectrosc.*, **42** (2011), 123.
- 16) H. Wu, K. Yip, F. Tian, Z. Xie and C. Z. Li: *Ind. Eng. Chem. Res.*, **48** (2009), 10431.
- 17) F. Jiménez, F. Mondragón and D. López: *J. Anal. Appl. Pyrol.*, **95** (2012), 164.
- 18) J. D. Brooks and G. H. Taylor: *Carbon*, **3** (1965), 185.
- 19) Y. Kubota, S. Nomura, T. Arima and K. Kato: *ISIJ Int.*, **51** (2011), No. 11, 1800.
- 20) J. W. Taylor and L. Hennah: *Fuel*, **70** (1991), 873.
- 21) K. Sudani, Y. Sugimoto and Y. Sunami: *Tetsu-to-Hagané*, **75**(9) (1989), 1426.
- 22) M. Okada, M. Tatsumi and N. Ohta: *Tanso*, **252** (2012), 54.