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Evaluation of Coal Properties Using High Temperature in-situ NMR Imaging Method

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Abstract

To monitor the dynamical changes in coals with temperature, an in-situ method must be used, therefore, we have applied single-point-imaging and have carried out the first systematic in-situ variable-temperature NMR imaging study of coals between 25 and 500℃ with our newly developed high temperature imaging probe and systems. It has been clarified that the macromolecular structure of coal is relaxed by the rapid heat treatment and in addition there is a close relation in hydrogen bond and relaxation of molecular structure of coal. Finally, we would like to propose the mechanism for the improvement of the coking property during this rapid heat treatment, which have the improvement of coal properties.

1. Introduction

The Gieseler plastometer method has long been widely used [1-4] to measure the coal softening and melting process. However, this method has a number of drawbacks. For example, it cannot be used to accurately evaluate the properties of non-caking/slightly-caking coal or clarify the differences in coal properties due to grain size. Concerning the rapid heated coal and raw coal that were studied for the next-generation coke process, the information on coal softening and melting properties obtained by the Gieseler plastometer method did not indicate any difference in coke strength between them despite the fact that a marked difference in coke strength does exist. The major problem with this method is that there is no close relationship between the principle of measurement and the change in the molecular coal structure that actually takes place in the coal heating process and that the method does not provide information about the molecular-level change in the coal structure during the softening and melting process.

To observe the structure of coal, polarizing and scanning microscopes have long been employed[5, 6]. The polarizing microscope is especially well suited to observe the mineral-like structures in coal, and there are various application examples[7]. However, these two types of microscope require pretreatment of the samples, etc., and because of their unique mechanisms, they have not been applied to in-situ observation of the coal softening and melting process.

In recent years, an attempt has been made to apply a micro-imaging technique based on the Nuclear Magnetic Resonance (NMR) method to coal since it is a nondestructive analytical technique that provides molecular-level chemical information[8, 9]. In the past, coal was not an object of direct observation by the NMR imaging method because the natural NMR absorption width of coal is comparatively large. In the previous technical report, we found that rapid heat treatment of coal increased the mobile component in the coal as the relaxation of coal structure was promoted by swelling the coal with pyridine-d5 vapor. In that method, however, it was impossible to distinguish between the effect of structural relaxation by swelling with solvent vapor and the effect of rapid heat treatment. Therefore, it was not possible to discuss the increase in mobile components quantitatively. Additionally, because of the absence of an in-situ structural analysis method, it was neither possible to mention nor to explicate the softening and melting behavior of the rapid heated coal.

This time, the authors developed and built the first system in the world to utilize the molecular-level chemical information provided by NMR imaging to permit not only direct observation of coal (without swelling of the coal with solvent vapor) but also in-situ observation of the coal softening and melting process[10, 11]. An attempt was

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made to apply the system to a wide variety of coals and to clarify the behavior of rapidly heated coal during the softening and melting process and the mechanism by which rapid heat treatment improves the coking property.

2. Experimentation

2.1 Samples

The coal used was Witbank coal (ash: 7.6%, volatile matter: 32%, total carbon: 75.8%, hydrogen: 4.76%, nitrogen: 1.90%, sulfur: 0.65%, maximum fluidity: 1.25 (log ddpm))–a representative of non-caking and slightly-caking coals. A total of three sample types were subjected to the experiments: coal heated rapidly to approximately 375℃ in an infrared heating furnace (heat-up rate: 100℃/min) ("grapid-heated coal"), coal heated slowly (heat-up rate: 10℃/min) ("gslow-heated coal") and coal not subjected to heat treatment ("graw coal"). All samples were made approximately 3 mm in size. The actual process that is expected to be used is so designed that the coal is retained in a temperature range in which the coal properties after rapid heat treatment are unaffected, and the coal properties in the present experiments are considered nearly the same as those in the actual process.

2.2 Experimental apparatus

The measurements of samples by NMR micro-imaging were done at 400.05 MHz using a Model α - 400 Spectrometer manufactured by JEOL Ltd. equipped with a micro-imaging unit that was developed. To obtain experimental samples, a piece of coal was inserted into a quartz sample tube for electron spin resonance (Wilmald CAT. No.702-PQ). For NMR micro-imaging, the sample temperature was raised from room temperature to 550℃ while passing nitrogen gas. The heat-up rate was set to 3℃/min as in an actual furnace. To determine the pulse sequence, the single-point imaging method developed was used by applying the concept of single-point sampling that was introduced to the spin echo method[12] and CRAMPS method[13] that are both standard imaging methods. The measuring time for each image in the in-situ measurement was about 8 minutes. Each of the temperatures shown in the following sections indicates the average value of the temperature at the start of measurement and the temperature at the end of measurement in 8-minute measurements. A thermocouple was used to directly measure the temperature of the sample in the sample tube.

The experimental sample scheme is shown in **Fig. 1**. The main measuring conditions optimized to observe the mobile component in coal were: excitation pulse 7 to 10 μs, echo time 80 μs, and cycle time 10 μs. The sampling point was set so that the resolution at the measuring surface was approximately 10 μm The resolution in the Z direction was approximately 100 μm and the same face was observed throughout the measurement. Generally speaking, coal tends to expand when it softens and melts, making it difficult to continue observing the same face. It was considered that this is not the case with the Witbank coal that was used in the present experiment since it does not expand significantly. The magnetic field gradient used was 89 T/cm for the X axis, 94 T/cm for the Y axis, and 109 T/cm for the Z axis.

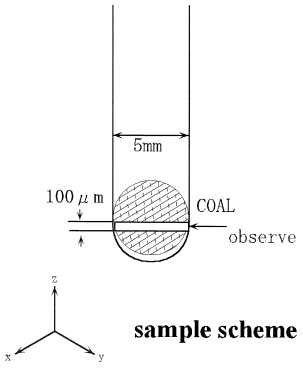

Fig. 1 Experimental sample scheme

3. Experimental Results

3.1 Results of NMR imaging of coal not swollen with solvent

In NMR micro-imaging of solid materials like coal, the NMR half-width (i.e., the length of T_2) is important. It has been known from a ^{1}H wide NMR spectrum that coal has two types of components: the mobile component whose half-width is several kHz and the immobile component whose half-width is tens of kHz[14]. The effects of swelling coal with pyridine-d5 were evident. As described in the previous technical report, the half-width decreased and the mobile component increased when the coal was swollen.

Fig. 2 shows the result of NMR imaging of raw coal swollen with solvent vapor. It is already known that pyridine-d5 enters the 3D cross-links of coal, causing a structural relaxation. This prevents a clear image of the interior of coal grain from being obtained. Besides, the accuracy of the image obtained is not very high since the coal contains substances which differ in magnetic susceptibility (e.g., the solvent used and inorganic components). Thus, although the increase in mobile component by rapid heat treatment can be understood qualitatively, it cannot be discussed quantitatively. In order to solve this problem, a Single Point Sampling-Imaging (SPI) method was developed[15].

The pulse sequence for single point imaging is shown in **Fig. 3**, and the characteristics of the SPI method are explained below. Un-

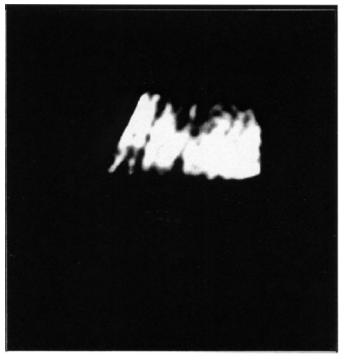

Fig. 2 2D images of raw coal and with swelling pyridine-d5 obtained by spin echo method

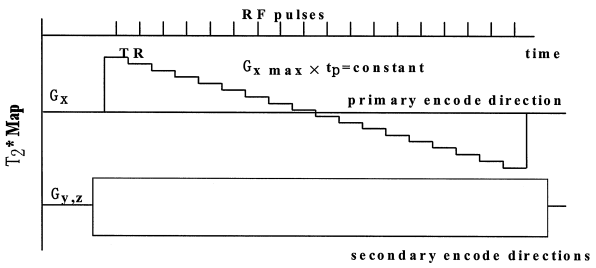

Fig. 3 Pulse sequence of single point imaging

like the conventional spin echo method, the SPI method depends not on the band selection pulse, but on the excitation band of the radio frequency (RF) pulse. Therefore, the reciprocal of the pulse width used for excitation must be greater than the product of the sample size (cm) and the magnetic field gradient (T/cm). Besides, the SPI method is an imaging technique that is based completely on phase encoding. In this respect, it is different from the conventional method, which is based on phase encoding and frequency encoding. In the SPI method, the signal is input during magnetic field inclination, at timing t = tp (tp time later) after a short RF pulse for excitation. Therefore, unlike the conventional spin echo method based on frequency encoding, it is completely free from the influence of unevenness of B_0 (static magnetic field), the influence of substances which are contained in coal in considerable amounts and which differ in magnetic susceptibility, the influence of image distortion caused by differences in chemical shift, etc.

Even with a coal sample whose T_2^* (transverse aggregate time when a magnetic field inclination exists) is short, the resolution is simply determined by the magnetic field inclination applied to the sample. Namely, the greater the magnetic field inclination that is applied to the sample, the higher the resolution. The signal intensity, S, that is obtained at a particular point can be described by using the density of hydrogen atoms, ρ, at that point. Thus,

$$S = \rho \exp(-tp / T_2^*) \times R(x) \quad (1)$$

where, $R(x) = (1 - \exp(-T_R / T_1)) / (1 - \cos\theta \exp(-T_R / T_1))$

From R (x) in Equation 1, it is possible to determine the cycle time (T_R) that depends on the shortest T_1 unique to the sample. The drawback of the SPI method is that a device which is capable of generating a large magnetic field gradient is indispensable and that the chemical shift information is lost. Nevertheless, as long as a generator of large magnetic field gradients and a suitable probe for measurement are available and the measuring conditions are optimized, the SPI method is very suitable for quantitative analysis of coal since, as can be seen from Equation 1, the signal intensity in the image can be expressed as the amount of the mobile component in the coal.

Examples of the images obtained by this method are given in **Fig. 4**. The images are really clear and free from the influence of any difference in magnetic susceptibility. Additionally, the samples need not be swollen by the solvent. Because of all this, it can quantitatively be seen from the images that rapid heat treatment increased the mobile component, that its domains increased in size and that their distribution in coal grains became uniform. It is very interesting to see that considering the size of macerals[16] contained in coal, the molecular cluster domains formed by the mobile component are tens to hundreds of micrometers in size and that they take part in the softening and melting of coal.

In view of the process of coal formation, it can hardly be considered that the coal structure is perfectly stable thermally. The temperature at which rapid heat treatment is implemented is not so high as to cause various chemical reactions to take place. Furthermore, since the heat treatment temperature is not very high, non-covalent bonds, such as the hydrogen bond, can break up more easily than covalent bonds. From all these facts, it is considered that the rapid heat treatment influences the intermolecular actions (e.g., hydrogen bond and $\pi - \pi$ interaction) that govern various 3D cross-links in coal, relaxing the cross-links and promoting the development of the mobile component. In the case of slow heat treatment, by contrast, it is considered that non-covalent bonds break up easily and at the same time, re-reactions can take place there, offsetting the structural relaxation effect.

3.2 Development of high temperature in-situ NMR imaging system

It is widely known that coal softens and melts at around 400℃. In order to implement in-situ observation of the softening and melting process, it is necessary to raise the temperature of the sample at a probe inserted into the narrow bore (89 mm in diameter) of a superconducting magnet up to 550℃ while keeping the bore interior at room temperature at the highest. When it comes to securing a high resolution with the SPI method that is free from the influences of uneven B_0 and substances which are contained in coal in considerable amounts and which differ in magnetic susceptibility as mentioned earlier, a large magnetic field gradient is indispensable. In this case, it is expected that the calorific value generated by the magnetic field gradient coil will become exceedingly high. Therefore, an original probe was designed and developed for high temperature in-situ imaging that should solve the above problems. The appearance of the probe is shown in **Fig. 5**, and the concept of development of the probe is explained below.

First, in order to prevent the heat generated by the magnetic field inclination coil and the heat radiated from the heater for heating the sample up to 600℃ from reaching the bore interior of the superconducting magnet, two independent cooling water pipe systems were provided for the probe. Next, to achieve a high magnetic field and secure a space for heat insulation, a rectangular copper wire, not the

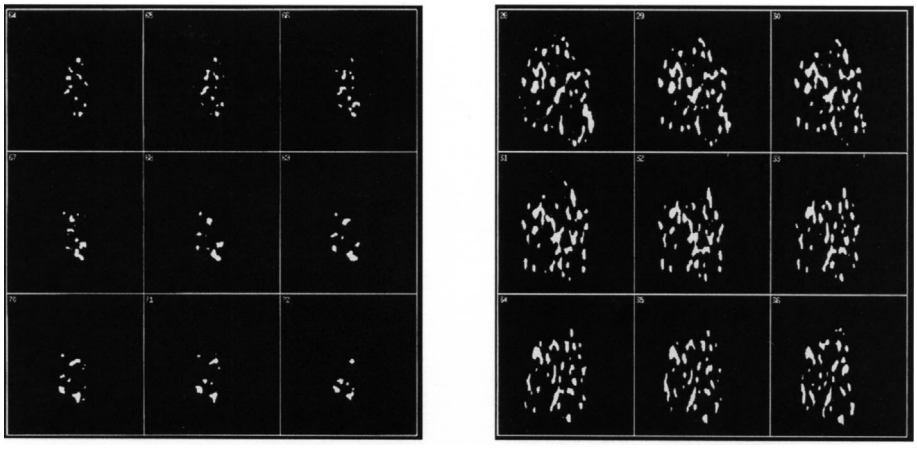

Fig. 4 The NMR 2D images of (a) raw coal, (b) rapid heated coal and (c) slow heated coal obatined by singel-point imaging

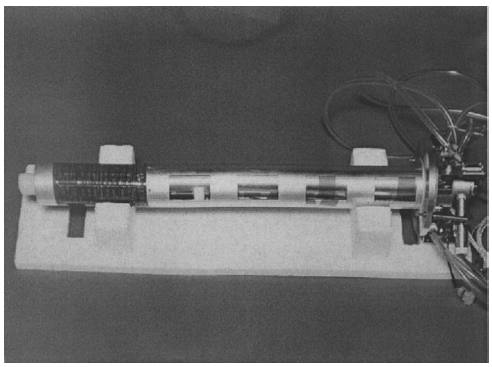

Fig. 5 Developed high temperature imaging probe

conventional round wire, was adopted to increase the space factor from 80% to 95%. The advantage of the rectangular copper wire is that the current and magnetic field efficiencies are high, whereas the thermal resistance is small.

The magnetic field inclination intensity depends on the current density. Since the space factor was increased, assuming that the cross-section area and the number of windings are the same, the copper wire offers a wider cross-section area and a smaller electrical resistance. Since the cross-section shape of the copper wire is rectangular, the copper wire produces a smaller air gap in multiple windings, allowing the windings to make closer contact with one another. As a result, the thermal resistance between wires can be reduced. Since copper wire has high heat conductivity, in order to secure sufficient effect of water cooling, it was necessary to reduce the thermal resistance of the magnetic field gradient coil as much as possible. The final design of the magnetic field inclination coil was made using a modified program for Fourier-Bessel expansion[17].

As the power supply for inclination of the magnetic field, a Techron Model 7782 available on the market was used for each of the X, Y and Z axes. At the current value of 50 A, the amount of inclination of the magnetic field was about 250 T/cm. The time constant of the power supply for magnetic field inclination was adjusted so that the output start-up time at that current value was about 100 μs or less. In order to obtain a uniform field of vision, a saddle-type coil was specially designed. The uniformity of the field of vision was improved from 80% to 95% and the quantitiveness of the signal intensity obtained from each image was improved significantly. As a result of all this, the newly developed probe achieved a heating temperature of 600℃, with the probe outer wall temperature being 35℃, allowing for in-situ observation of the coal softening and melting process for the first time. As already mentioned, the heat-up rate is 3℃/min and about eight minutes are required to obtain a single image. This means that the sample temperature rises by about 24℃ during measurement. The temperatures shown in **Fig. 6**, which gives examples of the results of in-situ NMR imaging applied to hard-caking Goonyella coal, indicate intermediate temperatures in the temperature change during in-situ NMR imaging.

The same point of the same coal in a region about 100 μm thick was observed. It can easily be seen that with the rise in temperature, the non-uniform domain of molecular clusters formed by the mobile component at room temperature gradually expands and spreads evenly within the coal grain. It can also be seen easily that in the case of hard-caking coals like Goonyella coal, there are parts in which almost all grain interiors have melted at a temperature near the maximum softening and melting temperature of 420℃. Thus, it was possible to confirm that the high temperature in-situ NMR imaging method provides valuable information in studying the softening and melting phenomenon of various brands of coal. In addition, with this method, it is possible to analyze the behavior of volatile matter in coal and quantify the volatile matter by making an in-depth study of the total NMR signal intensity obtained at each measuring temperature.

3.3 Explication of softening and melting phenomenon of rapid-heated coal by high temperature in-situ NMR imaging method

Fig. 7 shows the changes in the mobile component rate and NMR signal half-width reflecting the softening and melting condition, observed by the in-situ method at temperatures from room temperature to 550℃, for raw coal, rapid-heated coal and slow-heated coal. As

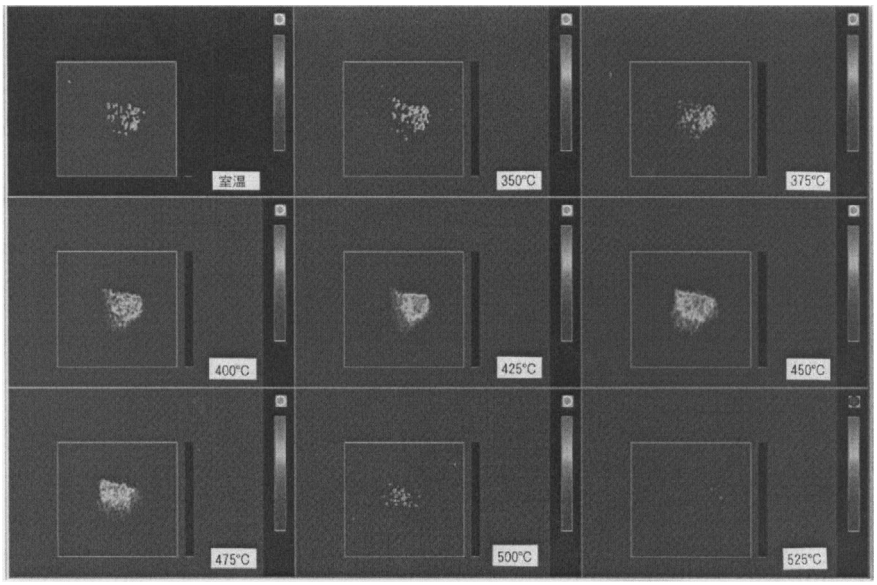

Fig. 6 in-situ NMR images of Goonyella coal at various temperatures (a)25℃, (b)350℃, (c)375℃, (d)400℃, (e)425℃, (f)450℃, (g)475℃, (h)500℃, (i)525℃

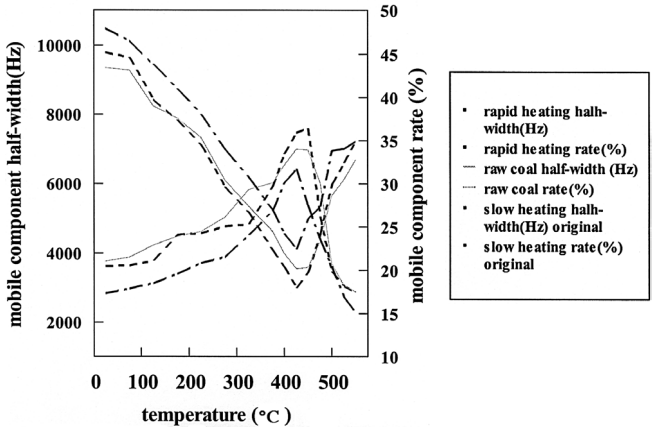

Fig. 7 Fractional intensity and their half width of mobile component as functions of temperature in three coals; raw coal, rapid heated coal and slow heated coal

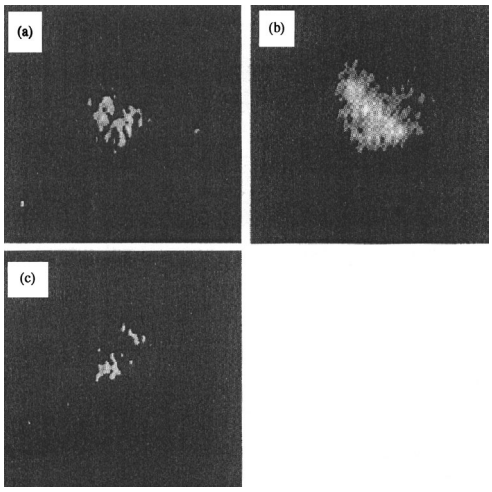

Fig. 8 in-situ NMR images of three coals: (a) raw coal, (b) rapid heated coal and (c) slow heated coal at the maximum mobility temperature, 400℃

already mentioned, because of the structural relaxation by heat treatment, the rapid-heated coal shows a large proportion of mobile component and a small half-width at room temperature. In these three coal sample types, with the rise in temperature, the mobile component rate increases and the half-width decreases gradually. At about 400℃, the mobile component rate reaches its maximum and the half-width decreases to the minimum. This temperature nearly coincides with the maximum softening and melting temperature that has been obtained by the Gieseler plastometer method. At 475℃, at which the re-solidification reaction begins to take place, the mobile component rate starts decreasing sharply and the half-width starts to increase[18].

Although the above behavior can be observed with all three types of coal, it is most conspicuous in the rapid-heated coal in terms of the rate of increase of mobile component and the rate of decrease of half-width. In particular, the rapid-heated coal shows a very small half-width at the maximum softening and melting temperature. Assuming that the coal composition remains the same, there is a correlation between the half-width of the NMR signal and the viscosity of solution: a small half-width corresponds to a low viscosity[19]. The implication is that in the above temperature range, grains of rapid-heated coal melt more than those of raw coal and hence, their viscosity is lower. On the other hand, the slow-heated coal contains more mobile component than the raw coal at room temperature, but with the rise in temperature the difference narrows down to become minimal in the temperature range 400℃ to 450℃, suggesting that the slow-heated coal develops a small amount of mobile component at high temperatures. Concerning the half-width too, the slow-heated coal shows a larger value than the raw coal at and above 400℃, indicating that the melting condition of the coal is not very good.

Fig. 8 shows the results of observation of the raw coal, rapid-heated coal and slow-heated coal by the in-situ NMR imaging method at the maximum mobility temperature. The images shown represent the results of in-situ measurements in exactly the same temperature range (388℃ to 412℃), since the maximum mobility temperature was nearly the same with the three types of coal (about 400℃). Evidently, the raw coal has both melted and solid parts. This is true with the slow-heated coal as well. By contrast, it can clearly be seen that with the rapid-heated coal, the melted zone within the coal grains is much wider.

4. Discussion

First, the discussion shall focus on the softening and melting phenomenon of coal. For the purpose of discussion, it is assumed that (1) coal is a multi-component group of molecules in which mobile and immobile components exist[20] and (2) coal has a coagulated structure because of the presence of many different intermolecular actions (hydrogen bond, $\pi-\pi$ interaction, van der Waals, hydrophobic interaction, etc.)[21]. As explained earlier, since our new method does not use any solvent to swell the coal, it has been confirmed that each of our coal samples contains a 3D molecular group domain tens to hundreds of micrometers in size which is formed by the mobile component and which is distributed unevenly[10].

In addition, by applying the high temperature in-situ NMR imaging method to coal samples, it has been found that the molecular group domain that is formed by the mobile component at room temperature expands with the rise in temperature and is evenly distributed within the coal grains. The implication is that with the mobile component domain observed at room temperature as the origin, the 3D cross-links that are formed by various intermolecular actions are relaxed with the rise in temperature and cause the softening phenomenon whereby the mobile component increases to occur. Then, as the structural relaxation region expands, the distribution of mobile component within the coal grain begins to increase and ultimately, the entire grain is filled with mobile component. At the same time, with the rise in temperature, the coagulation of molecules begins to melt as the molecules are liberated, and the liquid components flow through the entire grains while gradually losing their viscosity and continue melting the grains. It can be inferred that this is the phenomenon of softening and melting of coal. Now, on the basis of this concept, the discussion shall shift to the mechanism of coking property improvement by rapid heat treatment.

As described in the previous technical report, the rapid heat treatment did not cause the various molecular structures in coal to change noticeably, and only a change in the functional group that takes part in the hydrogen bond was observed. In addition, the rapid heat treatment shortened the longitudinal relaxation times, improved molecular-level mobility and made the spin dispersion phenomenon conspicuous. From all this, it was determined that the homogenization in the molecular group domain was proceeding. It was possible to

infer from this fact that the rapid heat treatment promoted the structural relaxation of coal. In addition, from the results of the present experiments, it was confirmed that raw coal contained an unevenly distributed molecular group domain tens to hundreds of micrometers in size formed by the mobile component and that the rapid heat treatment increased the amount and size of the molecular group domain formed by the mobile component at room temperature. Furthermore, from the results of an analysis using the high temperature in-situ method, it was found that with the rise in temperature, the mobile component rate increased and homogenization within the coal grain slowly proceeded, with the molecular group domain formed by the mobile component at room temperature as the origin.

The improvement in propagating and melting abilities of the mobile component at high temperatures can be explained by using a self-melting model[22] created based on the experimental results that Takanohashi et al. obtained using the solvent extraction method. Namely, the rapid heat treatment relaxed the intermolecular actions and increased the mobile component rate, thereby causing the molecular group domain to increase in size. As a result, similar molecular structures that had existed in the coal continuously melted easily with the rise in temperature, thereby promoting the phenomenon in which they melt one another. It can be inferred that this process improved the propagating and melting abilities of the mobile component at high temperatures.

5. Conclusion

By utilizing the molecular-level chemical information provided by NMR imaging, the world's first system was developed and built that enables direct, in-situ observation of the coal softening and melting process without using solvent vapor to swell the coal. With this system, it was possible to clearly grasp the changes in coal at the molecular and molecular group domain levels and the change in their behavior in the heating process. In addition, by using this system, the behavior of rapid-heated coal was clarified during softening and melting and the mechanism for improvement in coking properties of coal using rapid heat treatment. It has already been confirmed that rapid heat treatment of coal increases the drum strength of coke made from that coal. More specifically, it can be inferred that as a result of thermal structural relaxation by the rapid heat treatment, the mobile component that helps improve the coking property of coal increased and the propagating and melting abilities of the mobile component at high temperatures improved within the coal grains, thereby improving the coking property of rapid heated coal.

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