Characterization of Pitch-based Carbon Fibers (Part 1)
Carbonization Behavior of Stabilized Mesophase Pitch Fibers

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1. Introduction

Carbon or graphite fibers because of their light weight, high strength and modulus, are being used as an important reinforcing component of composite materials for various industrial applications. In recent years, pitch-based carbon fibers have been recognized as strategic materials because of their high strength per weight and low cost¹), and they have been intensively investigated²)-⁴), and successfully developed. Many authors⁵-⁶) reported that the performance of carbon fibers, as reinforced composites, depended to a large extent on the surface properties of carbon fibers and matrices, such as surface area, surface roughness, and surface functional groups which would yield a better chemical bonding between fibers and matrices.

Early works concerning surface features of carbon fibers have been performed on carbon fibers derived from polyacrylonitrile (PAN) or rayon⁷)-⁸). Rand and Robinson⁹) measured the surface micropore volume of commercial HT (Type II) fiber by nitrogen adsorption and desorption.

Greater part of the works was focused on the deliberation⁷)-⁹) regarding reactive functional groups on the fiber surface, using various sensitive methods such as XPS, NMR, IR, etc. Many other studies were also made to improve the surface so as to achieve maximum translation of fiber properties¹⁰)-¹²). However, some studies were carried out on the surface of pitch-based carbon fibers, which had emerged later years, especially on the carbonization process. This is due to the complexity of the chemical and physical changes involved in the process transferring the precursor fibers to carbon or graphite fibers. In general, the properties of carbon and graphite fibers are controlled to the greatest extent by the nature of the precursor and the methods of transformation from precursor to carbon and graphite. A systematic study was carried out in pitch-based carbon fibers in our laboratories.

In the present paper, changes in mass, specific surface area, surface functional groups, and mechanical character of precursor pitch-based carbon fibers for HPCF during carbonization in the range of 400—2,300°C were traced. The mechanism for carbonization of stabilized pitch fibers was described from the results obtained.
2. Experimental

The mesophase pitch fibers used in this study, prepared from coal tar pitch, were supplied from Nitto Boseki Co., Ltd. The spun pitch fibers used in some experiments were coated with graphite powder to prevent intermelt. Oxidation of spun pitch fibers was carried out in air at 310°C to stabilize them for successive carbonization. The elemental analyses and physical properties of raw pitch and pitch fibers after and before oxidation are listed in Table 1. The stabilized pitch fibers were heat-treated at 400 to 1,800°C in nitrogen atmosphere and at 2,000 to 2,300°C in argon atmosphere, then their surface areas and surface oxygen-containing functional groups were measured using BET and XPS, respectively. Nitrogen and argon used were both better than 99.999% in purity.

The specific surface areas of the stabilized pitch fibers, had been heat-treated under various temperatures, were measured by adsorption of krypton at liquid nitrogen temperature (-196°C) using a conventional BET volumetric apparatus. Before each adsorption run, the sample was evacuated at room temperature or at 400°C for 1 h below 10^-5 Torr. In order to examine the effects of evacuation temperature on the specific surface area or surface functional groups, the evacuation temperature was changed from room temperature to 400°C.

The stabilized pitch fibers, which had been heat-treated or evacuated under various temperatures, were characterized using XPS. A Shimadzu spectrometer (ESCA-850) with a MgKα ray was used. The base pressure in the sample chamber was below 10^-7 Torr. The binding energy of graphite peak C-1s of 284.6 eV was used for calibration.

3. Results

3.1 Thermal Behavior of Stabilized Pitch Fibers

Figure 1 shows the non-isothermal TG curves of stabilized pitch fibers at heating rate of 1.98 °C·min⁻¹ and 12.5 °C·min⁻¹, respectively. When the heating rate was 1.98 °C·min⁻¹, the weight loss of the pitch fibers commenced at about 300°C and terminated at about 800°C. When the heating rate was 12.5 °C·min⁻¹, the weight loss commenced at about 400°C and did not terminated until 1,000°C. The thermal behavior of stabilized pitch-based carbon fibers is completely different from that of sigrafil HF carbon fibers reported by Manocha, in the paper, the fibers showed a very small weight loss (1 wt%) although the carbon fibers were treated with concentrated nitric acid for various periods of time. Further it was pointed out that the weight loss at temperatures between 300 and 600°C was attributed to the evolution of CO₂ by decomposition of carboxyl groups, whereas at temperatures between 600 and 1,000°C to the evolution of CO from carbonyl and hydroxyl groups. In our system, however, the weight losses were found at temperatures between 300 and 800°C and showed a different behavior.

Table 1 Compositions and Physical Properties of Raw Pitch and Pitch Fibers

<table>
<thead>
<tr>
<th>Sample</th>
<th>Elemental analysis [wt%]</th>
<th>Composition [wt%]</th>
<th>Density [g/cm³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw pitch</td>
<td>C 92.10, H 4.90, N 1.03</td>
<td>HS 22.3</td>
<td>1.28</td>
</tr>
<tr>
<td>Spun carbon fibers</td>
<td>C 92.25, H 4.85, N 1.02</td>
<td>HIS-BS 51.5</td>
<td></td>
</tr>
<tr>
<td>Oxidized carbon fibers</td>
<td>C 83.66, H 2.94, N 1.14</td>
<td>BIS-THFS 12.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>THFIS 13.6</td>
<td></td>
</tr>
</tbody>
</table>

HS: Hexane soluble; HIS-BS: Hexane insoluble but benzene soluble; BIS-THFS: Benzene insoluble but tetrahydrofuran soluble; THFIS: Tetrahydrofuran insoluble.
higher value (about 20 wt%). It is clear that all of the weight losses observed at temperatures between 300 and 800°C would not be attributed to the decomposition of functional groups on the surface of oxidized carbon fibers. The evolution of small molecules and pyrolysis of pyrolytic components would be the significant factors that cause the weight loss. Moreover, this weight loss is greater than that of stabilized isotropic precursor (18 wt%) and that of mesophase precursor (13 wt%), both of which were obtained from a pilot-plant-scale production line. It is considered that overoxidation during stabilization and the high content of HS portion in raw pitch may be the factors other than these stated above that cause the weight loss. The content of oxygen of the stabilized pitch fibers was 12.26 wt% (Table 1), which is higher than that obtained from the pilot-plant-scale, or that reported in the oxidation of mesophase petroleum pitch fibers in which the content of oxygen at completion of stabilization was about 10 wt% of raw fiber.

3.2 Surface Properties

The stabilized pitch fibers were pretreated in the temperature range from 400 to 1,800°C in nitrogen atmosphere and from 2,000 to 2,500°C in argon atmosphere prior to their surface measurements. Full adsorption-desorption isotherms of krypton gas at liquid nitrogen temperature were obtained for the such heat-treated pitch fibers. Figure 2 shows typical adsorption-desorption isotherms for the carbon fiber heat-treated at 2,000°C. The common characteristics that the closed hysteresis loops indicating the presence of micropores as part of the total pore system could not be seen in Fig. 2.

Specific surface areas were obtained from the adsorption isotherms using the Brunauer-Emmet-Teller (BET) method in the conventional range of relative pressure, adopting a value of 0.185 nm² for the molecular area of krypton. The change of specific surface area with temperature is shown in Fig. 3. In the case of evacuation at room temperature, the curve in Fig. 3 can be classified into three ranges: below 800°C, 800–1,000°C, and above 1,000°C. In the first range, the specific surface did not change with temperature of heat treatment and was approximately constant at 0.4 m², even though the weight loss was considerable in this range (Fig. 1). In the second and third ranges, however, the specific surface area rapidly increased, and slightly decreased in the third range. In the case of evacuation at 400°C, similar results were obtained; but the increase in the specific surface area started at lower temperatures, and the extent of its increase in the second range was larger than that on evacuating at room temperature.

3.3 Surface Functional Groups

Figure 4 shows the C-1s spectra of the pitch fibers after spinning and the stabilized pitch fibers, which were heat-treated at various temperatures up to 2,300°C. A shoulder peak in the C-1s spectrum of stabilized pitch fibers was observed at 286–287 eV which was attributed to the formation
of oxygen-containing functional groups. The shoulder peak observed on the C-1s spectrum disappeared when the stabilized fibers were heat-treated at 600°C. This result indicates that the oxygen-containing functional groups produced by surface oxidation of the spun pitch fibers are decomposed at temperature below 600°C. These results are very similar to those of “commercial-type II” carbon fibers reported by Harvey et al.5) in which the oxide layer produced by oxidation with nitric acid was eliminated completely by heat-treating at below 1,000°C. However, the characteristic peaks of oxygen-containing functional groups reappeared when the heat-treatment temperature was raised to 1,000°C.

In order to clarify reasons for the reappearance of oxygen-containing functional groups at 1,000°C, the O-1s core level spectra of the inner part of carbon fibers were checked, and the effect of etching time on these spectra was measured. The ratio of O-1s/C-1s represents a good parameter to describe the degree of oxidation as shown in Table 2. The O-1s/C-1s ratios of carbon fibers treated at various temperatures with different etching times indicate that the oxygen concentrations of these carbon fibers are the highest on the surface as the ratios decreased with the increase in etching time. The O-1s/C-1s ratio of carbon fibers heat-treated at 800°C is the lowest which indicates that the oxygen-containing species are diminished by heat treatment at this temperature. These facts suggest that the increase in oxygen in the carbon fibers treated at higher temperatures than 800°C would be attributed a little to the contaminants in the nitrogen (or argon) stream used, and not to the movement of inner oxygen of carbon fibers itself.

The effect of etching time on C-1s spectrum treated at 1,000°C is shown in Fig. 5. The shoulder peak at 286 eV decreased suddenly in etching time of 2 min. The effects of etching time on the C-1s profiles treated at 1,500 to 2,300°C are the same as those of Fig. 5. These results indicate that the oxygen–carbon complexes are formed in the neighborhood of the surface layers of the carbon fibers.

Figure 6 shows the effects of evacuation temperature on C-1s spectra of stabilized pitch fibers, which were heat-treated at 2,000°C prior to the XPS measurements. The intensity of the characteristic peak of oxygen-containing functional-
al groups decreased with increasing evacuation temperature and disappeared at about 400°C; the result is different from that of the PAN-base carbon fibers obtained by Nishioka et al. This indicates that the oxygen-containing species produced by heat-treating can be decomposed at lower temperatures under reduced pressures.

A digital difference technique was applied to distinguish the types of oxygen-containing functional groups in Figs. 4 and 6. The oxygen-carbon complexes at 286.0, 287.0, and 288.6 eV of C-1s spectra can be assigned to the hydroxyl group (C-OH), the carbonyl group (C=O), and the carboxyl group (COOH), respectively. The area ratios of the chemically shifted species with respect to the main peak (C-OH) were obtained and shown in Figs. 7 and 8. In Fig. 7, the intensities of hydroxyl group and carbonyl group increased by increasing the heat treatment temperature except for the sample treated at 2,300°C. Since the specific surface area of carbon fibers was almost constant in that temperature range, the increase in hydroxyl group abundance on the carbon fibers does not depend on the surface area differences. The amount of carboxyl group does not change in this temperature range because of the oxidation conditions which are too mild to convert hydroxyl and carbonyl groups into a carboxyl group. These results agree with those of Takahagi’s report that the hydroxyl group is assigned to the main peak of the moderately oxidized carbon fibers and that the carboxyl peak is the largest for the extensively oxidized material. In Fig. 8, the main oxygen-containing functional group produced by heat treatment was hydroxyl, and it decomposed rapidly by increasing the evacuation temperature to 400°C. The carbonyl group had a lower abundance level in the original oxidized carbon fibers. The abundance level of carboxyl group was the lowest and was nearly unchanged with evacuation temperature.

### 3.4 Physical Properties

Table 3 shows the changes in elemental composition and physical properties with carbonization temperature. By raising the carbonization temperature, the content of carbon increased, but the contents of hydrogen and heteroatoms, such as nitrogen, oxygen, etc., decreased. Reactions of

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**Fig. 6** C-1s Spectra under Various Evacuation Temperatures for the Stabilized Pitch Fibers Heat-treated at 2,000°C

**Fig. 7** Relative Intensities of Three Different Functional Groups on Stabilized Pitch Fibers Heat-treated at Various Temperatures

**Fig. 8** Relative Intensities of Three Different Functional Groups on Carbonized Pitch Fibers Evacuated at Various Temperatures
dehydrogenation and deheteroatoms were basically completed before reaching 1,000°C. Only a little change in the elemental composition of carbon fibers was observed above 1,000°C. However, the physical properties, especially, the tensile elastic modulus, of carbon fibers continued to change, and it did not end until 2,300°C was reached. The tensile strength attained its maximum at 1,800°C, it then decreased gradually with increasing carbonization temperature. On the other hand, the tensile elastic modulus continuously increased, and the outside diameter and volume, resistivity, of the fibers continuously decreased. This decrease in tensile strength has been attributed according to Reynolds and Moreton to the surface flaws originated from the dust particles on the fiber surface by their reactions with the fiber surface itself at these high temperatures. They discovered that, when precursor fibers spun in clean-room conditions were used, the tensile strength of PAN-based carbon fibers was found to increase continuously up to the heat-treatment temperature of 2,500°C. These facts indicate that the major changes took place in the structure of carbon fibers above 1,000°C; i.e., they were transferred into the structure with high elasticity and electric conductivity as carbonization proceeded.

4. Discussion

The weight loss during the carbonization of stabilized pitch fibers at atmospheric pressure commenced at about 300°C and reached the maximum rate at 450—550°C (Fig. 1). The weight loss below 400°C was attributed largely to the physical removal of low molecular weight volatiles. The evolution of gases produced by pyrolysis of the branched chains in the aromatic rings and dehydrogenation and polymerization of aromatic rings occurred only above 400°C as reported in our previous paper. These facts indicate that the major changes took place in the structure of carbon fibers above 1,000°C; i.e., they were transferred into the structure with high elasticity and electric conductivity as carbonization proceeded.

Table 3 Analytical and Physical Data for Oxidized Carbon Fibers, Heat Treated at Various Temperatures

<table>
<thead>
<tr>
<th>Heat treatment temperature [ºC]</th>
<th>Elemental composition [wt%]</th>
<th>Physical properties</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C  H  N  O(diff.)</td>
<td>OD     TS    TE    VR    D</td>
</tr>
<tr>
<td>1,000</td>
<td>98.09 0.68 0.40 0.84</td>
<td>8.7    181    13.3 2.4x10^-3 1.74</td>
</tr>
<tr>
<td>1,500</td>
<td>98.77 0.51 0.23 0.49</td>
<td>8.3    180    17.7 1.5x10^-3 1.98</td>
</tr>
<tr>
<td>1,800</td>
<td>99.15 0.56 0.03 0.26</td>
<td>8.1    218    25.7 1.1x10^-4 1.92</td>
</tr>
<tr>
<td>2,000</td>
<td>99.57 0.51 0.00 0.00</td>
<td>8.5    204    28.1 1.0x10^-4 2.11</td>
</tr>
<tr>
<td>2,300</td>
<td>99.20 0.52 0.06 0.22</td>
<td>7.6    182    40.0 7.1x10^-4 2.06</td>
</tr>
</tbody>
</table>

OD: Outside diameter (µm); TS: Tensile strength (kg/mm²); TE: Tensile elastic modulus (t/mm²); VR: Volume resistivity (Ω·cm); D: Density (g/cm³).

The formation of functional groups on the surface of carbon fibers would be illustrated by Alberts mechanism for oxidation of coal. It is generally thought that the first step during the oxidation of coal is the formation of peroxide by oxidation of aliphatic and olefinic structures in

between pitch-based carbon fibers and PAN or rayon-based carbon fibers. Compared with the PAN or the rayon derived fibers, the precursor of carbon fibers derived from coal tar pitch has numerous molecular components and an extensive range of distribution of molecular weights.

However, the weight loss during heat treatment did not lead to an increase in the specific surface area of stabilized pitch fibers (Fig. 3), because it is considered that the carbon fibers are on a rheological state before they are transformed into infusible hydrocarbon polymers designated as coke, some holes did not remain on the surface of fibers. When the fibers are heated to about 1,000°C, the reactions of carbon—carbon bond cleavage and evaporation of volatile components have already taken place, and the main reactions are the removals of residual hydrogen and some of the substituent heteroatoms as reported in our previous paper. These reactions may lead to the formation of micro pores on the surface of the fibers, since the graphite-like structure has been formed in this stage. By increasing the temperature to 2,300°C, the specific surface area of the fibers decreased slightly. In addition, the outside diameters of carbon fibers are reduced from 8.5 (2,000°C) to 7.6 µm (2,300°C). It may be due to the fact that the crystal structure of carbon fibers generated a shrinkage as observed in the carbonization of carbon fibers derived from PAN. This presumption is supported by such facts, for example, a set of X-ray diffraction data for commercially available pitch-based carbon fibers with different degrees of graphitization obtained by Endo shows that, by raising the degree of graphitization of the fibers (HM50, HM60, HM80), the interlayer spacing, d002, decreased (0.3423, 0.3416, 0.3399 nm), and the crystallite thickness, Lc, increased (13, 15, 18 nm).

The formation of functional groups on the surface of carbon fibers would be illustrated by Alberts mechanism for oxidation of coal. It is generally thought that the first step during the oxidation of coal is the formation of peroxide by oxidation of aliphatic and olefinic structures in
coal, and then the production of phenol by transfer of the oxygen atom to the carbon in the aromatic ring\(^{24}\), as represented in the following schemes:

\[
\begin{align*}
\text{Ar} &= \text{Aromatic ring, } R, R' = \text{Aliphatic or olefinic structure.}
\end{align*}
\]

The phenolic structure can also be further oxidized to a structure with a carbonyl group. From the relative area ratios of chemically shifted species (Fig. 6), it is known that the hydroxyl is the main functional group on the surface of oxidized carbon fibers, and the initial relative area ratio of three oxygen-containing functional groups was hydroxyl (8): carbonyl (1): carboxyl (0.2). This ratio of functional groups is different from that of other fibers treated by nitric acid etc.\(^6\).

On heat-treating, graphitic oxides decomposed at temperatures below 600\(^\circ\)C as shown in Fig. 4. Taking account of the TG curve (Fig. 1) of stabilized pitch fibers, it was considered that part of the oxygen-containing species such as those combined onto aliphatic or olefinic structures on the surface of the fibers were removed by pyrolysis of the side chains in polynuclear aromatic hydrocarbons or by vaporization of the low molecular weight components. However, these oxygen-containing functional groups appeared again when the oxidized carbon fibers were heat-treated up to 1,000\(^\circ\)C. This phenomenon has been attributed to the contaminants in the atmospheric steam. The ratio of the three oxygen-containing functional groups produced by heat-treating at 1,000\(^\circ\)C is 7.6:1.5:1 (hydroxyl: carbonyl: carboxyl), which is different from that produced by oxidation of spun pitch fibers at 310\(^\circ\)C in air. This ratio slightly changed (11.7:2.6:1) when it was heat-treated in the range of temperature up to 2,300\(^\circ\)C. This means that the precursor pitch fibers were in a rheological state, i.e., the conversion of precursor pitch fibers to an infusible hydrocarbon polymer belonged to the liquid phase transfer process, involving an intermediate liquid crystalline state designated as mesophase. The rapid increase in the specific surface area at 800—1,000\(^\circ\)C would mean that the carbon framework close to that of graphite was formed in this range of temperature. Evaporation of light hydrocarbons produced by pyrolysis and polymerization of the stabilized pitch fibers resulted in the formation of some holes on the surface. The small decrease in the specific surface area above 1,000\(^\circ\)C could be attributed to the shrinkage of the crystal structures of carbon fibers.

The surface functional groups produced by surface oxidation of spun pitch fibers decomposed below 600\(^\circ\)C. However, the oxygen-containing functional groups reappeared when the carbonization temperature was raised to 1,000\(^\circ\)C. It was confirmed that surface oxides were produced by the reaction of the fibers with oxygen and/or water, both of which are contaminants of the stream.

5. Conclusions

The thermal behavior, changes of surface properties, and surface functional groups during carbonization of stabilized pitch fibers were investigated. The change in specific surface area with carbonization temperature was classified into three ranges: <300\(^\circ\)C, 800—1,000\(^\circ\)C, and >1,000\(^\circ\)C. The specific surface area was nearly constant below 800\(^\circ\)C although weight losses of fibers were considerable in this range of temperature. At 800—1,000\(^\circ\)C, the specific surface area rapidly increased but it decreased slightly above 1,000\(^\circ\)C. That the specific surface area of stabilized pitch fibers unchanged below 800\(^\circ\)C would mean that the precursor pitch fibers were in a rheological state, i.e., the conversion of precursor pitch fibers to an infusible hydrocarbon polymer belonged to the liquid phase transfer process, involving an intermediate liquid crystalline state designated as mesophase. The rapid increase in the specific surface area at 800—1,000\(^\circ\)C would mean that the carbon framework close to that of graphite was formed in this range of temperature. Evaporation of light hydrocarbons produced by pyrolysis and polymerization of the stabilized pitch fibers resulted in the formation of some holes on the surface. The small decrease in the specific surface area above 1,000\(^\circ\)C could be attributed to the shrinkage of the crystal structures of carbon fibers.

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References

要 旨

ビッチ系炭素繊維のキャラクタリゼーション（第１報）

不融化解ソフーズビッチ繊維の炭化挙動

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コールタールビッチから得られた高性能炭素繊維のプレカーサーである紡糸前後ビッチ繊維を表面不融化解処理し、室温から 2,300℃までのが温度範囲で不活性ガス雰囲気中加熱処理するにあたって、その重量、比表面積および表面酸化物の変化を TGA、BET および XPS を用いて追跡した。ソフーズビッチの紡糸により得られた紡糸後ビッチ繊維の不融化解処理は空気中、310℃で行い、その酸素含有量は紡糸後 1.88 ～ 12.26wt%まで増加した（Table 1）。

不融化解後ビッチ繊維の熱挿動をそれぞれ 1.98 と 12.5℃/分の昇温速度で非等温的に測定した（Fig. 1）。重量損失はともに 400～800℃の温度範囲で起こり、特に 450～550℃の温度範囲で重量の減少速度は最大となった。各温度で熱処理したサンプルの BET 表面積測定をそれぞれ室温および 400℃で排気して測定した結果、800℃までは比表面積がほとんど変化しなかった。800～1,000℃の温度範囲で激しく増加し、1,000℃以降では緩やかに減少していき（Fig. 3）。炭化過程における繊維の機械特性は継続的に変化している。特に炭化が黒鉱化温度に達すると、ビッチ繊維の抗張ミエラスの変化が著しい（Table 3）。これらの結果は、ビッチ系炭素繊維の表面積は炭化反応の進行速度によって起こるものではなく、纖維そのものの構造変化に関わっていることを示唆していた。

不融化解ビッチ繊維の表面酸化物の炭化温度による変化を XPS により追跡する結果、不融化解処理により形成した表面酸化物は 600℃以前に分解されるが、炭化が 1,000℃以上でも、酸化物の特徴ピークが観測された（Fig. 4）。各温度で加熱処理したビッチ繊維をエッチングして XPS を測定したところ、エッチング時間が 2 分に達すると、O-1s/C-1s 比は急激に減少した（Table 2, Fig. 5）。このことから熱処理にあたって、酸化物はおそらく纖維の表面で形成され、それらの表面酸化物は熱処理雰囲気中の不純物である酸素または水分等と炭素繊維の反応により生成したと推定される。

デジタル差分テクニックを利用して得られた XPS スペクトルを解析した結果、ビッチ繊維の表面酸化物は三種類の酸化酸化能基（水酸基、カルボン酸基およびカルボキシル基）に分けられる。これらの表面酸化酸化能基のほとんどは水酸基であり（Figs. 7, 8），それに減圧下温度の上昇につれて速やかに分解された（Fig. 8）。

Keywords
Coal tar pitch, Carbon fiber, Carbonization, Characterization, XPS

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