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SKIN-CORE STRUCTURE IN MESOPHASE PITCH-BASED CARBON FIBERS: CAUSES AND PREVENTION

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Abstract—To prohibit skin-core structure from appearing in mesophase pitch based carbon fiber (CF) with a large diameter (30–50 μm), measures such as decreasing oxidation temperature, prolonging holding time and increasing the oxygen partial pressure in the oxidative atmosphere were taken. EPMA (electron probe X-ray micro-analyzer) was utilized to detect the oxygen content distribution along the diameter of oxidized pitch fiber (OF). The transverse structure of OFs and CFs was observed under a scanning electron microscope (SEM). It was found with certainty that the skin-core structure in CFs is caused by steep oxygen content gradient along the diameter of their OFs. The oxygen distribution in OFs was controlled by the oxidative stabilization conditions. In this work, the CF whose precursor fiber had been oxidized at 240°C in a flow of pure oxygen for 10 hours exhibits no skin-core structure and possesses a high tensile strength. The kinetics of stabilization was also studied. It can be concluded that those factors which increase oxygen diffusion or depress oxidative reaction are effective in overcoming skin-core structure in CFs. © 1998 Elsevier Science Ltd. All rights reserved.

Key Words—A. Carbon fibers, mesophase, B. EPMA, D. Diffusion.

NOMENCLATURE

B	$\sqrt{(\rho_s k)/(D_{\text{eff}})}$
C	concentration of the oxygen in the fiber
C_s	its concentration at the surface
D_{eff}	diffusion coefficient of oxygen within the pitch fiber
E_a	activation energy
k_0	frequency coefficient
k	reaction rate constant
m	density of pitch fiber
r	transverse distance from the center of fibers
r_0	diameter of fibers
R	ideal gas constant
t	reaction time
T	reaction temperature
W_r	oxygen content at point r
ρ_s	active sites/unit volume
ψ	$r_0 B$.

1. INTRODUCTION

Carbon fiber has been drawing more and more attention since it appeared in the 1950s [1–4]. It is a strategic material in manufacture of composites [5]. Large diameter mesophase pitch based CF covered with SIC by chemical vapor deposition (CVD) can be more tightly combined with metals, resulting in excellent composites widely used in airplanes and rockets [6]. As-spun pitch fiber must be thermoset to prevent melting or microstructure changes upon carbonization. Oxidization stabilization, a conventional thermosetting method, is controlled by the

diffusion of oxygen and consequently the rates are exponentially related to the temperature. To avoid fusion and reorientation of mesophase, stabilization should be carried out at temperatures below glass transition temperature of the precursor [7]. However, skin-core structure is prone to appear in thick CFs, resulting from steep gradient oxygen distribution in the transverse section of oxidized fiber—OFs. Kowbel and Don observed the oxygen distribution in the stabilized pitch particles depending upon their stabilization conditions [8]. Mochida reported that blending PVC pitch enhanced the reactivity of the coal tar derived mesophase pitch to shorten the stabilization time significantly and, at the same time, to make the oxygen gradient steeper [9]. The influence of stabilization temperature on oxygen distribution in the mesophase pitch fiber was also studied in previous publications [10,11], showing that higher temperature resulted in steeper oxygen distribution gradient. Using conventional oxidation conditions, no skin-core structure can be introduced into fiber thinner than 10 μm . Singer *et al.* [12] agree with the point that thermosetting process is reaction-controlled rather than diffusion-controlled for small diameter. However, in another of Mochida's publications [13], a skin-core structure was introduced into thin pitch fibers of 10 μm by carrying out the stabilization in a lower oxygen partial pressure flowing gas than air. Therefore, low oxygen partial pressure seems to be a key factor in introducing a skin-core structure in their work; whether a higher oxygen partial pressure

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flow alone is sufficient to prohibit skin-core structure in thick carbon fiber is not known. In this work, thick (40–45 μm) mesophase pitch fiber (PF) was stabilized in a flow of pure oxygen and also at lower temperatures. The electron probe X-ray micro-analyzer (EMPA) was utilized to detect the oxygen distribution in oxidized fiber. Transverse structure of carbon fiber was examined as a function of oxygen distribution in oxidized pitch fiber.

2. EXPERIMENTAL

2.1 Preparing pitch fiber through spinning

Coal tar mesophase pitch, some properties of which are listed in Table 1, was spun into fiber from a steel spinneret ($D=0.3$ mm, $L/D=1$, where L and D mean the length and diameter of the nozzle, respectively) at 350°C by applying pressurized nitrogen (15 atm). The diameter of the fiber was controlled to be 40–45 μm .

2.2 Stabilization

The PFs were oxidized under different conditions of temperature, heating rate, holding time and oxidative atmosphere shown in Table 2.

2.3 Carbonization

All the OFs were carbonized under the same conditions as follows. They were heated up to 1000°C at a heating rate of 3°C/minute with the protection of inert nitrogen gas, held for 1 hour and then cooled down to room temperature naturally.

2.4 Measuring methods and instruments

The tensile strength of carbon fiber was determined by the average of 24 filaments tested on a YG-001 type apparatus. A Hitachi H-600 scanning electronic microscope (SEM) was used to observe the transverse features of OFs and CFs, an EPM-810 EPMA (electron probe X-ray micro-analyzer) to detect the gradient of oxygen content along the diameter direc-

tion and an FT-IR spectrometer to show the functional groups in PF and OFs.

3. RESULTS AND DISCUSSION

3.1 Functional groups and their changing during stabilization

The FT-IR spectra of PF and OFs shown in Fig. 1 identify functional groups in the pitch fibers and how they change during oxidative stabilization. The bands in the 3050–3045 cm^{-1} region in Fig. 1(a) are due to the stretching of unsaturated hydrocarbons. Those at 750 cm^{-1} are ascribed to the out-of-plane bending of aromatic four adjacent hydrogens and suggest the presence of aromatic hydrogen in the PF. Methyl and ethyl groups can be identified in the

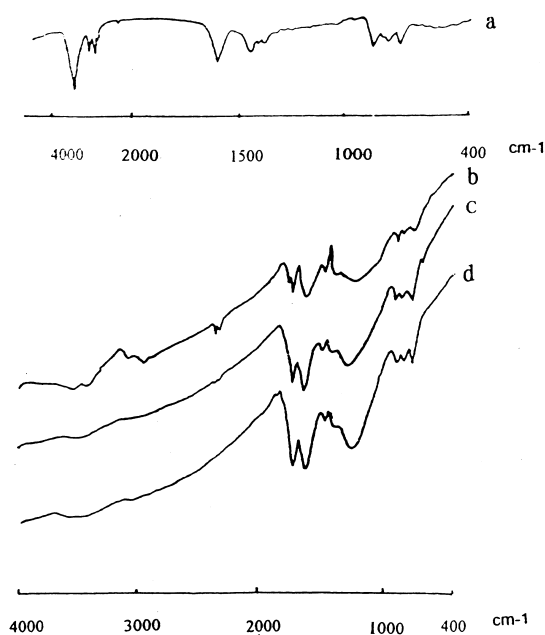


Fig. 1. The FT-IR spectra of PF and OFs: (a) PF; (b) OF1; (c) OF4; and (d) OF5.

Table 1. The properties of the mesophase pitch

Softening point (°C)	C(%)	H(%)	N+S+O(%)	C/H	BI(%)	PI(%)	BI-PS(%)	Anisotropic content (%)
300	94.8	5	0.2	1.58	86.2	44.5	41.7	70

Table 2. Stabilization conditions

No*	Atmosphere	Pressure	Gas velocity (m/s)	Temperature (°C)	Heating rate (°C/min)	Holding time (h)
1	Air	1	0.35	300	2	2
2	Air	1	0.35	300	2	12
3	Air	1	0.35	300	6	2
4	Air	1	0.35	240	2	20
5	Oxygen	1	1.31×10^{-3}	240	2	10
6	Oxygen	1	1.31×10^{-3}	240	2	5

*Carbon fibers and oxidized pitch fibers mentioned following will be named according to the number as CF1 or OF1 etc.

3000–2860 cm^{-1} region from the bands that result from stretching of the saturated hydrocarbons and in the 1440–1370 cm^{-1} region caused by the out-of-plane-bending of saturated aliphatic hydrogen. A little oxygen present in the PF as carbonyl is indicated at 1697 cm^{-1} . Oxidative stabilization generated some oxygen-containing groups with hydrogen gradually disappearing. OF1(b), obtained by oxidizing PF at 300°C for 2 hours in air, possesses more oxygen-containing groups than PF. Having been oxidized at 240°C for 20 hours in air, OF4(c) contains more oxygen and nearly no hydrogen compared with OF1. OF5(d), which had been oxidized at 240°C for 10 hours in a flow of pure oxygen, seems to be oxidized to the same degree and exhibits the same functional groups as OF4, showing that chemical reactions during stabilization in pure oxygen are the same as those in air. Therefore, oxidation in pure oxygen allows lower temperature and shorter holding time, which prevent the formation of skin-core structure in CFs.

3.2 The oxygen distribution along transverse section of OFs

The oxygen distribution along the diameter of OFs was demonstrated in Fig. 2. The numbers along the Y-axis denote the intensity of characteristic X-rays

liberated from oxygen atoms in a unit length along the diameter of fiber, while those on the X-axis denote the location when X-ray scanning from one side to the other along the diameter of fibers. It can be noted the oxygen distributions of OFs are very relevant to the oxidation conditions (Table 2). OF1(a), having been oxidized at 300°C for 2 hours in air, shows a much steeper gradient of oxygen content distribution. The reason for the result might be as follows. Oxidative reaction at high temperature is so quick that a cross-linkage was too soon formed on the surface, making oxygen diffusion much slower than the reaction. Despite the longer oxidation period (12 hours) for OF2(b), the oxygen distribution gradient remained very steep with the average content increasing. Heating rate is another factor, which makes the oxygen distribution steep. OF3(c) had been oxidized at 300°C for 2 hours with a more rapid heating rate of 6°C/minute. The gradient appears steeper than OF1 and the core region of low oxygen content is larger, which means the oxidation cannot be ignored during heating. Depressing the oxidation rate may be an effective method of making the gradient flatter. OF4(d) had been oxidized at a low temperature of 240°C for 20 hours in air, resulting in the distribution gradient of oxygen much flatter than OF1. However, a long holding time is not

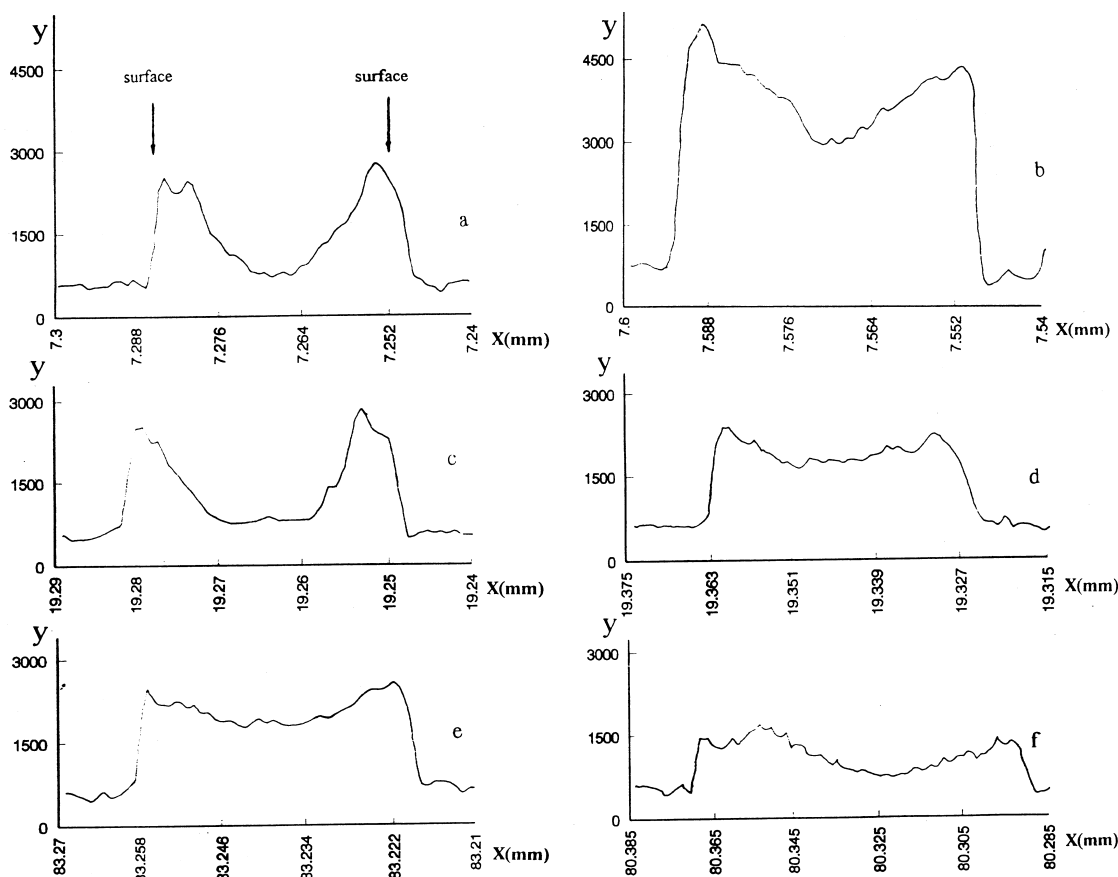


Fig. 2. The EPMA data of OFs: (a) OF1; (b) OF2; (c) OF3; (d) OF4; (e) OF5; and (f) OF6.

economical, so a method was needed by which oxidation was not depressed but oxygen diffusion was enhanced. For this reason, OF5 was oxidized in a flow of pure oxygen at the same temperature as OF4. It can be noticed that although the holding time was shortened to half of that for OF4, the oxygen content shows the same and the oxygen gradient is even flatter than OF4. OF6, also stabilized in the flow of pure oxygen with the holding time of 5h, exhibits an oxygen gradient as flat as OF5, but a low oxygen content. It is worth mentioning that the flow of pure oxygen is much less than that of air (Table 2), so that the oxygen concentration near surface of fibers was lower than that in the flow. If the pure oxygen flowed as fast as the air, the holding time can be reduced more. Therefore, the oxygen partial pressure is a key factor to increase both oxygen diffusion and chemical reaction. Furthermore, skin-core structure in CFs can surely be prevented as long as the oxygen distribution in OFs is flat.

3.3 The structure and properties of OFs and CFs

The morphologies of carbon layer planes in CFs depend on the degree of oxidation. The parts oxidized properly exhibit a fine mosaic texture, while those oxidized insufficiently exhibit a large domain texture because of fusibility. Figure 3 shows the features of OF1 and CFs' transverse structure. OF1(a), because of its very low oxygen content in the core [Fig. 2(a)], exhibits a molten core, resulting in serious skin-core structure in CF1(b). However, extensive oxidation causes significant fiber burn off during carbonization. OF2 having obtained a high average oxygen content with steep gradient [Fig. 2(b)] seems to be oxidized excessively; therefore, the skin of CF2 was burned

off and a crack was generated along the fiber because of shrinkage. Rapid heating rate in the process of stabilization made CF3(d) exhibit a thinner skin and a more molten core than CF1 and a large crack resulted because such a thin skin cannot contain such a large fusible core. Only the CF whose precursor was oxidized properly both at the surface and in the core can possess a fine transverse texture. This can be observed for CF4(e), which shows just a small core, but a thick skin as a result of appropriate oxidation. CF5(f) appears to have an even finer texture than CF4, owing to flatter oxygen content gradient for stabilization in a flow of pure oxygen. So it can be said stabilization in high oxygen partial pressure atmosphere had effectively prohibited skin-core structure. The tensile strength of CFs depends on their structure. From Table 3, it turns out that the finer the transverse structure of a CF, the higher tensile strength the CF possesses.

3.4 The kinetics of oxidative stabilization

The stabilization of pitch fiber is assumed to be achieved through oxidative condensation, oxygation and oxidative dehydrogenation of the pitch components of a highly aromatic nature, which remove their fusibility and maintain their fibrous shape and crystalline oriental alignment along fiber axis.

From the above discussion, it is known that degree of oxidation and distribution of oxygen in oxidized

Table 3. Strength of CFs

CFs	CF1	CF3	CF4	CF5
Tensile strength (MPa)	750	560	920	930

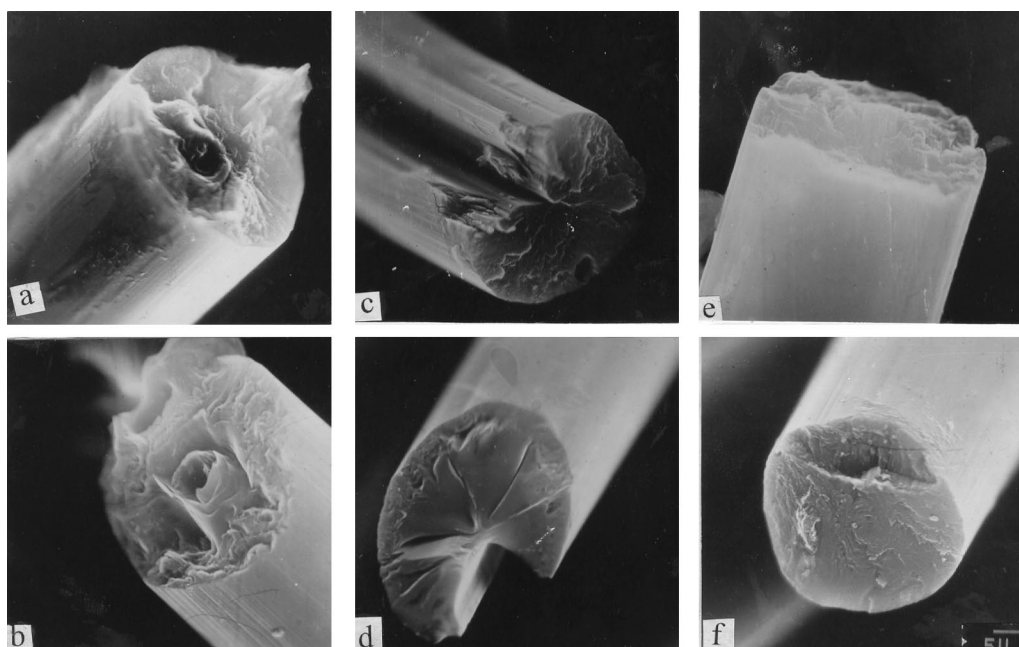


Fig. 3. The transverse structure of OF and CFs: (a) OF1; (b) CF1; (c) CF2; (d) CF3; (e) CF4; and (f) CF5.

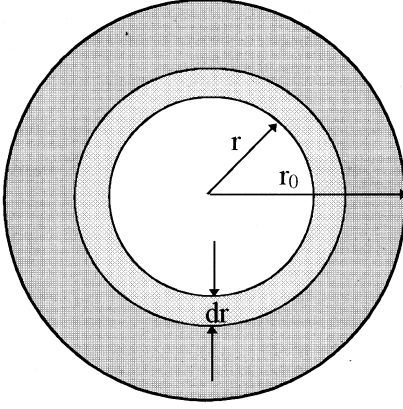


Fig. 4. The schematic drawing of pitch fiber.

pitch fiber are the key factors controlling the structure and properties of carbon fibers. Thus, it is necessary to study how and why oxidative conditions or even the reactivity and the diameter of pitch fiber influence the oxygen distribution. To clarify this problem, we first provide a simplified model considering pitch fiber to be an endless cylinder which exhibits no volume change during stabilization. The diffusion of oxygen is always perpendicular to the fiber axis. Take a coordinate r in this direction and set $r=0$ to denote the center of the fiber and $r=r_0$ the surface.

Let $C=C(r)$ =concentration of the oxygen in the fiber; $C_s=C(r_0)$ =its concentration at the surface; D_{eff} =diffusion coefficient of oxygen within the pitch fiber; ρ_s =active sites/unit volume; and k =reaction rate constant. Taking an element layer with width of dr (Fig. 4), then oxygen entering the element per unit time is:

$$2\pi(r+dr)D_{\text{eff}}\left(\frac{dC}{dr}\right)_{r+dr}, \quad (1)$$

that departing is

$$2\pi r D_{\text{eff}}\left(\frac{dC}{dr}\right)_r, \quad (2)$$

and that consumed is

$$2\pi r dr \rho_s k f(C). \quad (3)$$

Here, $f(C)$ represents a function to oxygen concentration. Considering the function to be of first order, then $f(C)=C$. Making a material balance over an element between the layers $r=r$ and $r=r+dr$, we derive in the usual way:

$$\frac{d^2C}{dr^2} + \frac{1}{r} \frac{dC}{dr} = \frac{\rho_s k}{D_{\text{eff}}} C. \quad (4)$$

Solving this equation in power series and defining $B=\sqrt{(\rho_s k)/(D_{\text{eff}})}$ we get:

$$C = \frac{C_s}{1 + \sum_{n=1}^{\infty} \frac{B^2 r_0^{2n}}{2^2 4^2 6^2 \dots (2n)^2}} \left[1 + \sum_{n=1}^{\infty} \frac{B^2 r_0^{2n}}{2^2 4^2 6^2 \dots (2n)^2} \left(\frac{r}{r_0}\right)^{2n} \right]. \quad (5)$$

The equation can be simplified into the following:

$$C \approx \frac{C_s}{1 + \psi^2/4} \left[1 + \left(\psi \frac{r}{r_0} \right)^2 / 4 \right], \quad (6)$$

in which

$$\psi = r_0 \sqrt{\frac{k \rho_s}{D_{\text{eff}}}}. \quad (7)$$

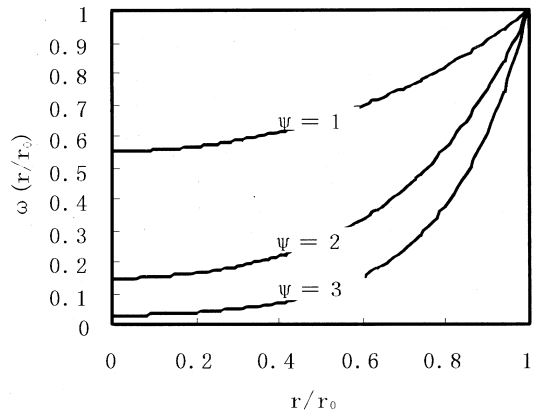
Thus, the oxygen content in $r(W_r)$ is similarly described as follows:

$$W_r = \frac{32}{m} k \rho_s t C_s \bar{\omega} \left(\frac{r}{r_0} \right), \quad (8)$$

in which m =density of pitch fiber, t is the reaction time and

$$\bar{\omega} \left(\frac{r}{r_0} \right) = \frac{1 + \left(\psi \frac{r}{r_0} \right)^2 / 4}{1 + \psi^2/4}. \quad (9)$$

From this equation, we generate Fig. 5, showing that the coefficient $\psi = r_0 \sqrt{(k \rho_s)/(D_{\text{eff}})}$ plays an important role in the oxygen distribution gradient along the transverse section of OFs. The larger the ψ , the steeper the gradient of oxygen distribution. A larger diameter (r_0) means a higher reaction rate constant ($k = k_0 e^{-E_a/RT}$, where k_0 is the frequency coefficient, E_a is the active energy, R is the idea gas constant and T is the reaction temperature); smaller diffusion coefficients D_{eff} and higher reactivity of pitch (ρ_s) produce larger ψ , which makes the oxygen distribution gradient steeper. This is why thick fiber is prone to exhibit a skin-core structure. From eqn (8), we know that to a certain oxygen content (W_r), the holding time decreases as oxygen concentration increases, without enhancing the gradient. Therefore, the fact above can be qualitatively explained according to this model. To reduce the gradient of oxygen content distribution along thick pitch fiber and not to increase the oxidation time, the most important things are to decrease the reaction temperature and enhance the oxygen partial pressure.

Fig. 5. The curves for $\bar{\omega}(r/r_0)$ varying with r/r_0 .

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