1. Introduction

In order to operate the blast furnace at lower temperature than usual, the highly reactive carbonaceous materials at low temperature should be developed. For that purpose, the reaction mechanism of various carbonaceous materials should be clarified. In the previous works,1,2) wide variety of materials from the activated carbon to glassy carbon were examined with respect to the reaction with CO 2 in the low temperature range between 823 and 1 173 K. The reaction rates were two orders of magnitude different from each other. In order to examine the difference, the effect of pore structure on the reaction kinetics was examined by following the change in reaction rate, specific surface area and pore structure with the reaction degree.3) The specific surface area does not influence the reaction rate so much. The change in the specific surface area accords well to the change in the volume of smaller pores than 10^-8 m. The reaction occurs exclusively on the surface of pores between 10^-8 to 10^-6 m in diameter. The effective surface area for the reaction is from 0.064 to 0.25 of the total surface area. In the present work, the Raman spectroscopy analysis was carried out to examine the reaction mechanism from the viewpoint of bonding structure of carbon atoms in various carbonaceous materials. Although many papers have been published on the structure analysis by the Raman spectroscopic analysis,4–12) the universal evaluation method has not yet been developed for materials which have widely different structure. The Raman spectra of various materials from natural graphite to glassy carbon were compared. The change in spectra with heat treatment at high temperature was examined to follow the structure change by the heat treatment. New parameter were derived to evaluate the structure and used to explain the difference in reaction rate among carbonaceous materials.

2. Experimentals

2.1. Materials

The material samples were (1) natural graphite (NG), (2) highly oriented pyrolytic graphite (HOPG), synthetic graphite: (3) (SGO), (4) (GS), (5) (IMF307), (6) glassy carbon (GC), (7) metallurgical coke, (8) wood charcoal (Bincho char which is carbonized oak) and (9) bamboo charcoal. The sample of HOPG and GC were in block...
shape. That of NG was flaky. The other samples were ground and sieved between 40 and 63 μm in size. The samples from (1) to (6) were classified as the ordered material, and those from (7) to (9), the disordered material. The latter samples were subjected to the heat treatment up to 2473 K. The composition of all materials is given in Table 1. The way to determine each component will be explained later.

2.2. Raman Spectroscopy

The laser Raman spectrum analyzer (NRS-1000, made by JASCO) was used. The laser source was green laser of 532.1 nm wave length and the maximum power of 14 mW. The unit was equipped with microscope so that the analysis of micro structure was possible. The beam diameter was 4 μm. The power was either 14 or 1.4 mW. The exposure time × accumulation times was 15 s × 3 or 15 s × 4 depending on the sample.

2.3. Heat Treatment

The sample weight was ca. 40 mg. In the case of metallurgical coke, it contained some amount of ash component which would react with carbon to change the structure when it was heated at high temperature. Therefore, the pre-treatment was carried out to reduce the ash content. It was dipped into the 9 wt% HF aqua solution and 5 vol% HCl aqua solution at the room temperature each for 24 h. Then, it was washed with distilled water and dried at 413 K.

Two kinds of equipment were used for low and high temperature range. The former was the differential thermo gravimetric balance (TG-DTA) which was normally used for the measurement of reaction rate with CO₂ as will be explained later. The temperature range was up to 1273 K. The sample was heated in N₂ stream of 2.5 × 10⁻⁵ m³/s (STP) at the heating rate of 2.5 K/min. The holding time was 300 s. The sample was cooled in N₂ steam with the same flow rate.

In the higher temperature range from 1373 to 2473 K, the induction unit was used which was usually used for levitation melting of metals. The schematic diagram of apparatus for high temperature range is shown in Fig. 1. The apparatus was composed of high frequency power generator (130 kHz, 60 kW), heating coil, reaction tube made of transparent silica, gas flow system and the thermometer of two colors eye. The graphite crucible of 11 mm inner diameter and 15 mm depth was put on the graphite pedestal with graphite cover and placed at the center of heating coil. The argon gas was introduced from the gas inlet at top with 1.7 × 10⁻⁴ m³/s (STP). The temperature on the graphite cover was measured through the prism by the thermometer of two colors eye. The holding time was 300 s. The sample was cooled in Ar stream.

2.4. Measurement of Reaction Rate with CO₂

Figure 2 shows the schematic diagram of experimental apparatus for the measurement of reaction rate. The furnace was the infrared radiation heating one with high heating and cooling rates. The thermo-balance unit was used to monitor the weight change of sample during reaction. The sample holder was made of pure alumina and of 13 mm diameter and 2 mm depth. Some of the exhaust gas was introduced to the infrared gas analyzer for determining the CO₂ content. The output from thermo-balance and gas analyzer was connected to the personal computer to acquire the data continuously, via RS-232C cable. The CO₂ and N₂ were used for reaction gas and flushing gas, respectively. The gases were dehydrated with silica gel tube. The CO₂ component in N₂ was eliminated by passing the gas through soda line tube.

The sample of about 30 mg was put into the sample holder and set at the center of the furnace. It was heated in N₂ stream of 2.5 × 10⁻⁵ m³/s (STP) at the heating rate of 0.3 K/s to 573 K and kept at the temperature for 1.8 ks in order to eliminate volatile matter and moisture. It was cooled to the room temperature to change the gas stream from N₂ to CO₂. Then, it was heated to the experimental temperature of 1173 K at the heating rate of 2.5 K/s. The weight change was monitored from the time when the temperature reached to the experimental temperature and the
steady change started. After the predetermined reaction degree of 10%, the sample was cooled to the room temperature in CO$_2$ stream. Then, the sample was heated again in N$_2$ stream to the same temperature at the heating rate of 2.5 K/s. The CO content in exhaust gas was monitored by the gas analyzer to evaluate the amount of surface oxygen complex which will be explained later, or the adsorbed CO on the reaction site of sample. The area under the curve of CO content change was integrated to evaluate the reactive surface area, RSA, which was the amount of adsorbed CO per unit mass of sample.

The initial amount of fixed carbon, $W_C$, was evaluated by subtracting volatile matter, moisture and ash component from the initial weight. The amount of former two was estimated by the weight loss when the sample was kept at 573 K in N$_2$ stream. The ash content was estimated from the amount of residue when the sample was fully burnt in the air at 1 273 K.

The reaction degree, $X(\%)$, was defined as

$$X=100\left(W_0-W_t\right)/W_C$$ ..........................(1)

where $W_0$ was the weight at the beginning of reaction in CO$_2$ stream and $W_t$ was the weight at time $t$. The reaction degree was plotted against time. The reaction rate, $r$ (1/s), was estimated from the slope of plotted curve as

$$r=\left(dX/dt\right)/100$$ .............................(2)

3. Results and Discussion

3.1. Raman Spectrum of Materials

Figure 3 shows the Raman spectra of ordered structure materials. A very sharp peak appeared at 1 580 cm$^{-1}$ for NG and HOPG. The peak is known as that of G band, which is related to the energy of sp$^2$ bonding and assigned to the normal graphite structure. The other peaks appeared at 1 360 cm$^{-1}$ and 1 620 cm$^{-1}$ for SGO, GS and IMF. Those peaks are known as that of D and D' bands, respectively, which are originated from defect structure of graphite. The peak for diamond appears at 1 332 cm$^{-1}$. Thus, the present peak at 1 360 cm$^{-1}$ should not be assigned to diamond structure. The relative height of D band peak to G band peak is known to have inverse relation to the lateral size of graphite structure. Therefore, D band might be assigned to the edge carbon of graphite structure. The D' band peak might be assigned to the defect carbon on the aromatic plain of graphite, because it appears near to G band. It is seen from the spectra that NG and HOPG have perfect graphite structure. The relative height of D band peak to G band peak is known to have inverse relation to the lateral size of graphite structure. Therefore, D band might be assigned to the edge carbon of graphite structure. The D' band peak might be assigned to the defect carbon on the aromatic plain of graphite, because it appears near to G band. It is seen from the spectra that NG and HOPG have perfect graphite structure. The others have the graphite structure with many defects. Although there appeared three similar peaks for GC, the meaning of these peaks would be different from that for graphite structure, because GC is glassy carbon.

Figure 4 shows the Raman spectra of disordered materials. Different from those of ordered materials, only two broad peaks appeared near 1 600 cm$^{-1}$ and 1 360 cm$^{-1}$. The peaks are designated as G* band peak and D* band peak, respectively. But this designation does not mean physically the graphite and its defect structure. The spectra of coke and wood charcoal are similar to each other, but that of bamboo charcoal is different from those of them. Therefore, D band might be assigned to the edge carbon of graphite structure. The D' band peak might be assigned to the defect carbon on the aromatic plain of graphite, because it appears near to G band. It is seen from the spectra that NG and HOPG have perfect graphite structure. The others have the graphite structure with many defects. Although there appeared three similar peaks for GC, the meaning of these peaks would be different from that for graphite structure, because GC is glassy carbon.

3.2. Change in Spectrum of Disordered Materials by Heat Treatment

Figure 5 shows the change in the Raman spectrum of coke by the heat treatment. The vertical broken lines show the peak position of G, D and D' bands of graphite structure. Up to the heat treatment temperature of 1 573 K, there was no change in the spectrum. At 1 923 K, the spectrum changed slightly. Both of G* band peak and D* band peak became sharper. At 2 033 K, the peaks became far sharper. The G* band peak seemed to split into two peaks. At 2073 K, the G* band peak was split remarkably into two peaks. At 2 473 K, the spectrum became similar to that of synthetic graphite.

Figure 6 shows the change in the Raman spectrum of bamboo charcoal. No remarkable change was observed up to 773 K. At 1 073 K, the several peaks between 1 100 cm$^{-1}$ and 1 500 cm$^{-1}$ in the spectrum of bamboo charcoal.
sharper. At 2473 K, the spectrum approached to that of synthetic graphite, although the relative height of D* band peak was larger, compared to that of synthetic graphite. Figure 7 shows the change in the Raman spectrum of wood charcoal. No change was observed up to 1673 K. At higher temperature, the spectrum approached to that of synthetic graphite, although the relative height of D* band peak was far larger, compared to that of synthetic graphite. But the spectrum at 2473 K seemed to become that of GC.

3.3. Evaluation Method of Carbonaceous Materials with Raman Spectrum Analysis

There have been many reports on the evaluation method of ordered materials with Raman spectrum analysis, namely, 1) peak intensity ratio, 2) peak area ratio, 3) half width of peak. The peak ratio of D band peak to G band peak is called R ratio, \( R = \frac{I_D}{I_G} \). The R ratio was compared to the size of graphite structure of La which was determined by XRD. The R ratio decreased with the increase of La. Thus, the R ratio can be used to evaluate perfection degree of graphite structure. Katagiri et al. made the map using R ratio and half width of peak for the more precise characterization of materials. The evaluation method of ordered materials seems well established.

There also have been many reports on the evaluation method of disordered materials. They are the similar R ratio as above, but using the ratio of \( \frac{I_{D*}}{I_{G*}} \) band separation, ratio of peak to background and combination of \( R* \), and \( I_{V}/I_{G*} \) where \( I_V \) is the intensity of minimum point between two peaks. But the universal evaluation method for the carbonaceous materials from ordered to disordered structure has not yet been established.

In the present paper, new parameters which can be used for all carbonaceous materials will be developed as follows. Examining the change in Raman spectrum with the temperature, two broad peaks of G* and D* become sharper at higher temperature and G* peak slits to G and D peak at further higher temperature. It can be seen that the spectrum should be the superimpose of several peaks. The curve fitting with four peaks, G*, D*, R1 and R2 was tried, as shown in Figure 8. In order to reproduce the experimentally obtained spectrum, it was necessary to assume additional peaks of R1 and R2. The R1 peak appeared around 1510 to 1527 cm\(^{-1}\) and R2, around 1239–1280 cm\(^{-1}\), respectively. These two peaks are assigned to the so-called turbostratic or random structure. The peak position of respective band is plotted against the temperature in Figure 9. The position of D* and D' peak did not change with the temperature, while that of G* changed from 1998 to 2173 K. At higher temperature than 2173 K, the peak position was constant at 1580 cm\(^{-1}\) which corresponded to that of G band of graphite structure. At higher temperature than 2073 K, the D' peak appeared. Therefore, the G* peak can be considered as the combined peaks of G and D'. These peaks could be identified by curve fitting at higher temperature than 2073 K. The fraction of area under D' peak to the total area is plotted against...
the temperature in Fig. 10. With the decrease in temperature, the fraction increased linearly. At lower temperature than 2,073 K, D’ peak could not be identified. The fraction was extrapolated down to 1,923 K. At farther lower temperature, the peak position of G* band did not change. Thus, the fraction was considered constant at the lower temperature.

New parameters are defined using the area of respective band peak as follows:

\[
\text{G Fraction (\%)} = 100 \left( \frac{G_A}{T_A} \right) \quad \text{(3)}
\]
\[
\text{D Fraction (\%)} = 100 \left( \frac{D_A + D’_A}{T_A} \right) \quad \text{(4)}
\]
\[
\text{R Fraction (\%)} = 100 \left( \frac{R_{1_A} + R_{2_A}}{T_A} \right) \quad \text{(5)}
\]

where the suffix A denotes the area of respective band peak and \(T_A\) is the total area.

### 3.4. Structure Evaluation by New Parameters

The change in G, D and R fractions for coke with the temperature is shown in Fig. 11. The R fraction decreased monotonously with the temperature from 1,373 K. The D fraction increased from 1,373 to 1,988 K but decreased remarkably from 2,033 K. The G fraction started to increase slightly from 1,373 K and remarkably from 2,033 K. The followings can be seen from the figure. The structure changing starts to occur at 1,373 K. The random structure changes to the graphite structure with many defects up to 2,033 K. And the graphite grains grow remarkably at higher temperature than 2,033 K. Figure 12 shows the change in G, D and R fractions for bamboo charcoal with the temperature. The similar changes to those in Fig. 11 can be seen. But the increase in D fraction and decrease in R fraction started at lower temperature of 1,073 K. Figure 13 shows the change in G, D and R fractions for wood charcoal with the temperature. Three fractions did not change up to 1,673 K. At higher temperature, D and R fractions decreased and that of G fraction increased. No increase in D fraction was observed. The difference between bamboo charcoal and wood charcoal would be due to the difference of carbonization temperature. Namely, the bamboo is carbonized at 673 to 993 K, while the wood of this kind, higher than 1,273 K. Thus, the transition from random structure to
the graphite structure with many defects would be finished for wood charcoal. **Figure 14** shows the construction of coke, bamboo charcoal and wood charcoal before heat treatment. The construction of coke and bamboo are similar to each other, namely, 45% of random structure, 45% of graphite structure with many defects and 10% of graphite structure. On the contrary, the wood charcoal consists of 70% of graphite structure with many defects, 20% of random structure and 10% of graphite structure. By the heat treatment at 1273 K, the construction of bamboo charcoal approached to that of wood charcoal.

### 3.5. Reaction Rate

**Figure 15** shows the plot of reaction degree with time of disordered materials, as examples. The plots lay almost on the straight line, showing the constant reaction rate. From the slope of line, the reaction rate constant was evaluated and listed in **Table 2**.

### 3.6. RSA

**Figure 16** shows an example of transient response of CO removal from the reactive site. The area under the hatched part was integrated and multiplied by the gas flow rate of $2.5 \times 10^{-3}$ m$^3$/s (STP) to estimate the volume of CO which was converted to the amount in mole unit using the state equation for the ideal gas. Then, the amount was divided by the weight at the reaction end, $W_f$, to obtain RSA (mol/g). The obtained results are shown in **Table 3**.

### 3.7. Reaction Rate Constant

In the present work, the following equation was derived to defined the rate constant of $k_1$ (g/mol/s) as

$$r = k_1 \text{RSA} \quad \text{(6)}$$

for simplicity. The $k_1$ was obtained from the data in Tables 2 and 3 and listed in **Table 4**.

In the previous work, the reaction rate, $r_2$, was estimated in the unit of mol/m$^2$/s and related to the surface concentration of CO molecules, $I_{CO}$ (mol/m$^2$), as
where, \( k \) (1/s) was defined as the rate constant. The equation of the present reaction can be divided into the following two equations:

\[
\begin{align*}
C_t + CO_2(g) & \rightarrow C(O) + CO(g) \quad (8) \\
C(O) & \rightarrow C_t + CO(g) \quad (9)
\end{align*}
\]

where, \( C_t \) is the reactive carbon, \( C(O) \) is the surface oxygen complex\(^{(14)} \) which will leave the material as the adsorbed \( CO \). It has been considered that the Eq. (9) should be the rate controlling step.\(^{(15)} \) Therefore, the Eq. (7) seems acceptable because the \( G \) can be considered as the surface concentration of surface oxygen complex. In the previous work,\(^{3)} \) the specific surface area was shown to have no significance. But, the area term in \( k \) cancelled out. Therefore, \( k \) can be considered independent of the specific surface area.

\[
r_j = k \Gamma_{CO} \quad \text{(7)}
\]

where, \( k \) (1/s) was defined as the rate constant. The equation of the present reaction can be divided into the following two equations:

\[
\begin{align*}
C_t + CO_2(g) & \rightarrow C(O) + CO(g) \quad (8) \\
C(O) & \rightarrow C_t + CO(g) \quad (9)
\end{align*}
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where, \( C_t \) is the reactive carbon, \( C(O) \) is the surface oxygen complex\(^{(14)} \) which will leave the material as the adsorbed \( CO \). It has been considered that the Eq. (9) should be the rate controlling step.\(^{(15)} \) Therefore, the Eq. (7) seems acceptable because the \( \Gamma_{CO} \) can be considered as the surface concentration of surface oxygen complex. In the previous work,\(^{3)} \) the specific surface area was shown to have no significance. But, the area term in \( k \) cancelled out. Therefore, \( k \) can be considered independent of the specific surface area.

\[
k_t = 12(W_c/W_t)k \quad \text{(10)}
\]
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