JOURNAL OF MATERIALS SCIENCE **34** (1999) 4613–4622

Sublimation and deposition of carbon during internal resistance heating of carbon fibers

H. S. KIM, M. SHIOYA*, A. TAKAKU‡
Department of Organic and Polymeric Materials, Tokyo Institute of Technology, 2-12-1 O-okayama, Meguro-ku, Tokyo 152, Japan
E-mail: mshioya@o.cc.titech.ac.jp

A carbon fiber tow subjected to internal resistance heating often breaks when its surface temperature is raised higher than about 2200 °C. In this study, the cause of the tow breakage was investigated. Internal resistance heating gives rise to a large temperature distribution in the tow cross section, the temperature being at a maximum in the central region of the tow cross section. Because of this temperature distribution, carbon filaments in the tow are sublimated from the central region of the tow cross section, leaving a growing cavity; as a result the tow breaks. Some of the sublimated carbon deposits on the filaments in the low temperature region surrounding the sublimating region, forming a laminar texture around the filament surface. The structure of the deposited carbon was investigated by reflected light microscopy, by scanning electron and transmission electron microscopy, and by electron and wide-angle X-ray diffraction. The deposited carbon was found to be composed of carbon layer stacks with low in-plane stacking regularity.

1. Introduction

Polyacrylonitrile (PAN)- and pitch-based carbon fibers are conventionally produced through the processes of stabilization and carbonization. The stabilization process is a low temperature heat treatment in an oxidative atmosphere to render precursors infusible. The succeeding carbonization process is a high temperature heat treatment in a non-oxidative atmosphere to eliminate non-carbon atoms from oxidized precursors. The carbonization is carried out by using an electric furnace.

A partially carbonized fiber, which is obtained by carbonization at around 1000 °C, has increased electrical conductivity. Thus, it is possible to heat-treat the partially carbonized fiber at a higher temperature by use of the Joule heat generated by passing electric current through the fiber [1]. By internal resistance heating, a high temperature treatment can easily be achieved with a relatively low consumption of electric power. Internal resistance heating has also been applied as a means of heating carbon fibers to deposit pyrolytic carbon on the fiber surface by chemical vapor deposition [2].

With internal resistance heating, carbon fibers can be heated to desired temperatures almost instantaneously, and carbon fibers can be heated and cooled down in a step-wise manner by turning on and off electric current to the fibers. This is advantageous especially for studying kinetics of the carbonization process. That is, the heat treatment at desired temperatures for quite short and long periods can be achieved and the heat treatment times can be varied by several orders [3–5]. The structural development of carbons by heat treatment at high temperature involves a thermally activated kinetic process which depends on both the temperature and the time of heat treatment. It has been reported previously for PAN- and pitch-based carbon fibers that by applying the temperature-time superposition to the changes of resistivity during isothermal heat treatment at various temperatures by internal resistance heating, smooth composite curves of resistivity versus heat-treatment time may be obtained. The temperature-time superposition using the shift factor determined on the superposition of the resistivity has been also applied successfully to construct the composite curves of material parameters, such as the density and the microvoid and crystallite parameters, versus heat-treatment time [6].

With internal resistance heating, it was often experienced that carbon fiber tows broke when elevating their surface temperature to about 2200 °C or higher than that. In order to utilize more widely internal resistance heating as a means of heating carbon fiber tows, the cause of tow breakage at high temperature should be clarified. This paper reports that the tow breakage at high temperature is due to sublimation and thinning of carbon fibers in the central region of tow cross section, given rise to by temperature distribution in the tow. A part of the subliminated carbon is deposited on carbon filaments in the outer region of the tow cross section.

* Author to whom all correspondence should be addressed.
‡ *Present address*: Seitoku University, Sagamidai 531, Matsudo, Chiba 271, Japan.

The structure of the deposited carbon is also studied in this work.

2. Experiments

2.1. Materials

PAN- and coal pitch-based carbon fiber tows processed at about 1250 and 1000 °C at maximum, respectively, were used. The characteristics of these carbon fiber tows are shown in Table I. In this paper, the starting carbon fibers will be called untreated fibers.

2.2. Internal resistance heating

The apparatus used for internal resistance heating is schematically illustrated in Fig. 1. In a Pyrex glass tube, a carbon fiber tow was extended under a tension of 7.8 N in contact with four graphite pulleys of 2 cm in diameter. A pair of inner pulleys 10 cm apart worked as electrodes. A twist of one turn per 5 cm was given to the tow in order to bind closely the filaments in the tow. In the glass tube, nitrogen gas was caused to flow at a rate of 5 l min^{-1}.

Current was applied across the tow between the two electrode pulleys so that the surface temperature of the tow changed according to an appropriate temperature-time profile. The surface temperature of the tow was measured with an infrared radiation thermometer (Minolta IR-630) from the outside of the glass tube. Infrared wavelengths detectable with this thermometer range from 0.8 to 1.1 μm. The infrared transmittance at these wavelengths measured through the glass tube was 0.81. The emissivity of carbon fiber tows was assumed to be 0.9. In determination of the surface temperature, these values of the transmittance and the emissivity were used.

TABLE I Characteristics of carbon fiber tows

Precursor	Pyrolysis temperature (°C)	Number of filaments per tow	Linear density of tow (g m^{-1})	Diameter of filament (μm)
PAN	1250	3000	0.202	6.9
Coal pitch	1000	3000	0.475	10.5

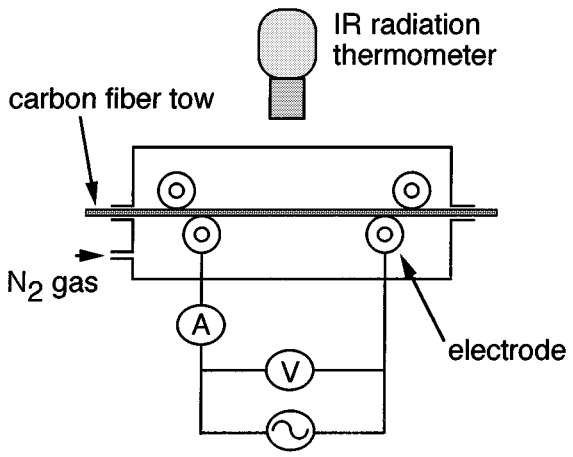

Figure 1 Schematic illustration of apparatus used for heat treatment of carbon fiber tows by internal resistance heating.

The heat treatment of the carbon fiber tows by internal resistance heating was carried out according to the following procedure. First, a current was passed through the tow until the surface temperature reached 600 °C; this temperature was maintained for 30 min for conditioning. Then, the tow was heated up to a desired temperature at a rate of 100 °C min^{-1}. After keeping the tow at this temperature for 1 min, the current was turned off, and the tow was left cooling in the heating apparatus; the surface temperature decreased to room temperature within a few seconds.

2.3. Polarized reflected light microscopy

The cross sections of the tows were examined with a polarized reflected light microscope. In order to keep the tow configuration as was formed during internal resistance heating, the heat-treated tows were carefully removed from the heating apparatus and impregnated in a low viscosity epoxy resin. The stiff strands obtained by curing the impregnated resin were further embedded in an epoxy resin for easy handling, and tow cross sections cut. Any void, if left in the cross sections, was filled with an extra resin. The cross sections were polished using a waterproof abrasive, and coarse and fine alumina powders in order. The cross-section observation was made on a part of the tow situated at the mid point between the two electrodes during internal resistance heating.

2.4. Electron microscopy

The fracture ends of the carbon fibers were gold-sputtered and examined with a scanning electron microscope (SEM).

The ultra-thin sections of carbon deposited on carbon fibers during internal resistance heating was examined with a transmission electron microscope (TEM). Selected area electron diffraction patterns were also made on these thin sections. The thin sections were prepared by cutting with an ultramicrotome the carbon fibers embedded in an epoxy resin.

2.5. Wide-angle X-ray diffraction

The wide-angle X-ray diffraction (WAXD) of the carbon fibers was carried out by using a diffractometer, a position-sensitive proportional counter and Ni-filtered CuK_α radiation. The X-ray specimens were prepared by aligning the fibers in parallel to form a rectangular cross section.

3. Results

3.1. Changes in morphology of tow cross sections

Polarized reflected light micrographs of the cross sections of the pitch-based carbon fiber tows, heat-treated at 2050, 2150, 2250 and 2350 °C by internal resistance heating, are shown in Fig. 2. No marked change can be observed in the cross section of the tow heat-treated at 2050 °C as compared with the untreated tow. However,

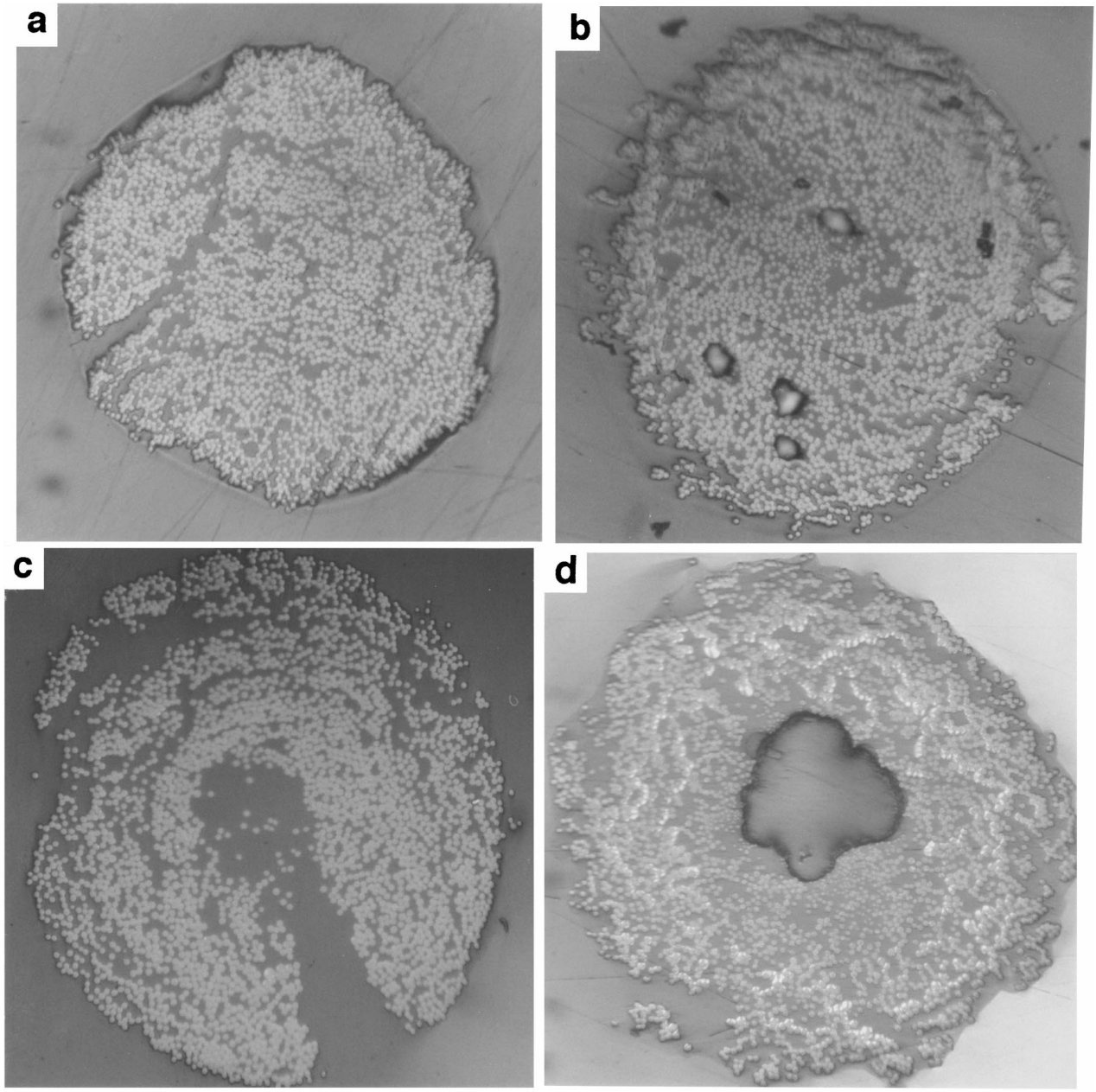

Figure 2 Polarized reflected light micrographs of cross section of pitch-based carbon fiber tow. Heat-treatment temperature: (a) 2050, (b) 2150, (c) 2250 and (d) 2350 °C.

in the tow heat-treated at 2150 °C, filaments smaller in diameter than the untreated ones are observed. At a heat-treatment temperature of 2250 °C, the filaments in the central region of the tow cross section disappear leaving a cavity, and in the vicinity of this cavity, some thinned filaments are observed. At a heat treatment of 2350 °C, the cavity grows larger, and the tow becomes tubular.

In Fig. 3, the cross sections of the PAN-based carbon fiber tows heat-treated at 2050 and 2450 °C by internal resistance heating are shown. A marked cavity is developed in the cross section at 2450 °C, and in the vicinity of the cavity, thinned filaments are found.

Fig. 4 shows a polarized reflected light micrograph of the cross section near the surface of the PAN-based carbon fiber tow heat-treated at 2450 °C. A few filaments thickened several times larger than the original filaments are evident.

For the pitch-based carbon fiber, the changes in tow cross section with internal resistance heating are summarized schematically in Fig. 5. When a tow is heated to a surface temperature higher than about 2050 °C, the carbon filaments locating in the central region of tow cross section become sublimated. A part of the sublimated carbon deposits on filaments in the vicinity of the sublimating filaments. However, the sublimated carbon does not deposit uniformly over the filaments surrounding the sublimating filaments but deposits preferentially on a small number of filaments. With increasing surface temperature, the cross-section region where the sublimation occurs extends toward the tow surface. Simultaneously, the region where the deposition takes place extends toward the tow surface.

It has been often experienced that a carbon fiber tow breaks when heated to a temperature higher than about 2200 °C by internal resistance heating. It can be stated

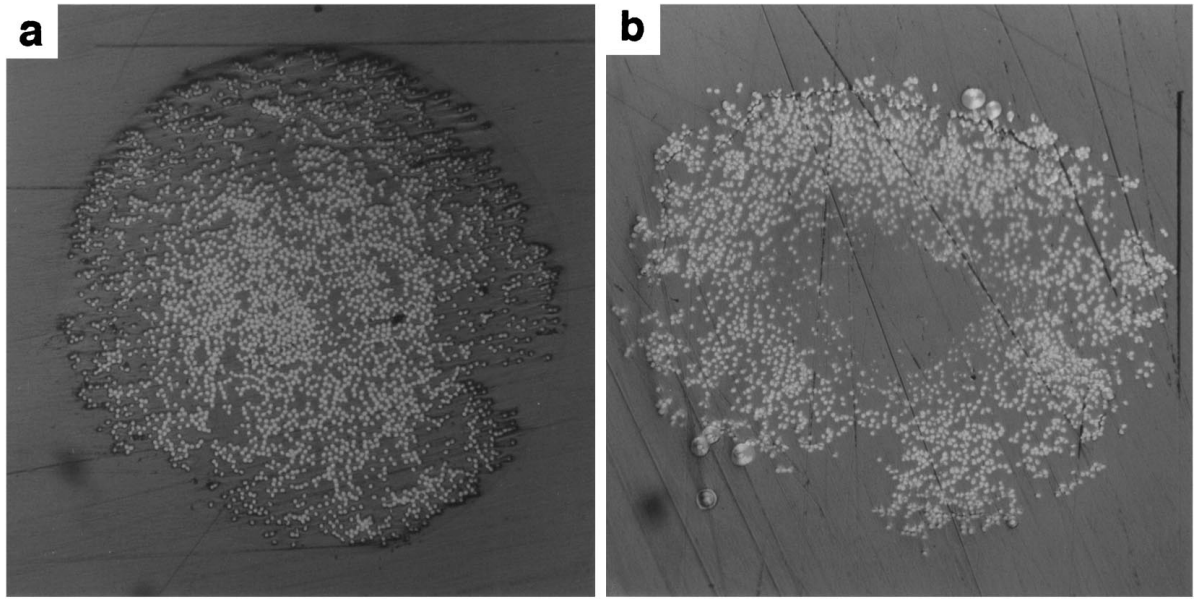

Figure 3 Polarized reflected light micrographs of cross section of PAN-based carbon fiber tow. Heat-treatment temperature: (a) 2050 and (b) 2450 °C.

Figure 4 A polarized reflected light micrograph of cross section near surface of a PAN-based carbon fiber tow heat-treated at 2450 °C.

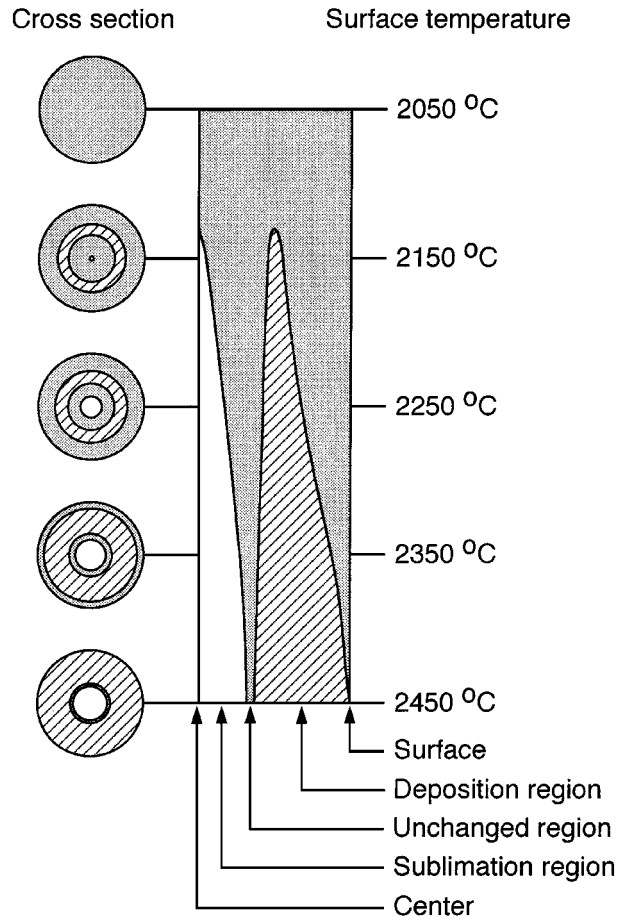

Figure 5 Changes of the sublimation and deposition regions in cross section of pitch-based carbon fiber tow with heat treatment.

that the tow breakage of this type is caused by the sublimation of carbon, beginning with the filaments in the central region of the tow cross section.

3.2. Morphology and structure of deposited carbon

Fig. 6a–e are SEM images of the untreated pitch-based carbon filament and the filaments collected from various parts of the tow heat-treated at 2450 °C. It is found that at the initial stage of the deposition, the sublimated carbon deposits as granular aggregates on the filament surface (Fig. 6b). As the deposition increases in amount, the granular aggregates are piled up and form a laminar texture (Fig. 6c). In the cross section of the deposited carbon, the concentric laminar texture is

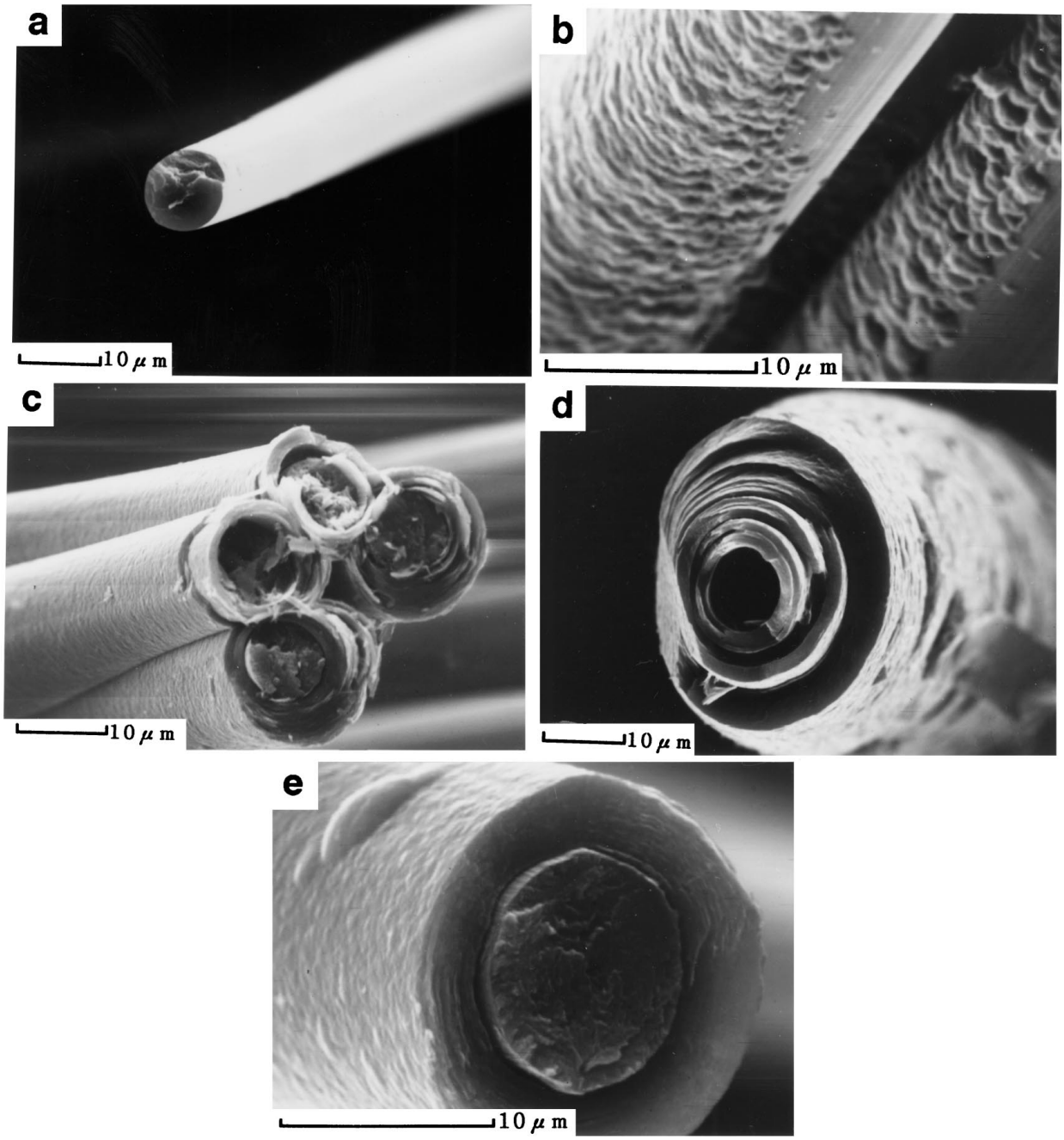

Figure 6 Scanning electron micrographs of pitch-based carbon filaments: (a) untreated and (b–e) heat-treated at 2450 °C.

clearly shown (Fig. 6d). For some filaments, cleavage is observed between the deposited laminar carbon and the substrate filament (Fig. 6e). This cleavage is developed probably in the cooling process of the heat treatment owing to the difference in thermal expansion between the deposited laminar carbon and the substrate filament.

As will be shown later, the deposited carbon comprises the carbon layer stacks similar to those of graphite. The graphite is an optically uniaxial negative crystal [7], and the refractive index of the carbon layer stacks is smaller in the direction normal to the carbon layer plane than in the in-plane direction. Thus the orientation of the stacks in the deposited carbon can be found by examining the birefringence in the cross section of the deposited carbon. In the present work, the birefringence was examined by setting a sensitive color plate having a retardation of 530 nm in a diagonal position between crossed polaroids. Then, if the cross section of the deposited carbon is optically isotropic, the cross section will be seen in the sensitive color, red. If the carbon layer normals are oriented in parallel with the fast direction of the sensitive color plate, i.e. the direction in which the refractive index of the sensitive color plate being smallest, the deposited carbon will be seen in blue. On the other hand, if the carbon layer normals are oriented perpendicularly to the fast direction of the sensitive color plate, the deposited carbon will be seen in yellow.

Fig. 7 shows a micrograph of a typically thickened pitch-based carbon filament; the fast direction of the sensitive color plate being indicated by an arrow. In this figure, the bright (yellow) and the dark (blue) regions in the deposited carbon extend along the radial directions perpendicular to and parallel to the fast direction

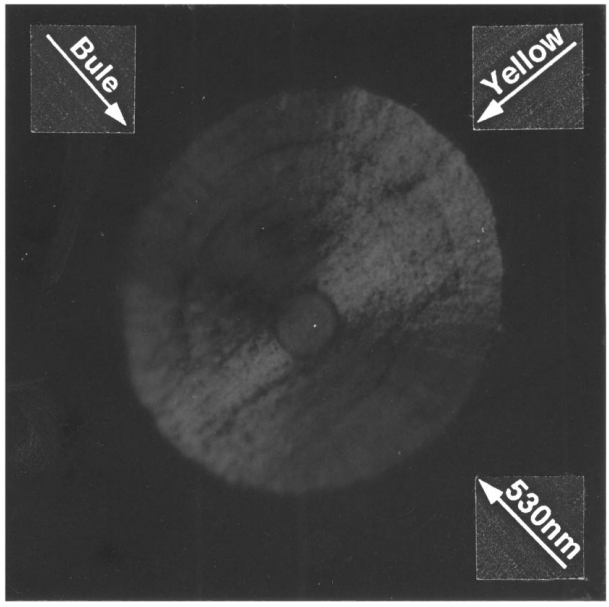

Figure 7 A polarized reflected light micrograph of cross section of a pitch-based carbon filament heat-treated at 2450 °C. The arrow indicates the fast direction of the sensitive color plate.

of the sensitive color plate, respectively. Thus, in the bright and the dark regions, the carbon layer normals are oriented in the radial direction of the thickened filament. The carbon layers are oriented concentric with the filament surface producing onion skin structure.

A bright field TEM image of a thin section, cut perpendicularly to the filament axis from the carbon deposited on the pitch-based carbon fiber at 2450 °C, is shown in Fig. 8a and b. In Fig. 8a, a laminar texture grown around the filament surface is observed. Fig. 9a and b are TEM images of a thin section cut along the filament axis from the outermost area of the carbon deposited on the pitch-based carbon fiber at 2450 °C. In Fig. 9a, a fibrillar texture extending perpendicular to the filament axis is observed.

The insets in Figs 8b and 9b are the selected area electron diffraction patterns. The electron diffraction angles are very small, so that the lattice spacing d can be calculated using the equation,

$$d = \frac{\lambda L}{r} \tag{1}$$

where λ is the wavelength of the incident electron beam, L the camera length and r the distance from the position of the incident electron beam to the diffraction spot on the recording film.

The electron diffraction patterns obtained experimentally and the Miller indices determined by assuming that the deposited carbon has the same structure as graphite are shown schematically in Fig. 10. In Table II, the lattice spacings calculated from the diffraction patterns are compared with those of graphite. Although most of the lattice spacings for the deposited carbon are comparable with those for graphite, the deposited carbon shows a greater value of the (002) spacing than graphite. The deposited carbon does not produce *hkl* diffractions with $l \neq 0$ other than the 00*l* diffractions.

TABLE II Lattice spacings measured from electron diffraction patterns of thin sections of deposited carbon, cut perpendicularly and in parallel to filament axis, in comparison with lattice spacings and Miller indices of graphite

	Lattice spacing (nm)		
Miller index	Graphite	Thin section perpendicular to filament axis	Thin section parallel to filament axis
002	0.335	0.341	0.341
004	0.168	0.170	0.170
006	0.112	0.113	0.113
100	0.213	0.211	0.211
200	0.107	0.104	0.104
110	0.123	0.121	0.121

This indicates that the regularity in the layer-plane direction of the carbon layer stacks is quite low. The material is of a typical 'turbostratic' structure.

In the diffraction pattern of Fig. 8b, the azimuth of the 00*l* diffractions coincides with the radial direction of the filament. This indicates that these diffractions originate from the carbon layer stacks orienting their layer normals toward the radial direction of filament. The azimuth of the 00*l* diffractions in Fig. 9b coincides with the filament-axis direction, and this shows the presence of the stacks orienting their layer normals toward the filament-axis direction.

The *hk*0 diffractions in Figs 8b and 9b appear in circles having arc-like parts at the azimuthal angle corresponding to the tangential direction of the filament surface. The *hk*0 reciprocal lattice image of the turbostratic structure is of a cylindrical shape oriented in the layer-normal direction [8]. Thus, according to the orientation mode of the layer normals, the diffraction pattern represents the following characteristics: (1) when the layer normals are parallel with the incident electron beam, a circular *hk*0 diffraction pattern will appear; (2) when the layer normals are perpendicular to the incident electron beam, a streak-like *hk*0 diffraction pattern elongated to the layer-normal direction will appear; (3) when the layer normals are distributed symmetrically around a certain axis perpendicular to the incident electron beam, the *hk*0 diffraction will show a circular pattern having an intense part on the outer region of the circle at an azimuthal angle corresponding to the direction of the symmetry axis. The *hk*0 diffraction patterns in Figs 8b and 9b correspond to the last case, which indicates the distribution of the layer normals in the plane perpendicular to the tangential direction of the filament surface.

It is stated from the electron diffraction patterns of Figs 8b and 9b, therefore, that the deposited carbon is composed of the carbon layer stacks whose layer normals have the orientation distribution in a plane perpendicular to the tangential direction of the filament surface. It appears that the carbon layer normals oriented in the tangential direction of the filament surface are scarce.

In order to confirm that the existence of the carbon layers whose normals are oriented in the filament-axis direction does not result from the disturbance of the

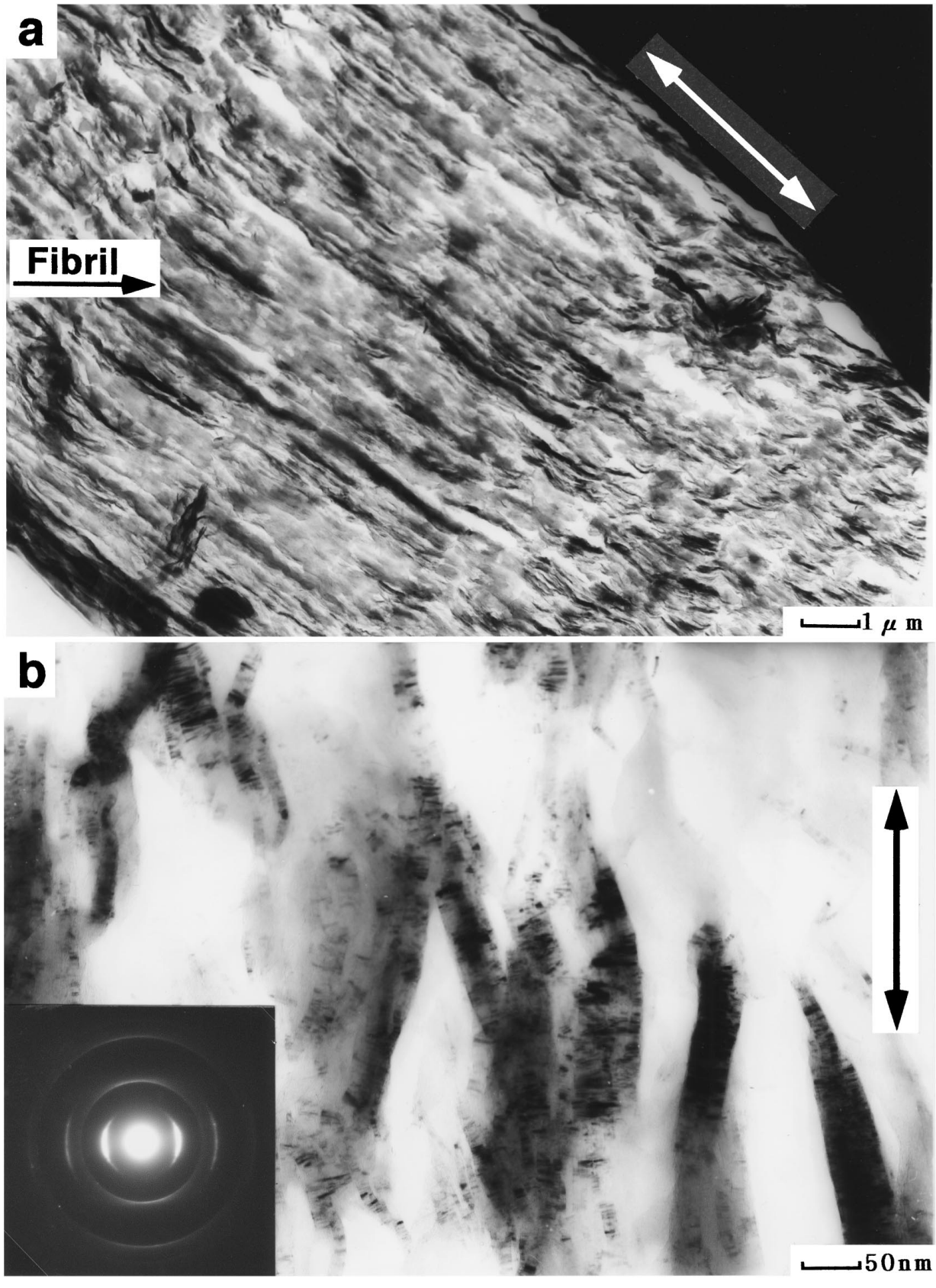

Figure 8 Bright field transmission electron microscopy images of a thin section cut perpendicularly to the filament axis from carbon deposited on a pitch-based carbon filament at 2450 °C. The inset is a selected area electron diffraction pattern. The arrows indicate the tangential direction of filament surface.

layer orientation during the ultra-thin sectioning process for TEM observation, WAXD measurements were carried out on aligned carbon fibers. The meridional WAXD intensity distributions of the untreated pitch-based carbon fiber and the heat-treated ones at 1900 and 2450 °C are shown in Fig. 11. These intensity distributions have been normalized to a constant specimen thickness after giving necessary corrections for X-ray absorption by the specimens and air scattering to as-measured intensity distributions.

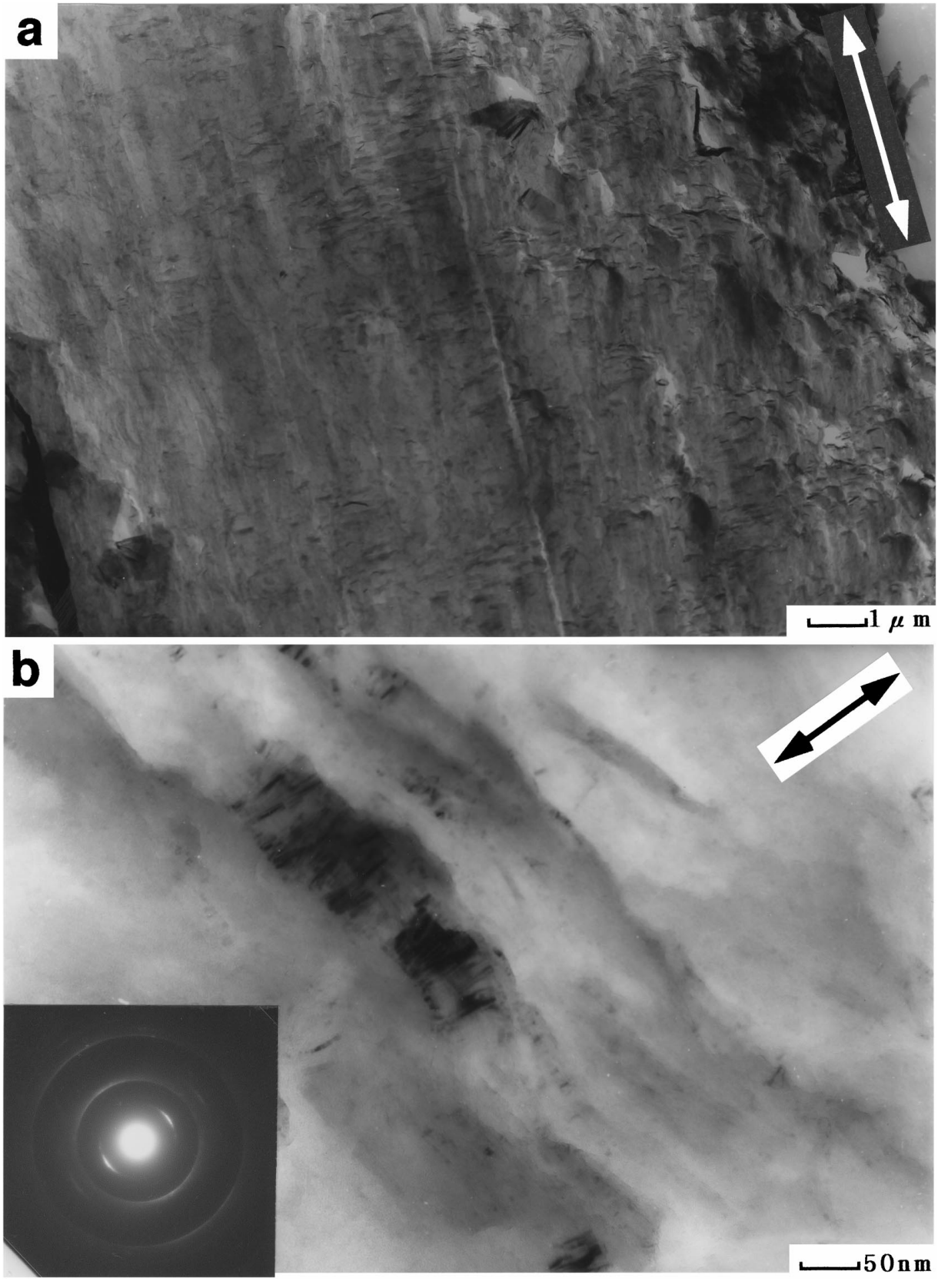

Figure 9 Bright field transmission electron microscopy images of a thin section cut along the filament axis from a part near surface of carbon deposited on a pitch-based carbon filament at 2450 °C. The inset is a selected area electron diffraction pattern. The arrows indicate the filament-axis direction.

The peaks at diffraction angles of about 43° and 78°, observed commonly for the untreated and the heat-treated fibers, are respectively assigned to the 10 and the 11 diffractions. Among the fibers in Fig. 11, the fiber heat-treated at 2450 °C holds the deposited carbon. In the 10 and the 11 diffractions of this fiber, therefore, a certain contribution from the corresponding diffractions of the deposited carbon will be involved. However, the contribution from the deposited carbon is considered to be very small, since the amount of the deposited carbon contained in the heat-treated fiber was only a few percent in volume.

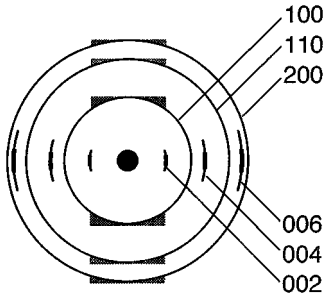

Figure 10 Miller indices of electron diffraction patterns shown in Figs 8b and 9b.

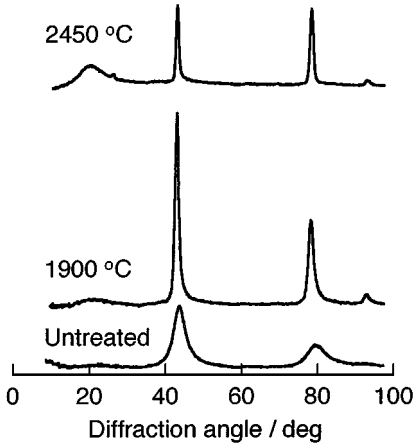

Figure 11 Meridional wide-angle X-ray diffraction intensity distributions of untreated pitch-based carbon fibers and the fibers heat-treated at 1900 and 2450 °C.

In Fig. 11, the carbon fiber heat-treated at 2450 °C shows a broad diffraction composed of the overlap of the diffraction peaks at about 20° and 26°. These diffraction peaks can be attributed to the deposited carbon, since these peaks are not seen for the fiber heat-treated at 1900 °C where the sublimation and deposition of carbon do not occur. The diffraction peak at about 26° is due to the stacks whose layer normals are oriented in the filament-axis direction. These results of the WAXD measurements are consistent with those of the electron diffraction measurements.

4. Discussion

When a carbon fiber tow is heat-treated in a uniform temperature atmosphere such as in heat treatment using a conventional electric furnace, the temperature distribution in the tow cross section will be very small. In the case of internal resistance heating, the heat is evolved by the tow itself and is dissipated from the tow surface via thermal radiation and convection. Hence, a considerable temperature distribution will appear in the tow cross section, and the temperature will be higher in the central region than at the tow surface.

Kikutani *et al.* [4] have considered the temperature distribution produced in the cross section of a carbon fiber tow during internal resistance heating at constant surface temperature, and have shown that when the heat evolution and the thermal conductivity are uniform over the tow cross section, the temperature T at a radial

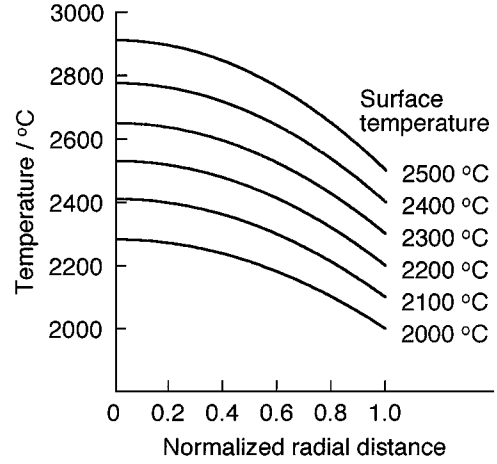

Figure 12 Temperature distributions in cross section of carbon fiber tow at various surface temperatures during internal resistance heating.

distance r in the tow having the radius r_S and the length L is given by

$$T = T_S + \frac{W}{4\pi kL}\left[1 - \left(\frac{r}{r_S}\right)^2\right] \qquad (2)$$

where T_S is the surface temperature of the tow, W the supplied electric power and k the apparent thermal conductivity of the tow. The temperature in the central region of the tow, calculated by Equation 2, gives an intermediate value between two values; one calculated by assuming that the heat evolution is uniform but the thermal conductivity changes along tow radius, and the other calculated by assuming that both the heat evolution and the thermal conductivity change along the tow radius.

Fig. 12 shows the temperature distributions calculated by Equation 2 for surface temperatures from 2050 to 2450 °C. The results of calculation indicate that the temperature at the tow center is higher by 300 to 390 °C than at the surface. The sublimation of carbon fibers becomes evident in the central region of a tow when the surface temperature is raised to about 2100 °C. It is estimated from the results in Fig. 12 that at the surface temperature of 2100 °C, the central region is heated to about 2450 °C. That is, the sublimation of carbon fibers will start occurring from about 2450 °C. With increasing surface temperature, this high temperature region and accordingly the sublimating region extend toward the outer region.

When condensed hexagonal carbon layer fragments, sublimated from the carbon filaments in the high temperature region of the tow cross section, are deposited in a probabilistic manner on a carbon filament in a lower temperature region surrounding the sublimating filaments, the resistance of the filament coated with deposited carbon will decrease. This decreases the heat generation, and thereby decreases the temperature of the filament. That is, these filaments which first start adsorbing the sublimated carbon can adsorb more sublimated carbon as they cool, so that they grow to remarkably thickened filaments as observed in Fig. 4.

In the sublimation process of carbon filaments, the filaments on thinning increase the heat generation and

temperature. That is, once the thinning is started, the thinning will be automatically accelerated. This should contribute to create the prominent cavity observed in the tow cross section.

5. Conclusions

It is found that the breakage of carbon fiber tows during internal resistance heating at high temperatures is caused by the sublimation of carbon filaments. In internal resistance heating, there is a range of temperature through the tow cross section, the temperature being greatest in the center. The sublimation starts occurring at the central region of tow cross section, when the temperature of this region becomes higher than about 2450 °C. A part of the sublimated carbon deposits in a probabilistic manner on a relatively small number of filaments in a lower temperature region surrounding the sublimating region. With increasing heat-treatment temperature, the sublimating region extends toward the outer region in the tow cross section, and simultaneously the deposition region extends toward the outer region.

The sublimated carbon deposits as granular aggregates on the filament surface, and the granular aggregates are piled up forming a laminar texture around the filament surface. The deposited carbon is composed of carbon layer stacks with a relatively low in-plane stacking regularity. The layer normals of the stacks have an orientation distribution in a plane perpendicular to the tangential direction of the filament surface but mostly oriented perpendicularly to the filament surface.

References

1. G. Z. CRANCH and J. S. SHINKO, US Patent no. 1.313.597.
2. D. J. PINCHIN and R. T. WOODHAMS, *J. Mater. Sci.* **9** (1974) 300.
3. K. YAMAMOTO, T. KIKUTANI and A. TAKAKU, *Tanso (Japan)* **146** (1991) 8.
4. *Idem., ibid.* **148** (1991) 142.
5. A. TAKAKU, T. MANGANZI and M. SHIOYA, *ibid.* **163** (1994) 119.
6. *Idem., Carbon* **34** (1996) 1449.
7. R. A. FORREST, H. MARSH and C. CONFORD, in "Chemistry and Physics of Carbon," Vol. 19 (Marcel Dekker, New York, 1984) p. 239.
8. W. RULAND and H. TOMPA, *Acta Cryst.* **A24** (1968) 93.

Received 27 January 1997
and accepted 7 December 1998