主 論 文 の 要 約

論文題目 **Study on coal reactivity with molecular structural analysis toward developing coke manufacturing technology**
（分子構造解析による石炭反応性評価のコークス製造基盤技術への展開）

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論 文 内 容 の 要 約

In this doctoral thesis, chemical structural analysis for coal tar which is byproducts of coke making process and coals which is an important fossil resource and widely produced around the world was focused on. Especially, coal is mainly used in the steel industry as fuel for power generation, raw material for coke, heat source in blast furnaces (pulverized coal for blowing in), and as a component adjuster in converter furnaces (coal additive). Although, there is currently some momentum to decrease the use of fossil fuel resources for de-carbonization, it will be difficult to reach a rapid decrease in the use of fossil resources due to the need to maintain the living standards of people in developed countries and the development and population growth of developing countries. I anticipate a world in which we will have used fossil resources while continuing to develop and improve efficient utilization process, and use renewable energy as much as possible, during proceeding the developing and commercializing technologies for CO_2 separation and capture. Therefore, coal will continue to be an important resources for mankind that should be effectively utilized.

In chapter 1, several coke making methods for using the low-quality coal, chemical structural models for coal, studies about spontaneous heating of coal and the technique of Nuclear Magnetic Resonance (NMR) measurements were described because there is an urgent need to reduce costs by shifting from high-priced hard coking coal to low-priced non-coking coal and low-coking coal, and optimization of processes for reduction of CO_2. The chemical structural analysis using NMR is a powerful tool for these achievement of the objects. In the future, it is considered that further reduction

of the utilization ratio of hardly coking coal and utilization of non-coking carbon sources such as biomass must be desired, and it will be important to advance the technology of using coal tar as a coking binder for coal. It is first necessary to develop a technology to elucidate the molecular structure of coal. In the previous molecular structural analysis for coal, detailed molecular structural models have been constructed in three dimensions, and attempts have been made to calculate the intermolecular forces that are considered to play an important role in the development of coking properties. However, there have been few reports comparing the molecular structure and intermolecular forces between coals with different thermal properties such as dilatation and fluidity. The low-quality coals have higher spontaneous heating nature than high-quality coals and have a higher potential for disaster. Therefore, it is important for companies not only to develop the coke manufacturing technology, but also to construct technologies to safely store and manage coals. Some previous research about spontaneous heating of coals were also summarized in this chapter. In order to manage coals safely in iron making process, it is important to understand the oxidation mechanism of coal at low temperature for example at less than 80°C. However, there is little previous research focusing on chemical structural changes during oxidation at less than 80°C.

In Chapter 2, two-dimensional average molecular structure models for two types of coking coals were constructed to discuss the dilatation and fluidity of coal in terms of its chemical structures. The chemical structure models of the extractions and residues were constructed using a support program. The mean molecular weight of the coal extractions, which is an important structural parameter when constructing models, was obtained via Gel Permeation Chromatography (GPC) measurements; polycyclic aromatic hydrocarbons with structures similar to those of coal molecules were used as standard substances to realize a calibration line. In this manner, more accurate extraction models, as compared to those in literature, with structural parameters that were similar to the analytical values were obtained. These models can suitably indicate the differences between the types of coals. In particular, they indicated significant differences in the number of aromatic rings and cluster sizes. Thus, it was concluded that the PI fraction in coal, which has a mean molecular weight of approximately 2000 and 6-7 aromatic rings in one cluster, might serve as an essential component for the coking property and the cluster size in the MI fraction, while also affecting the softening property of the coal.

In Chapter 3, the two-dimensional average molecular structure model presented in Chapter 2 was used to obtain the most energetically stable three-dimensional aggregated structural models constructed by molecular dynamics calculations, and the intermolecular interactions in the aggregation structure were clarified. It was found that the tendency of the modeled densities was consistent with the actual densities of the samples. The qualitative trends of the T_g^{exp} and T_g^{calc} values obtained for the AS, PS, and PI fractions, which comprise the three-dimensional aggregated structural models of coal A, were consistent. These fraction and aggregated structural models

qualitatively described the relaxation trends of coal. The cohesive energy density (CED) of coal B was larger than that of coal A at temperatures below the T_g, and the CED of coal A was similar to that of coal B at temperatures above the T_g. This implies that the aggregated interaction among molecules in coal A was stronger than that in coal B at low temperatures due to hydrogen bonding. It was concluded that the differences in the molecular and cohesive structures of the coal led to differences in the distribution of van der Waals energy and electric energy at different temperatures. The van der Waals energy decreased 0.34 and 0.37 J/cm^3 for every 1°C increase, and it changed from attraction to repulsion at about 450°C and 285°C in coals A and B, respectively. Electric energy decreased from 0.13 to 0.26 J/cm^3 for every 1°C increase, and it remained an attractive force, even with increasing temperature. The mechanism for the 13°C difference in the calculated T_g of the coal types was due to the composition of the cohesive energy, which reflected the distribution of the molecular structure.

In chapter 4, to elucidate the mechanism of oxidation reaction below 80°C, which is important for managing the risk of spontaneous heat generation in coal, an R70 test to understand temperature rise behavior, quantitative analysis of generated gas, and chemical structure analysis of oxidized coal by solid-state NMR were conducted using dry coking coal X and Y. As a result, it was found that the rate of temperature increase in coal Y was significantly larger than in coal X, furthermore, both coals showed a rapid temperature increase from around 60°C. The analysis of the generated gas showed that although the rate of CO_2 and CO generation was greater for coal Y than for coal X over the entire temperature range, the total amount generated was almost the same when compared at the same attained temperature. Results of chemical analysis of the oxidized coal suggested that more water was adsorbed on coal Y than on coal X, and ^1H MAS NMR analysis supported adsorbed water being the main component. Furthermore, carbon structure analysis using ^{13}C MAS NMR suggested that oxidation of both coals produces aldehyde and carboxyl groups and that the formation reaction of carboxyl groups from aldehyde groups is accelerated in coal Y in particular. In contrast to previous findings, the potential that aromatic carbon may have contributed to the oxidation reaction was newly demonstrated. The average molecular structure analysis of coal X and Y before oxidation showed that the main difference was in the number of aromatic rings, which may have led to differences in the stability of aromatic carbon radicals and further led to differences in spontaneous heating.

In chapter 5, direct observation of functional groups generated in coking coals during oxidation using ^{17}O isotope oxygen gas and solid state ^{17}O MAS NMR spectra measurement was implemented in order to understand detail oxidation mechanism for coal. In this research, coal was oxidized under $^{17}O_2$ atmosphere and solid state ^{17}O MAS NMR spectra were measured using Oldfield echo pulse sequence. The site B / site A values showed the temperature dependence on the oxidation reaction mechanism, and the main reactions at higher temperatures were hydroxyl group generation, carboxyl group generation, and CO, CO_2 generation. Furthermore, it was found that the temperature at which this reaction changed depended on the coal type. The generation of aldehyde groups, which was unclear

in the one-dimensional measurement, was successfully observed by the high sensitivity of Cryo-MAS-Probe and the elimination of spinning side using the pulse sequence of pjMATPASS. In conclusion, the identification of oxygen functional groups by high-resolution 2D NMR spectroscopy such as ^{17}O 3QMAS NMR will advance the detailed analysis of coal oxidation reactions. Therefore, the combination of sample preparation using $^{17}O_2$ enriched gas and solid state ^{17}O MAS NMR spectroscopy will be an important tool for analyzing the oxidation reaction mechanism of coals.

In chapter 6, two kinds of coal tar which is byproducts of coke making process were analyzed using FD-MS and liquid state ^{1}H NMR. From the analysis of FD-MS mass spectra and ^{1}H NMR spectra, the properties of raw material coals affect the molecular structures of primary coal tars were clarified. These analytical methods are expected to contribute the development of use of the coal tar.

Finally, in Chapter 7, future prospects in this research were summarized. The detailed chemical structural analysis of coal and coal tar will provide important knowledge for expanding the use of low-quality coal in the steel industry and will be developed into a basic technology for coke manufacturing, which I believe is of great industrial importance.