

Kinetics of gasification of glass-like carbons heat-treated at various temperatures with CO₂

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Reaction rates based on the Boudouard reaction using a Langmuir-Hinshelwood type equation were analyzed to investigate the effect of the heat treatment temperature on the reactivity of glass-like carbon made from furan resin with carbon dioxide. Glass-like carbons were prepared from furan resin at 1000 °C, 1500 °C and 2000 °C. Oxidation was performed in the range from 925 °C to 1100 °C in a batch reactor. The binding energy of carbon-carbon in the glass-like carbon was found to increase with increasing heat treatment temperature. Contrarily, the binding energy between carbon and oxygen in a functional group was found to decrease with increasing heat treatment temperature. The oxidation resistance of glass-like carbons especially those heat-treated at high temperatures was concluded to be relatively excellent compared with other carbons such as graphite because the functional group containing oxygen was hard to form on glass-like carbon and the decomposition of the functional group into carbon monoxide was thought to be difficult.

Key words: Glass-like carbon, Oxidation, Langmuir-Hinshelwood Equation, Boudouard Reaction.

Introduction

Glass-like carbons have been thought to have a cell type structure with nano-sized closed pores. They have some excellent characteristics such as extremely low gas-permeability, high chemical stability, low density and relatively high mechanical strength. Because of these qualities which are important to there applications, they are widely used for parts of semiconductor-making tools, electrodes, fuel cells, substrate of hard disks, electro conductive jigs etc [1-3].

It is well known that the oxidation resistance of glass-like carbons is relatively high compared with other carbon materials and that the oxidation resistance increases with increasing heat treatment temperature [4]. Also, effect for transitional metal oxides such as TiO₂ and Ta₂O₅ to enhance the oxidation resistance of glass-like carbon has been reported [5]. The reason given was that the transitional metals suppress the production of oxygen-containing functional groups formed on the surface [6]. The surface oxides forming during oxidation are closely connected with the oxidation resistance [7]. The reactivity of carbon with oxidant substances depends on the carbon structure. Carbon with a high degree of graphitization is known to have a high oxidation resistance [8, 9]. However, the oxidation resistance of glass-like carbons having no graphitized

structure is confirmed to be higher than those of general artificial graphites [4]. This fact means that factors other than the crystal structure are strongly correlated with the reactivity. However, the details of the factors and reasons are obscure as yet.

To clarify the intrinsic reactivity of carbon materials, kinetic analysis of reaction rates performed under the condition where the chemical reaction is the rate-determining step is important. For the purpose, the application of a Langmuir-Hinshelwood type equation (abbreviated L-H equation) is considered to be essential [10-13]. The reaction rates of carbons such as artificial graphites, coals, and carbon blacks etc. with carbon dioxide and water vapor have been analyzed using a L-H equation by some researchers [14-20]. The authors of this paper have reported the analytical results of the reaction rates of glass-like carbon with carbon dioxide using a L-H equation [21]. We discussed the binding energies between carbon-carbon atoms and between carbon-oxygen.

In this paper, the effect of heat treatment temperature of glass-like carbon on the oxidation resistance is investigated.

Experimental

Preparation of glass-like carbon

Furan resin for the raw material of glass-like carbon was prepared from furfuryl alcohol with p-toluene sulfonic acid as a curing agent. Furfuryl alcohol was mixed with 0.3 wt% p-toluene sulfonic acid at room temperature for 1h, then the temperature of the solution was elevated to 50 °C whilst stirring. Three hours later,

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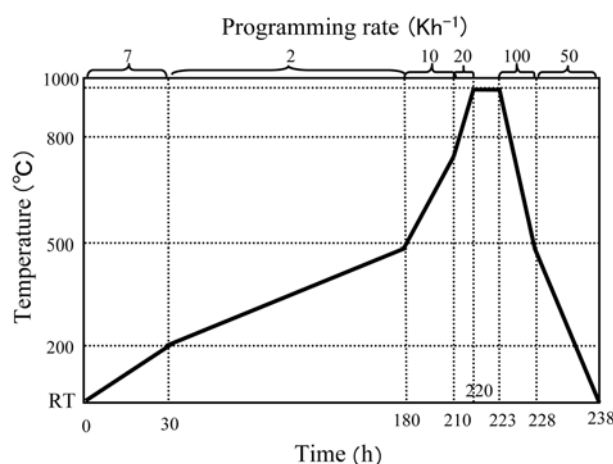


Fig. 1. Heating pattern for carbonization in nitrogen.

defoaming at room temperature was conducted in a deaerator to eliminate as much as possible of the water produced during polymerization. The solution was then transferred into a flat vessel and cured at 50 °C for 72h. Through this process, a resin block with a size of 50×50×5 mm was obtained.

The furan resin was carbonized at 1000 °C in nitrogen according to the heating pattern shown in Fig. 1. The resulting carbonaceous product was heated up to 1500 and 2000 °C and kept for 1h. The product was crushed and grains with sizes of 20 to 30 mesh (250 to 315 μm) were used for the oxidation experiments. The specimens heat-treated at 1000, 1500 and 2000 °C are hereinafter abbreviated as GC1000, GC1500 and GC2000, respectively.

The specimens were characterized by measurements of specific surface area, bulk density, interlayer spacing and crystalline size. The specific surface area was calculated by BET plots of the N₂ adsorption isotherm measured at -196 °C. The bulk density was measured by the Archimedes' method using distilled water. The average interlayer spacing d_{002} and the crystallite size $L_c(002)$ were determined from the (002) peak, respectively, and the crystallite size $L_a(110)$ was evaluated from the (110) peak in the XRD profiles.

Measurement of the Boudouard reaction rate

The Boudouard reaction means the reaction of carbon with carbon dioxide to produce carbon monoxide as expressed by equation (1):



The Rate of the Boudouard reaction was measured using a batch reactor schematically illustrated in Fig. 2. The major components of the apparatus are an electrical furnace for oxidation, a device to measure the oxygen potential pressure in the reactant gas, a circulation system for the gas phase, and a gas supply system. A flexible tedlar bag was attached to keep the gas phase at atmospheric pressure, because the volume in the

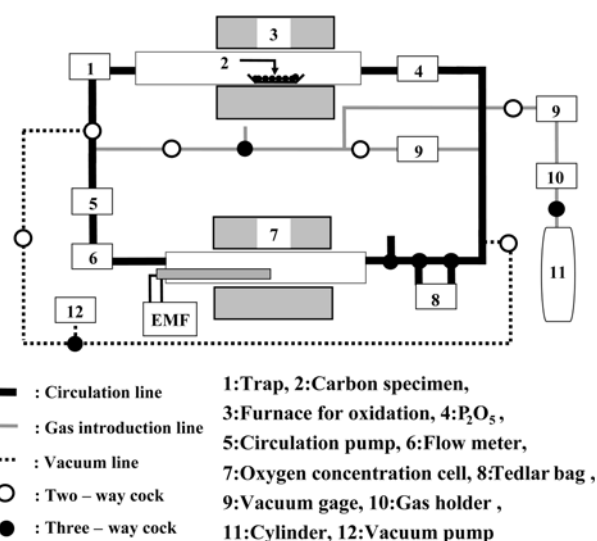


Fig. 2. Schematic diagram of the experimental apparatus for oxidation.

reaction system increases with the progress of the Boudouard reaction. Diphosphorus pentoxide was used for perfect dehydration of the gas phase in the reaction system.

After an alumina boat containing a 3.0g specimen was placed in the center of the reactor tube, the reaction line was evacuated and then carbon dioxide or carbon dioxide plus nitrogen were introduced in the reaction line through the gas supply system. The volume of gas introduced was estimated by measuring the pressure of the gas stored. Then, the specimen was heated to the prescribed temperature. The gas phase was kept circulating during the reaction. The volume of the gas introduced in the system was about 3.0 liter at room temperature. The reaction was performed at temperatures ranging from 925 to 1100 °C.

As the reaction proceeded, the gas phase began to contain carbon monoxide. In a gas mixture containing carbon dioxide and carbon monoxide, the oxygen potential P_{O_2} in the gas phase is determined by the ratio of the partial pressures of carbon dioxide (P_{CO_2}) to carbon monoxide (P_{CO}). Therefore, the exact concentrations or the partial pressures of carbon dioxide and carbon monoxide can be calculated from P_{O_2} in the gas. The P_{O_2} was determined using an oxygen concentration cell (stabilized zirconia was adopted). Air was used for the cell reference. The amount of carbon gasified, %burnt-off, was estimated through the initial amount of carbon and P_{CO_2} . The reaction rate, R (%burnt-off/minute⁻¹), was determined from the relation between the reaction time and %burnt-off. The relationship between P_{CO_2} and %burnt-off/minute⁻¹ of the carbon specimen was calculated to analyze the reaction rate.

Analysis of the Boudouard reaction rate by Langmuir-Hinshelwood type equation

The reaction rates were applied to a L-H equation.

The Boudouard reaction (1) is composed of two elementary reactions (2) and (3) [12]:



$$[Ct^*] = [C^*] + [C(O)] \quad (4)$$

Here, C^* indicates the active site to be oxidized and i_1 , i_2 and i_3 are the kinetic rate constants. The reaction (2) is called the oxygen exchange reaction. It is known that an equilibrium is easily attained [12]. In this reaction, active carbon reacts with carbon dioxide to form a surface oxide, $C(O)$, and to release carbon monoxide. The reaction (3) is the decomposition of the surface oxide to produce carbon monoxide and active sites. The total active sites, Ct^* , is expressed as equation (4). Since the surface oxide concentration is obtained by the theory of the steady state method ($d[C(O)]/dt=0$) and equation (4), the reaction rate of equation (1), $R=i_3[C(O)]$, is expressed as equation (5) [12]:

$$R = \frac{i_1[Ct^*]P_{CO_2}}{1 + \frac{i_2}{i_3}P_{CO} + \frac{i_1}{i_3}P_{CO_2}} \quad (5)$$

Replacing $i_1[Ct]$, i_2/i_3 , and i_1/i_3 by K_1 , K_2 , and K_3 yields equation (6) which is called the L-H equation:

$$R = \frac{K_1 P_{CO_2}}{1 + K_2 P_{CO} + K_3 P_{CO_2}} \quad (6)$$

Equation (7) is obtained from equation (6) under the condition of $P_{CO_2} + P_{CO} = 1(\text{atm})$. Equation (7) shows that $1/R$ and $1/P_{CO_2}$ are linearly related. However, we cannot solve the constants through linear plots of $1/R$ and $1/P_{CO_2}$ because equation (7) has three constants. Then another experiment is required to be conducted under a different total pressure. In this study, oxidation was performed in a reaction system containing nitrogen at atmospheric pressure. The relation between $1/R$ and $1/P_{CO_2}$ in equation (8) is not exactly liner, because P_{N_2} changes as the oxidation proceeds. However, the intercept of equation (8) is identical to that of equation (7). Since the region where the change of P_{N_2} can be almost negligible gives a straight line as well, we can thus determine the values of K_1 , K_2 , and K_3 , through experiments in the reaction systems (CO_2 -CO) and (CO_2 -CO- N_2):

$$\left(\frac{1}{R}\right) = \frac{1 + K_2}{K_1} \left(\frac{1}{P_{CO_2}}\right) + \frac{K_3 - K_2}{K_1} \quad (7)$$

$$\left(\frac{1}{R}\right) = \frac{1 + K_2 - K_2 P_{N_2}}{K_1} \left(\frac{1}{P_{CO_2}}\right) + \frac{K_3 - K_2}{K_1} \quad (8)$$

These constants, K_1 , K_2 and K_3 , depend on the reaction temperature. K_1 , K_2 and K_3 , can be expressed as equation (9):

$$K_j (j=1,2,3) = A_k \exp\left[\frac{-E_k}{RgT}\right] \quad (9)$$

The kinetic constants, i_1 , i_2 and i_3 are expressed as the following:

$$i_1 = A_{i_1} \exp\left[\frac{-E_{i_1}}{RgT}\right] = \frac{A_{k_1}}{[Ct^*]} \exp\left[\frac{-E_{k_1}}{RgT}\right] \quad (10)$$

$$i_2 = A_{i_2} \exp\left[\frac{-E_{i_2}}{RgT}\right] = \frac{(A_{k_1} A_{k_2})}{(A_{k_3})} \frac{1}{[Ct^*]} \exp\left[\frac{-E_{k_1} - E_{k_2} + E_{k_3}}{RgT}\right] \quad (11)$$

$$i_3 = A_{i_3} \exp\left[\frac{-E_{i_3}}{RgT}\right] = \frac{(A_{k_1})}{(A_{k_3})} \frac{1}{[Ct^*]} \exp\left[\frac{-E_{k_1} + E_{k_3}}{RgT}\right] \quad (12)$$

Therefore, E_{k_1} , E_{k_2} and E_{k_3} can be calculated from equations (13), (14), and (15).

$$E_{i_1} = E_{k_1} \quad (13)$$

$$E_{i_2} = E_{k_1} + E_{k_2} - E_{k_3} \quad (14)$$

$$E_{i_3} = E_{k_1} - E_{k_3} \quad (15)$$

The enthalpy change, ΔH , in the oxygen exchange reaction expressed by equation (2) is evaluated from equation (16). Also the formation enthalpy of the surface oxide $C(O)$, $H_{C(O)}$, is calculated using equation (17).

$$\Delta H = E_{i_1} - E_{i_2} = E_{k_3} - E_{k_2} \quad (16)$$

$$H_{C(O)} = \Delta H - H_{CO} + H_{CO_2} + H_{C^*} \quad (17)$$

Results and Discussion

Characterization of specimens prepared

The bulk density, BET surface area, interlayer spacing and crystalline size are summarized in Table 1. The bulk density slightly decreased with a rise of heat treatment temperature. The BET specific surface area considerably decreased between 1000 °C and 1500 °C. The interlayer spacing also slightly decreased and the crystalline sizes increased with increasing heat treatment temperature. Almost no difference between 1500 °C and 2000 °C was observed.

Table 1. properties of glass-like carbon prepared in this study

specimen	GC1000	GC150	GC200
Item			
d_{002} (nm)	0.355 ₅	0.349 ₉	0.345 ₈
L_c (002) (nm)	1.4 ₅	2.2 ₈	2.3 ₉
L_a (110) (nm)	3.0 ₀	2.9 ₇	3.4 ₉
Specific surface area (m ² /g)	2.1	1.4	1.3
Bulk density (g/cm ³)	1.52	1.51	1.49

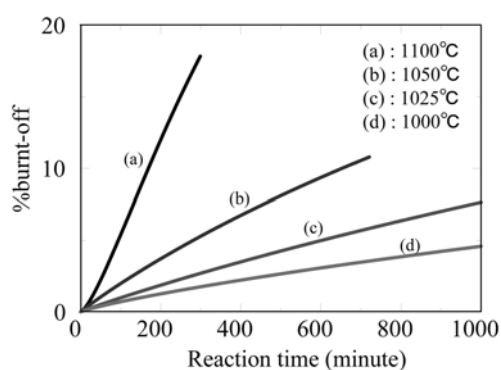


Fig. 3. Relationship between burn-off and reaction time.

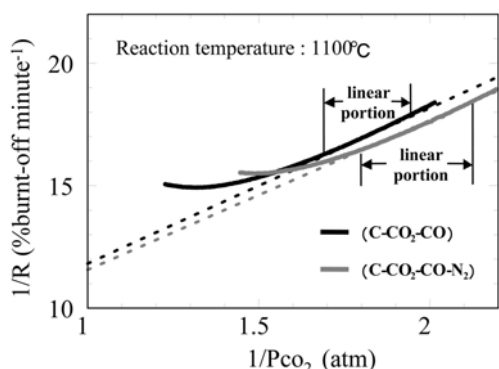


Fig. 4. Typical linear plots of reciprocal reaction rate (1/R) vs CO₂ partial pressure (1/P_{CO2}).

Boudouard reaction rate and constants, K₁, K₂ and K₃ in the L-H Equation

Figure 3 illustrates the relationship between burn-off and reaction time. Since the oxidation was performed in a batch reactor, the results of Fig. 3 cannot be directly applied to zero-order or first-order kinetics because P_{CO2} varies with the reaction time. The reaction rate R at a specified time is determined from the tangent of the curve at that moment.

Typical examples of relations between 1/R and 1/P_{CO2} are illustrated in Fig. 4. The region of the reaction, at least in the linear portions, is believed to be in the rate-determining step. Table 2 summarizes the results obtained from the linear relations at various temperatures.

To compare the reactivity of the specimens, reaction rates in equation (6) were calculated using the constants summarized in Table 2. A condition of P_{CO2}+P_{CO}=1(atm) was adopted. The resultant reaction rates of

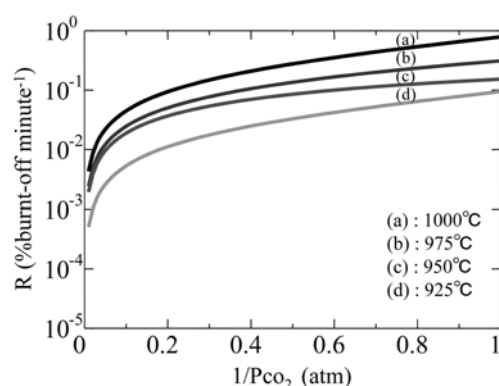


Fig. 5. Boudouard reaction rates at various temperatures for GC1000.

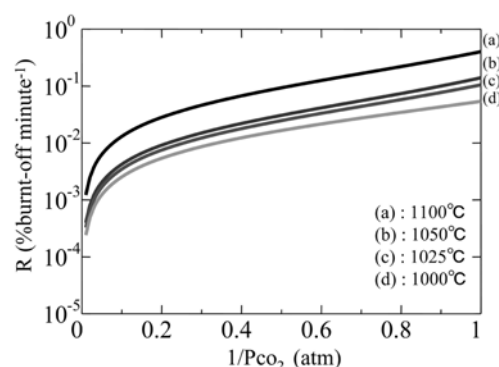


Fig. 6. Boudouard reaction rates at various temperatures for GC1500.

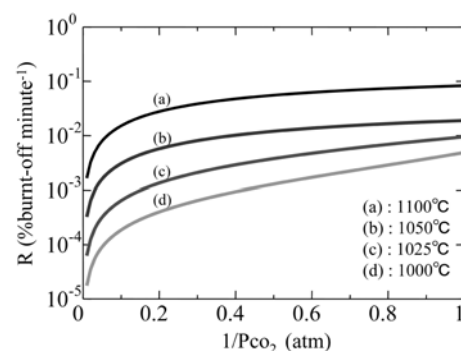


Fig. 7. Boudouard reaction rates at various temperatures for GC2000.

GC1000, GC1500 and GC2000 are shown in Fig. 5, Fig. 6 and Fig. 7, respectively. In all specimens, the reaction rates are confirmed to increase with increasing reaction temperature. The reaction rates gradually de-

Table 2. properties of glass-like carbons prepared in this study

Specimen	GC1000				GC1500				GC2000			
Reaction temperature/°C	925	950	975	1000	1000	1025	1050	1100	1000	1025	1050	1100
K ₁ /(%burnt-off·minute ⁻¹ ·atm ⁻¹)	8.102	3.3808	0.197	0.898	0.059	0.190	0.296	0.848	0.007	0.019	0.091	0.255
K ₂ /atm ⁻¹	21.064	17.263	2.909	4.133	1.469	4.863	6.542	5.971	3.175	2.099	1.775	0.538
K ₃ /atmv	1.1014	6.155	1.073	3.405	0.097	0.805	1.112	1.100	0.491	1.040	3.794	2.076

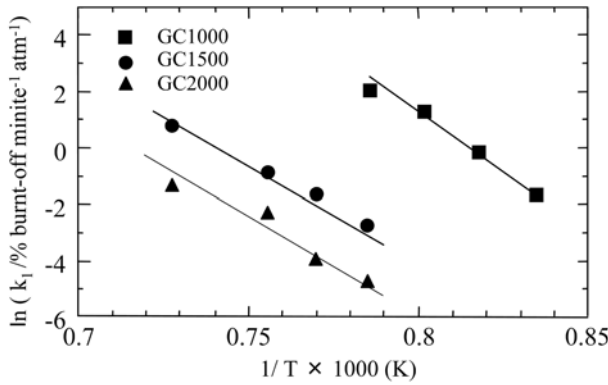


Fig. 8. Arrhenius plots for K1.

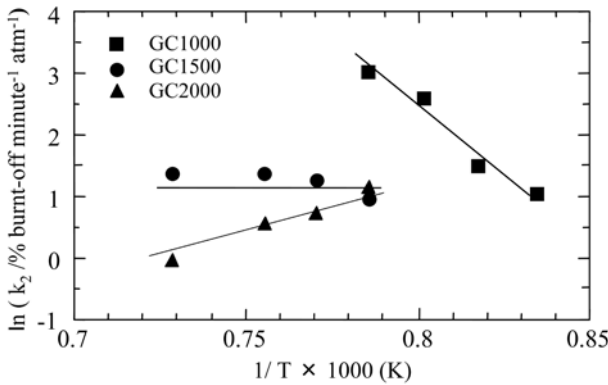


Fig. 9. Arrhenius plots for K2.

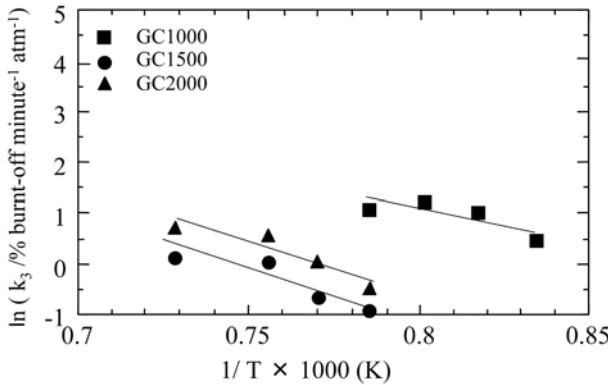


Fig. 10. Arrhenius plots for K3.

crease with decreasing CO₂ concentration and steeply fall in the region of low partial pressure of CO, indicating that CO inhibits the oxidation.

The results of the Arrhenius plots for K₁, K₂ and K₃ are shown in Fig. 8, Fig. 9, and Fig. 10, respectively. The value of K₁ becomes high as the reaction temperature increases, and it increases with increasing preparation temperature. A tendency for K₂ to decrease with increasing preparation temperature is seen. The temperature dependence on the K₃ is considered to be the same as K₁.

E, ΔH and H_{C(O)}

The values of E, ΔH and H_{C(O)} are shown in Table 3. For reference, some reported values are summarized in Table 4 [14–20]. E_{i1} is related to the temperature dependence for the oxygen exchange reaction. As is clear in Table 4, E_{i1} values of carbon black and activated carbon whose oxidation reactivity is relatively high are seen to be low [16–20]. However, natural graphite with a low reactivity has high value of E_{i1} [14]. The values of glass-like carbons examined in this study are recognized to be higher than that of graphite. It has been reported that the reactivity of glass-like carbon is lower than that of natural graphite [4].

E_{i2} is the activation energy of the reverse reaction of equation (2). E_{i2} decreases with the rise of heat treatment temperature. The values of all specimens are positive and smaller than those of E_{i1}. Since the reaction of carbon dioxide with carbon is endothermic reaction, E_{i2} must be smaller than E_{i1}. However, Lewis et al. [15] reported that E_{i1} is almost equal to E_{i2} for anthracite, and Bandyopadhyay and Ehosu [20] reported that E_{i2} is larger than E_{i1} for carbon from a coconut shell-based carbon. Since the carbons [17–20] contain a lot of minerals, the oxidation reaction mechanism can

Table 3. E, ΔH and H_{C(O)}

Specimen	E _{i1} /kJ·mol ⁻¹	E _{i2} /kJ·mol ⁻¹	E _{i3} /kJ·mol ⁻¹	ΔH /kJ·mol ⁻¹	H _{C(O)} /kJ·mol ⁻¹
GC1000	641	453	289	188	-95
GC1500	563	342	338	221	-62
GC2000	503	277	390	226	-57

Table 4. E, ΔH and H_{C(O)} reported by other researchers

	material	E _{i1}	E _{i2}	E _{i3}	ΔH	H _{C(O)}
Strange & Walker [14]	Natural graphite	414	310	364	105	-178
Lewis et al. [15]	Anthracite	136	135	205	1.3	-282
Menster & Ergun [16]	Carbon black	222	151	243	71	-212
Ollero et al. [17]	Olive	60	38	167	22	-212
Barrio and Hustad [18]	Birch	165	21	236	144	-139
Rathmann et al. [19]	Straw	100	-7	155	107	-176
Bandyopadhyay and Ehosu [20]	Coconut	157	243	408	-86	-379

not be discussed in detail.

The enthalpy ΔH of the oxygen exchange reaction can be evaluated from the values of E_{i1} and E_{i2} . The values of ΔH for GC1000, GC1500 and GC2000 were calculated to be 188, 221, and 226 kJ/mol. It is noteworthy that the difference between 1000 and 1500 °C is large.

Based on the enthalpy change, ΔH , in reaction (2) and the formation enthalpies of carbon dioxide and carbon monoxide, the formation enthalpies of surface oxide $\text{H}_{\text{C(O)}}$ were calculated to be -95, -62, and -57 kJ/mol for GC1000, GC1500 and GC2000. $\text{H}_{\text{C(O)}}$ expresses the stability of C(O) in the oxygen exchange reaction of equation (2). High values of formation enthalpy of the surface oxide indicate that the binding force between the carbon of the active site and the oxygen dissociated from carbon dioxide is strong [22]. The values of glass-like carbons are very small compared with the other carbon materials as is shown in Table 4. Therefore, the binding force between oxygen and carbon of glass-like carbon is concluded to be very weak and then the surface oxide is very unstable. It is thought that the functional group containing oxygen is hard to form on glass-like carbon. Furthermore, since $\text{H}_{\text{C(O)}}$ increases with the rise of heat treatment temperature, the functional group containing oxygen becomes harder to form on glass-like carbon with the rise of heat treatment temperature.

It is known that the edge plane of the graphite structure is more reactive than the basal plane [23, 24]. The concentration of edges on the carbons heat-treated at lower temperatures is higher than that on the carbons heat-treated at higher temperatures. Also this concentration increases in the process of oxidation [25]. Since carbons with high edge concentration contain many functional groups, the reactivity of the carbons should be reasonably high. Activated carbons are considered to have a high concentration of edges. We can confirm in Table 4 that $\text{H}_{\text{C(O)}}$ of such activated carbons [15-19] is relatively high and that of natural graphite [20] is low. The glass-like carbons prepared in this study have lower $\text{H}_{\text{C(O)}}$ than that of natural graphite. The structure of glass-like carbons is said to be cell type [1] by which the edge concentration is expected to be low. The strain energy must be high because the plane has a bent form. Furthermore, the strain energy becomes small when glass-like carbon is heated at high temperatures because the cell size is known to grow with increasing temperature [26, 27]. This means that a functional group is difficult to form on glass-like carbon. Then, $\text{H}_{\text{C(O)}}$ of glass-like carbon is thought to become smaller with increasing heat-treatment temperature.

The activation energy of equation (3), E_{i3} , is considered to be proportional to the binding energy between neighboring carbon active sites [28]. The specimens GC1000, GC1500 and GC2000 have E_{i3} values of 289, 338, and 390 kJ/mol, respectively. E_{i3} increases by 50

kJ/mol every 500 °C of heat treatment temperature, indicating that the binding energy becomes higher with increasing heating temperature. E_{i3} of GC2000 is almost the same as natural graphite, indicating that the decomposition of the surface oxide is significantly difficult.

In some of the thermodynamic parameters, E_{i1} , E_{i3} , and $\text{H}_{\text{C(O)}}$ of glass-like carbon are found to be relatively high compared with those of other carbons. The Boudouard reaction of glass-like carbon doesn't appear to be easy to initiate because of the cell type structure with low edge concentration. Since and the combination of carbon with dissociated oxygen is weak and the binding energy between carbons of glass-like carbon was estimated to be high, the functional group containing oxygen was hard to form on glass-like carbon and the decomposition of the functional group into carbon monoxide was thought to be difficult. These are the reasons that the oxidation resistance of glass-like carbon is excellent.

Conclusions

In this study, the relationship between heat treatment temperature of glass-like carbon and the reactivity with carbon dioxide was investigated. The main results and conclusions are as follows.

1. E_{i1} and E_{i2} decreased and E_{i3} increased with increasing heat treatment temperature. The binding energy between carbons of glass-like carbon was considered to become high with increasing heat treatment temperature.
2. ΔH of glass-like carbon considerably increased between 1000 °C and 1500 °C and remained unchanged between 1500 °C and 2000 °C.
3. The binding energy of carbon with oxygen dissociated from carbon dioxide on glass-like carbon was estimated to be weak, and small values of the energy compared with other carbon materials were established.
4. Since the combination of carbon with dissociated oxygen is weak and the binding energy between carbons of glass-like carbon was estimated to be high, the functional group containing oxygen was hard to form on glass-like carbon and the decomposition of the functional group into carbon monoxide was thought to be difficult. For this reason, the oxidation resistance of glass-like carbon was concluded to be relatively high.

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