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Structure of mesophase pitch-based carbon fibres

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The structure of five samples of commercially available carbon fibres with ultra-high modulus produced from mesophase pitch was studied by the complementary techniques of high resolution electronmicroscopy, X-ray diffraction and transverse magnetoresistance effect. The fibres with high strength and elongation to failure were found to be composed of turbostratic carbon structure, which was different from the three-dimensional graphite structure in ultra-high modulus carbon fibres. Transmission electronmicroscope examination revealed that the mesophase pitch-based fibres with high strength have a basic structure unit with folded sheets arranged nearly parallel to the fibre axis similar to those of high modulus carbon fibres produced from PAN. The present fold structure was suggested to contribute consequently to the lower graphitizability of the fibres and to the strong effects on the fibre strength. By controlling the microstructure, it is expected that the crystallographic as well as the mechanical properties could be improved significantly even from the same kind of precursor materials such as mesophase pitch.

1. Introduction

Carbon fibres are classified in two groups from the precursor materials: those from PAN and those from pitch. The carbon fibres from pitch are further classified into two subgroups: those from isotropic pitch for general use grade and those from mesophase pitch with advanced properties of ultra-high modulus of elasticity, which have been investigated intensively in recent years [1–6] and successfully developed commercially.

Oberlin *et al.* [7–10] have clarified the microtexture and structure of carbon fibres from PAN with the aid of a high-resolution transmission electron microscope (TEM).

The high-modulus PAN-based carbon fibres are composed of stackings of hexagonal net layers of carbon, the microstructure of which has strong effects on the mechanical and electrical properties. Oberlin *et al.* [7–9] have also established a structure model which can provide more quantitative interpretation for their mechanical properties of high strength and high modulus carbon fibres from PAN. For mesophase pitch-based carbon fibres, on the other hand, there has been little discussion of its microstructure [11, 12], but more detailed and comprehensive structural studies have been focused mostly on the manner of macroscopic structural analysis by means of a polarized microscope and scanning electron microscopy [1–5] or toward indirect analysis of crystallographic structure by X-ray diffraction and transport properties such as electrical conductivity. The mesophase pitch-based carbon fibres have a so-called radial, random and onion-type cross-sectional morphology in macroscopic structure. On the other hand, a high degree of graphitizability of the fibres has been shown, whereas PAN-based fibres are non-graphitizable [13].

Not only macroscopic structural analysis but also combined microscopic visual observation of the microtexture as well as a crystallographic structural analysis yield information on the structural sensitive factors which improve the mechanical properties of the mesophase pitch-based carbon fibres.

In the present paper, the microtexture and structure of some commercially available mesophase pitch-based carbon fibres are studied, and the structural factors, on which the mechanical properties of mesophase pitch-based carbon fibres predominantly depend, are discussed. Furthermore, a newly determined microtexture which gives rise to a high performance of the mechanical properties of mesophase pitch-based carbon fibres is demonstrated. Based on the proposed structural model, pitch-based carbon fibres with various advanced properties such as high strength and high elongation, in addition to the ultra-high modulus of elasticity, which has been developed successfully in commercialized mesophase pitch-based carbon fibre, will be expected.

2. Experimental procedure

Test samples of ultra-high modulus carbon fibre (CF) were prepared from Thornel P100 and P120 (commercially available products of AMOCO Performance Products, Inc.) and Carbonic HM50, HM60, and HM80, (Kashima Oil Co.), all of which are from the mesophase pitch, and Torayca M46 (Toray Co.) from PAN with high modulus of elasticity. Some basic physical properties for text samples are given in Table I.

The CFs were examined by the complementary

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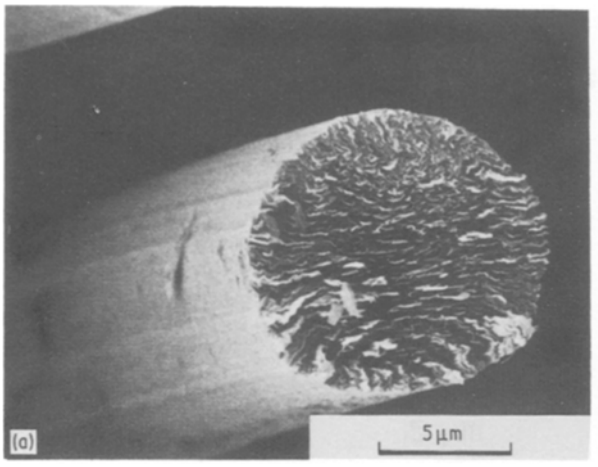

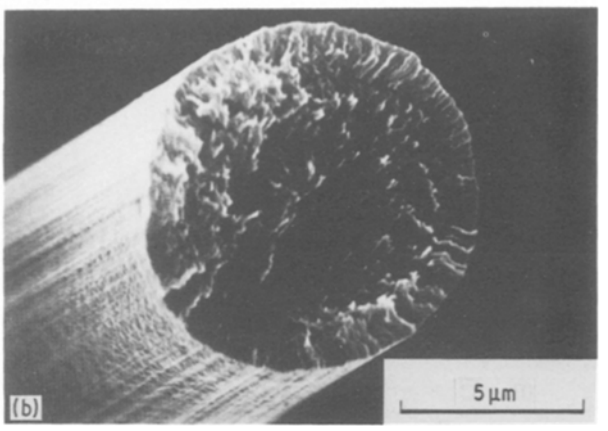

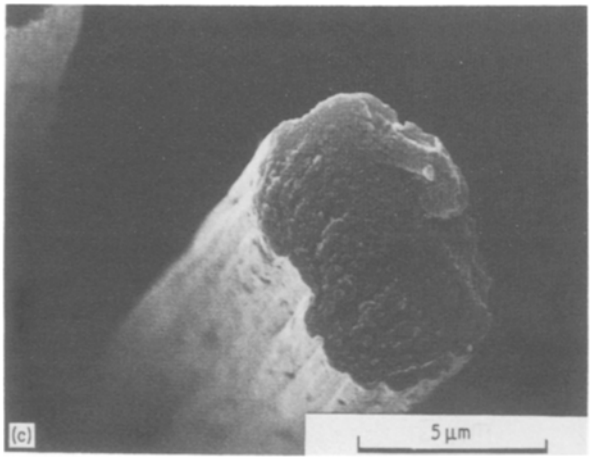

Figure 1 Scanning electron micrographs showing the morphology of the samples used. (a) Thornel P-120, (b) Carbonic HM60, (c) Torayca M46.

means of X-ray diffraction, transmission electron-microscopy (TEM) and transverse magnetoresistance measurements of the fibres. In the X-ray diffraction examination, Cu$K\alpha$ radiation and the powder method were applied to determine the diffraction patterns of 0 0 2, 1 0 0 and 1 1 2 lines. Silicon powders (10 wt %) of X-ray diffraction grade were mixed into the pulverized fibre sample. After the deviation of diffraction angle was compensated, the interlayer spacing, d_{002}, and the crystallite thickness, L_c, were determined from the diffraction peak and half maximum width of 0 0 2 diffraction, which was also calibrated by the 1 1 1 diffraction peak of silicon.

In TEM observation, after embedding the test sample in a suitable resin, it was thinly sectioned using an ultramicrotome fitted with a diamond knife. Transverse and longitudinal thin sections as well as thin fragments formed by gentle grinding in an agate mortar were examined. The sections and fragments were put on the microgrid with carbon film. For thin sectioned samples, evaporation of carbon was carried out.

TABLE I Mechanical properties of various carbon fibres used

Sample name		Tensile strength (GPa)	Tensile modulus (GPa)	Elongation (%)
Thornel	P100	2.2	690	0.3
	P120	2.4	830	0.3
Carbonic	HM50	2.8	490	0.6
	HM60	3.0	590	0.5
	HM80	3.5	790	0.4
Torayca	M46	2.4	450	0.5

TEM observation was made at an acceleration voltage of 350 kV, and the microstructure of the CF was analysed by selected-area electron diffraction (SAD), bright-field observation, 0 0 2 dark-field image (DF image) and (0 0 2) lattice images, in accordance with the method established by Oberlin and Oberlin [10]. In addition, magnetoresistivity was measured, at 77 K, with liquid nitrogen and with a sample of single filament about 1 cm long, for comparable evaluation of the degree of graphitization. By the four-terminal method, passing a direct current of 1 mA under the magnetic field of 0 to 10 kG applied perpendicular to the fibre axis, the transverse magnetoresistivity ($\Delta\varrho/\varrho_0$) of the fibres was obtained. The techniques used for magnetoresistance measurement are the same as reported by Endo *et al.* [14].

3. Results and discussion

3.1. Observation using scanning electron microscopy (SEM)

Fig. 1 shows the SEM observation results of Thornel P120, Carbonic HM60 and Torayca M46. The characteristic bent shape of the orientation of the core structure of Thornel P120 and radial structure of Carbonic HM60 are clearly observed. In the case of Torayca M46 of high-modulus CF from PAN, the macroscopic structure was not clearly observed, beside the non-circular cross-section.

3.2. X-ray diffraction

Fig. 2. shows the X-ray diffraction patterns of the respective as-received CF, and Table II gives the structural parameters obtained from those patterns. Judging from the interlayer spacing, d_{002}, obtained from the

TABLE II Structural parameters determined by X-ray diffraction on various carbon fibres used

Sample name		d_{002} (nm)	L_c (nm)
Thornel	P100	0.3392	24
	P120	0.3378	28
Carbonic	HM50	0.3423	13
	HM60	0.3416	15
	HM80	0.3399	18
Torayca	M46	0.3434	6.2

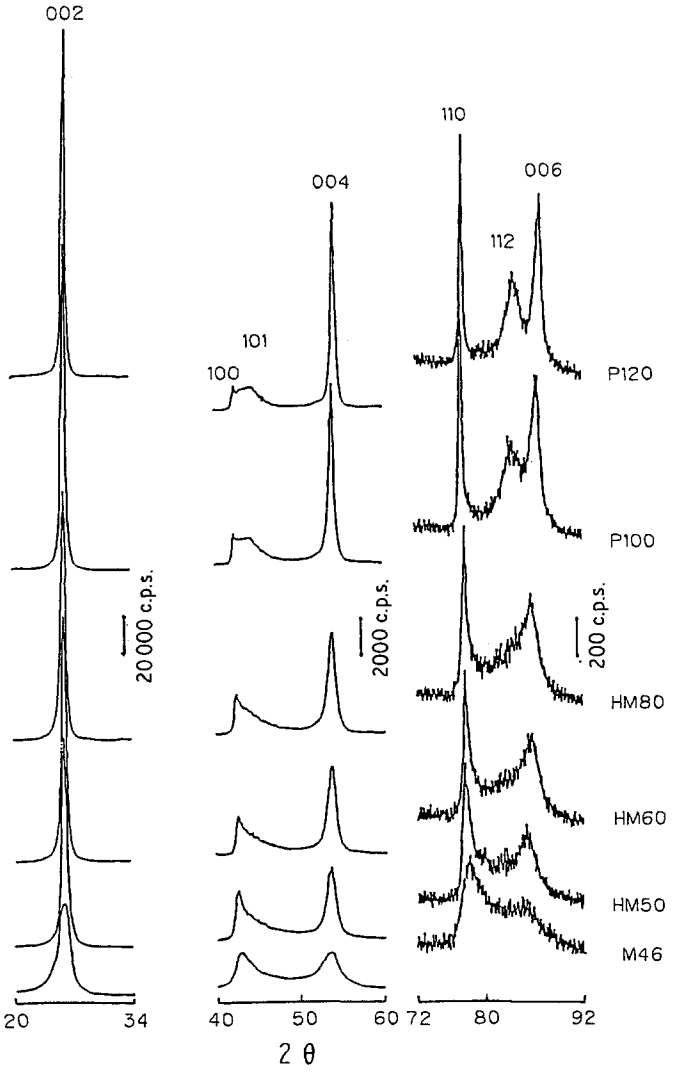

Figure 2 X-ray diffraction pattern showing the 0 0 2, 1 0, 1 1 and 1 1 2 peaks of carbon fibres used.

0 0 2 diffraction line, the degree of graphitization increases sequentially from Torayca to Carbonic to Thornel. Therefore, Carbonic is a CF with an intermediate degree of graphitization between Torayca and Thornel in the performance category of high-modulus carbon fibres.

It should be noted that the crystallite thickness, $L_c(0\,0\,2)$ of Carbonic is about half of those Thornel P100 and P120 even though it is from the same kind of precursor material, and it is 2 to 3 times as large as that of Torayca M46. Namely, Carbonic is meant to be composed of crystallites that are rather thin compared to other CFs produced from mesophase pitch.

The X-ray diffraction pattern shown in Fig. 2 further indicates the different crystal structure between Thornel and Carbonic. The separation of diffraction line 1 0 into two lines of 1 0 0 and 1 0 1 is observed in the diffraction pattern for Thornel P100 and P120. The definite appearance of the diffraction line 1 1 2, which indicates the existence of a three-dimensional stacking order of graphite layers, is also clear in the figure. On the other hand, the observed patterns of Carbonic HM50, HM60 and HM80 consist neither of a separation of line 1 0 to 1 0 0 and 1 0 1, nor line 1 1 2 for three-dimensional diffraction. These results suggest the crystallographic interpretation that Thornels are composed of a graphite-like crystal structure of a comparatively larger size, which has three-dimensional ordering. On the other hand, Carbonics are composed of a turbostratic layer structure, and the crystallite units are comparatively small in size, being recognized as a structure similar to that of the high-modulus CF produced from PAN, as seen in the figure.

3.3. TEM observations

Fig. 3 shows the SAD patterns for Thornel P120 and Carbonic HM60. Both are seen from Fig. 3 to have a conventional structure of CF with a high degree of preferred orientation of carbon layers arranged in parallel to the fibre axis. However, Thornel P120 has a spot-type orientation of 0 0 1 at an average angle of 90° to the fibre axis, though other irregular orientation is rarely found in the shape of 0 0 1 spots. In the case of Carbonic HM60, the 0 0 1 arc indicates a little scattered preferred orientation. The orientation of the hexagonal net plane of carbon to fibre axis has some degree of distortion, about 15°, in comparison to Thornel P120. Therefore, Carbonic is considered to be less oriented than conventional mesophase pitch fibre, and very similar to that of high-modulus PAN-based fibre, a detailed analysis of which have been reported [7–9]. Furthermore, Guigon and Oberlin [7–9] have reported a close correlation between the distortion of layer orientation and the increase of elongation degree of the CF in the case of high modulus CF from PAN. A comparatively larger amount of elongation of

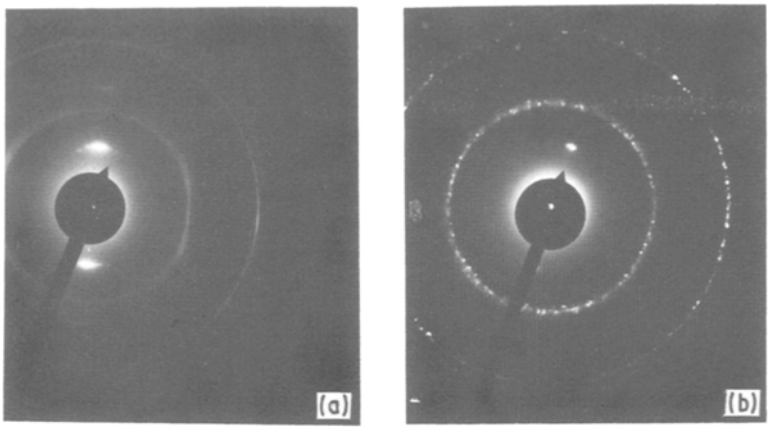

Figure 3 SAD patterns on (a) HM60 and (b) P-120.

Carbonic HM60, 0.5%, is assumed to be similarly caused by the distortion of less preferred orientation even in the mesophase pitch-based CF.

In examination of the SAD pattern for Thornel P120, diffraction line 0 1 was separated into two lines of 1 0 0 and 1 0 1, and line 1 1 2 also appeared. In case of Carbonic HM60, neither separation of line 0 1, nor the appearance of those of the X-ray diffraction pattern as mentioned above, was seen. It may be concluded that Thornel P120 is characterized by a distinct high degree of preferred orientation and a three-dimensional graphitic structure, and Carbonic HM60 is characterized by a carbon-like crystal structure with a turbostratic layer and by a distorted orientation. The respective structure of the carbon fibre is considered to have an effect on the properties of higher modulus of elasticity in Thornel, and larger elongation, in Carbonic. These structures also give rise to the high performance of Thornel in thermal and electrical conductivity.

Dark-field images were observed with an objective aperture of 15 μm diameter. In this case, an aperture was given at about 15° on the 0 0 2 diffraction arc, and crystallites with *c*-axis orientation of about 0° to 8° inclination to the fibre axis were brightened in the image. As shown in Fig. 4, and as demonstrated by Guigon *et al.* [7, 8], 0 0 2 DF image varies, depending on the extent of folding of the basic structure unit. When the basic structure units of fibre layers which compose the fibre are folded parallel to the fibre axis, and an electron beam is given also perpendicular to the fibre axis, crystallites are observed as a bright band where the basal planes lie parallel to the incident beam. Then, by measuring the distance between the bright bands running along the fibre axis, the radius of the fold is estimated. By measuring the thickness of the band, the thickness of the parallel stackings of the carbon layer along the fibre radius is estimated. In other words, the pitch of the bright bands varies depending on the extent of the folded structure of carbon layers. Guigon and Oberlin [8] have proposed a structure model of high-modulus PAN-based carbon fibres after such combined TEM analysis.

By the same methods, Thornel P120 was observed and typical results are shown in Fig. 5a. A few bright bands were observed and with a long pitch, about 30 nm. This indicates that the basic structure units of Thornel P120 are in a plane-like structure. It was also observed that the thickness of the layers was not so homogeneous. In observations of Carbonic HM60, bright bands were found more frequently with a shorter pitch, about 10 nm, and with even thickness in each band, as shown in Fig. 5b. It is indicated that the basic structure units are of a well-folded structure similar to the structure model illustrated in Fig. 4. In other words, a comprehensive structure model for PAN-based high-modulus CF given by Oberlin may be reliably applied to the microtexture of Carbonic, as far as the longitudinal structure is concerned.

Fig. 6a shows the bright-field image of a transverse cross-section of Thornel, indicating a plate-like morphology of stacked carbon layers. On the other hand, as indicated in the 0 0 2 dark-field image, the transverse cross-section of Carbonic (Fig. 6b) is clearly characterized as rather folded stackings of carbon layers. As seen in the lattice image of Fig. 7a, bent 0 0 2 layers are observed.

The lattice fringe along the fibre axis for Carbonic

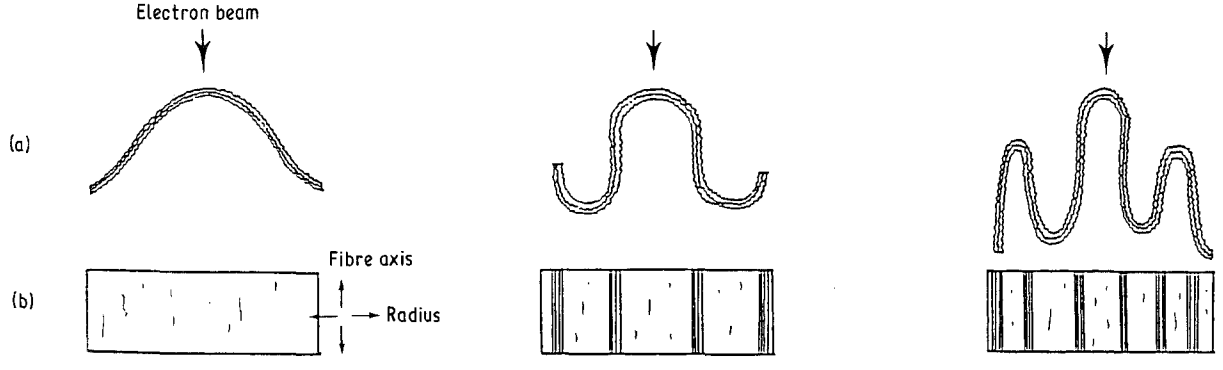

Figure 4 Fold structure model. (a) Profile of basic structure unit. (b) 0 0 2 DF image.

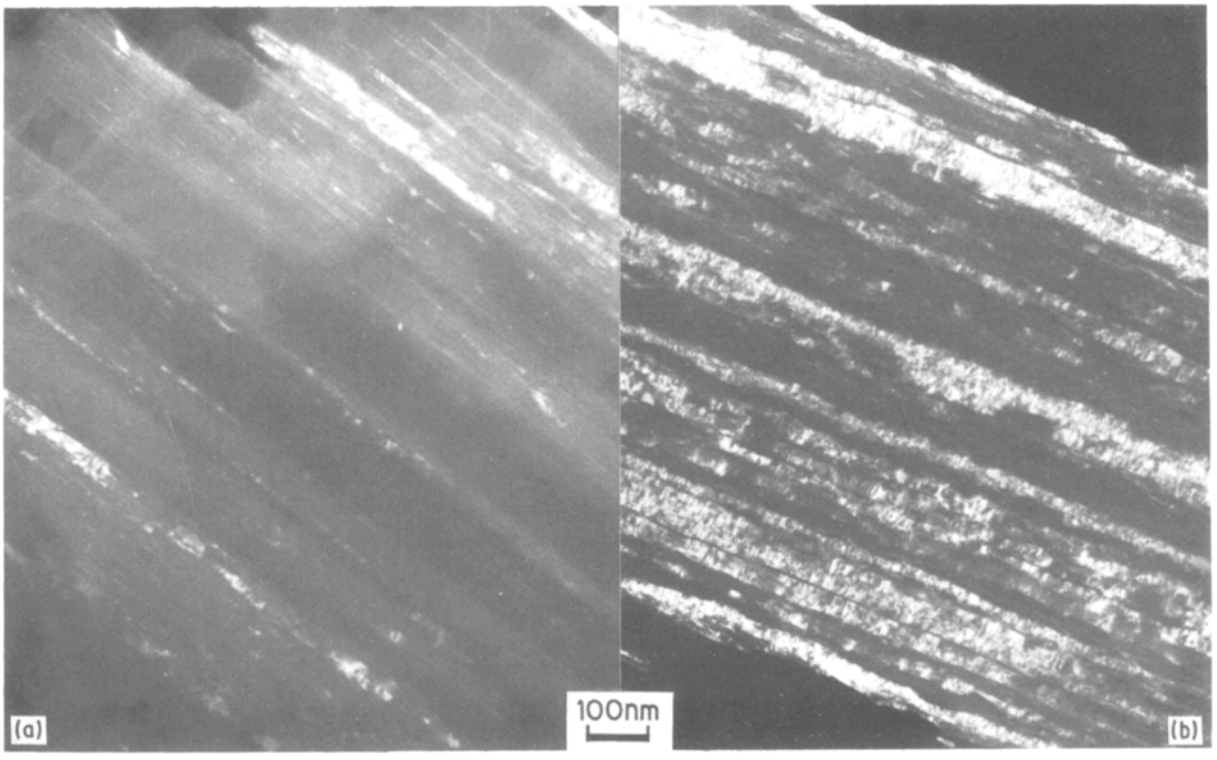

Figure 5 0 0 2 dark-field image on (a) P-120 and (b) HM60.

HM60 is shown in Fig. 7b. It indicates a comparatively long layer with slack folds oriented parallel to the fibre axis.

3.4. Transverse magnetoresistivity

Magnetoresistivity ($\Delta\varrho/\varrho_0$) is a phenomenon of electron transportation, reflecting the energy band structure depending on the graphitization degree of the carbon materials in macroscopic order [14]. When ($\Delta\varrho/\varrho_0$) is positive, under a magnetic field applied parallel to the *c*-axis of the crystallites, the materials are mainly composed of crystallite units with three-dimensional graphitic structure. And when negative, the materials are mainly composed of a turbostratic layer structure [15].

Fig. 8 shows measurements of the magnetoresistivity in relation to a magnetic field, *B*. They are classified in two groups: the positive group for Thornel P100 and

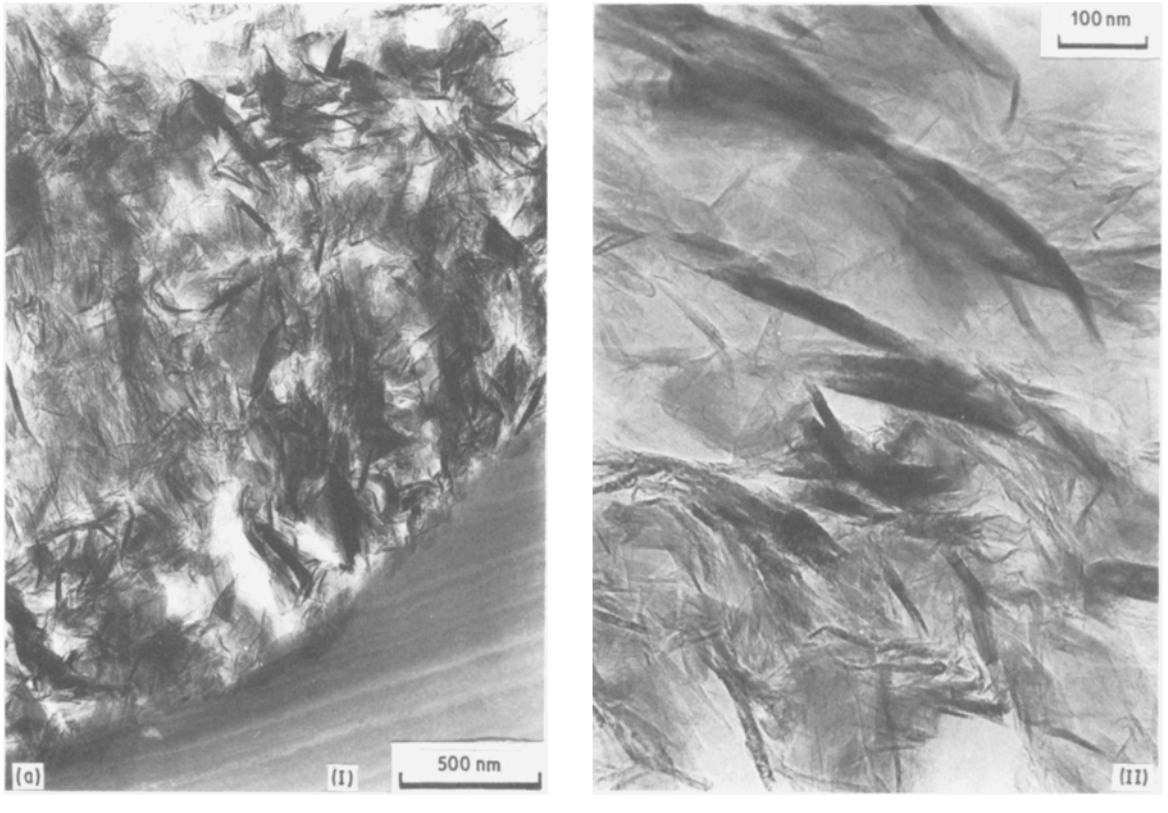

Figure 6 (a) Bright-field images (I; low magnification and II; enlarged view) on (a) cross-section of P-120, (b) cross-section of HM60.

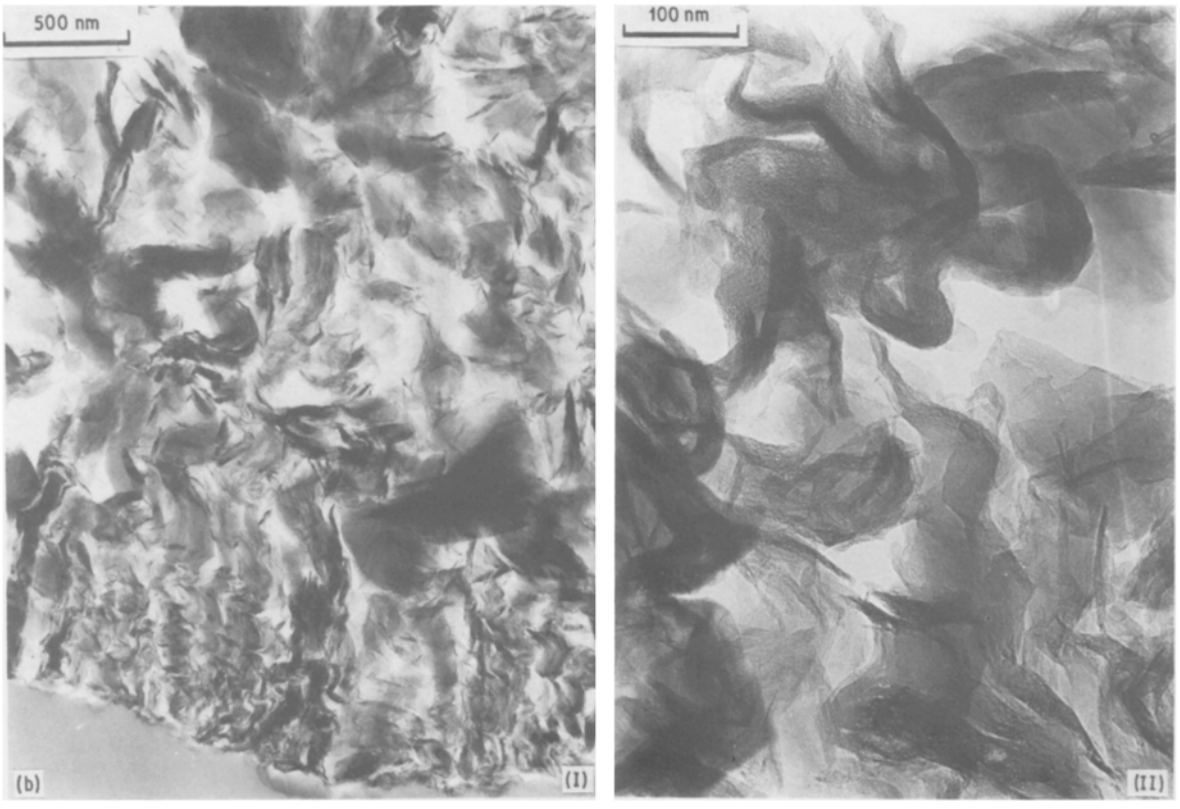

Figure 6 Continued

P120, and the negative group for Carbonic HM50, HM60 and HM80, and for M46. The former is characterized as carbon fibres mainly composed of graphitic structure, and the latter are carbon fibres of turbostratic layer structure. These correspond well with the results of X-ray diffraction and TEM observation as previously described. In the case of Carbonic HM50, HM60 and HM80, and also in P100 and P120, different absolute values of $(\Delta\varrho/\varrho_0)$ reflect the growing stages of the graphitic structure, because they are characterized as having similar preferred orientation of the carbon layers along the fibre axis in each

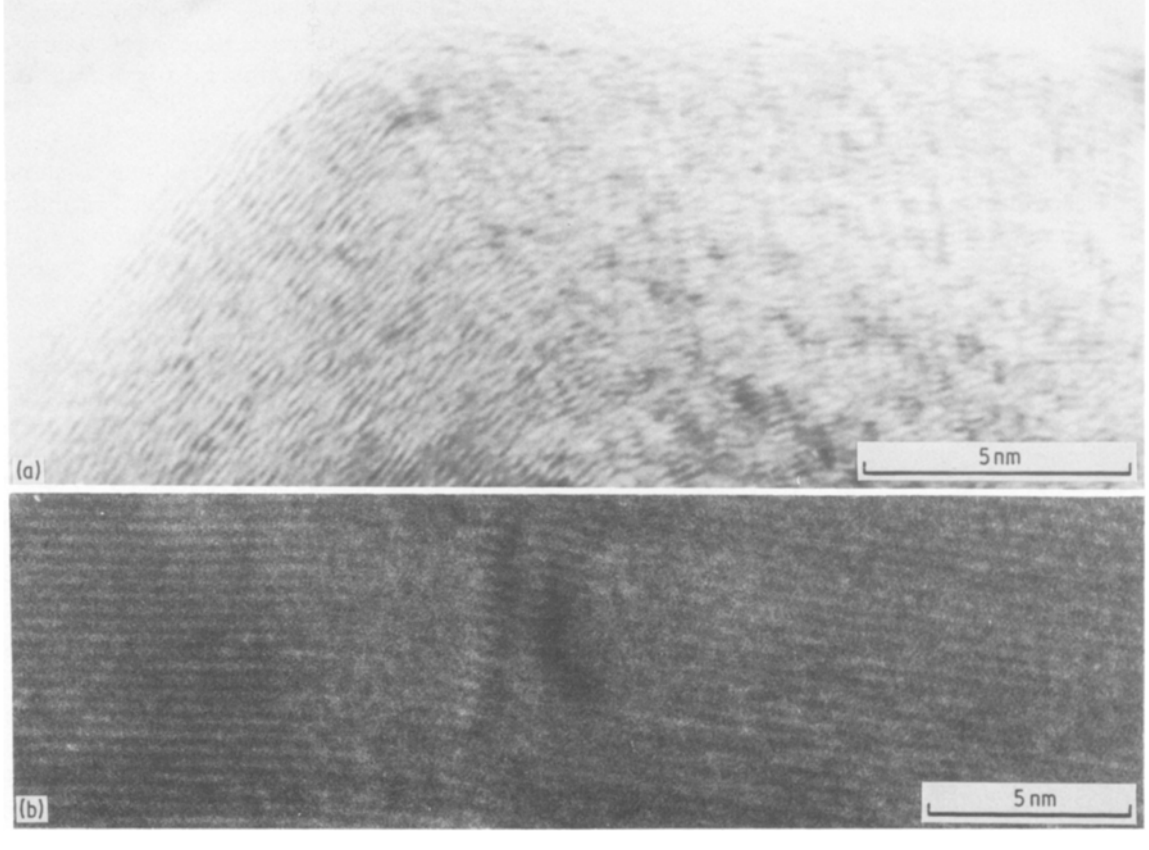

Figure 7 0 0 2 lattice fringes of (a) cross-section and (b) longitudinal section of HM60.

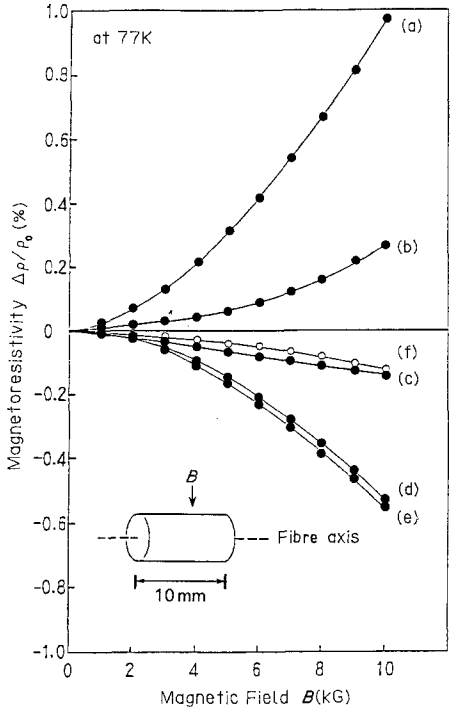

Figure 8 Transverse magnetoresistivity for samples measured at 77 K as a function of magnetic field B. (a) Thornel P-120, (b) Thornel P-100, (c) Carbonic HM80, (d) Carbonic HM50, (e) Carbonic HM60, (f) Torayca M46.

category. It is noteworthy that mesophase pitch-based HM80 and PAN-based M46 have similar $(\Delta\varrho/\varrho_0)$–$B$ characteristics, which indicates the turbostratic structure.

As shown in Fig. 9, after heat treatment at 2850° C in argon atmosphere for 15 min, Carbonic still has a negative value indicating turbostratic structure, even though the absolute values decrease, and this behaviour is similar to that of PAN-based fibres [15].

3.5. Structure–properties relationship

Based on the results described above as a whole, the microtexture and structure model of Thornel and Carbonic are visualized in the form as shown in Fig. 10. Thornel has an oriented core structure with a relatively flat plane in cross-section, and has an extremely well-oriented 0 0 2 plane in the direction of the fibre axis. Therefore, it is a CF with well-developed three-dimensional graphitic structure. Carbonic has a good preferred orientation in the direction of the fibre axis,

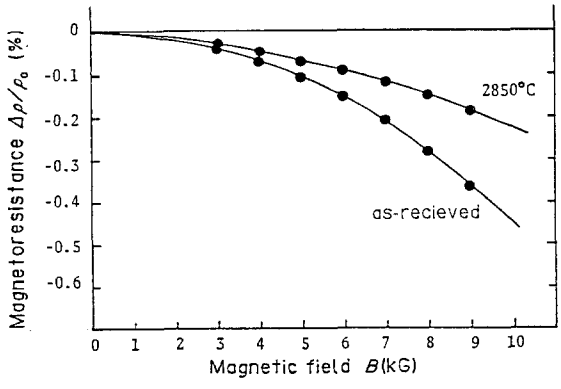

Figure 9 Transverse magnetoresistance measured at 77 K on as-received HM50 and heat treated at 2850° C for 15 min.

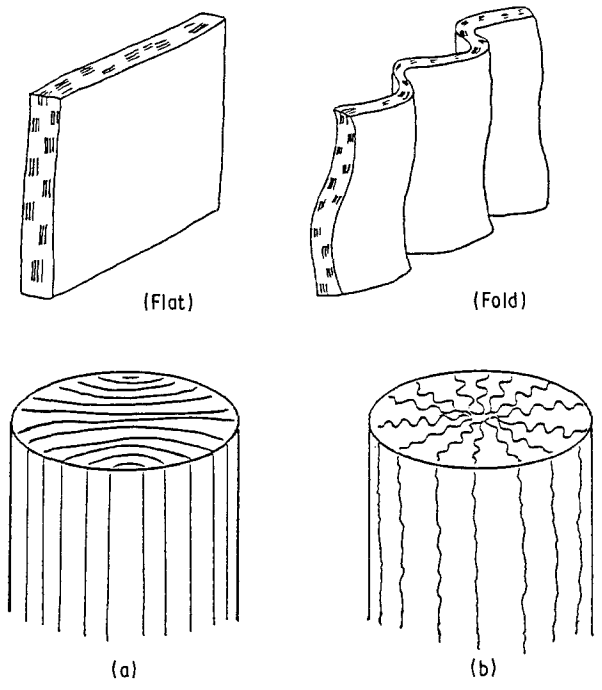

Figure 10 Structure model of mesophase pitch-based carbon fibres, (a) Thornel, (b) Carbonic.

though its orientation is not so sharp as that of Thornel. In cross section, it shows a folded layer structure, which results in keeping the turbostratic layer structure even after the high-temperature process, instead of three dimensional graphitic structure. Because Thornel is composed of a flat basic structure unit, it is assumed to have more shrinkage between the 0 0 2 planes along the c-axis, while graphitization proceeds and to make the interlayer spacing come close to d_{002} of an ideal graphite crystal. On the other hand, as Carbonic has folded carbon sheets, it is somewhat restricted in shrinkage along the c-axis while the graphitization proceeds, resulting in a turbostratic layer structure even after high-temperature heat treatment.

As shown in Table I, Thornel has a larger modulus of elasticity than Carbonic, but Carbonic is about 1.5 times as high as Thornel is in strength. This difference can be analysed from the viewpoint of structure. Modulus of elasticity depends on the orientation along the 0 0 2 plane in the direction of the fibre axis, and it is assumed to be disturbed very little by the limited distortion of orientation in the case of Carbonic. However, there is some difference in strength, the reason for which is supposed to lie in the difference in cross-sectional microtexture. Let us think of a fracture crack starting from a defective part, as shown in Fig. 11. In the case of a fibre with a flat layer structure, the crack propagation speed will be fast. In other words, the resistance to crack propagation could be low. In the case of a fibre with a folded layer structure, the propagation speed of a fractured crack will possibly be disturbed by following a plane after a fold, and the resistance to crack propagation will be increased, resulting in an improved strength of the material. Many microcracks not extending to catastrophic fracture lead to an increased elongation of these fibres. These assumptions coincide, though qualitatively, with the comprehensive structural model proposed by

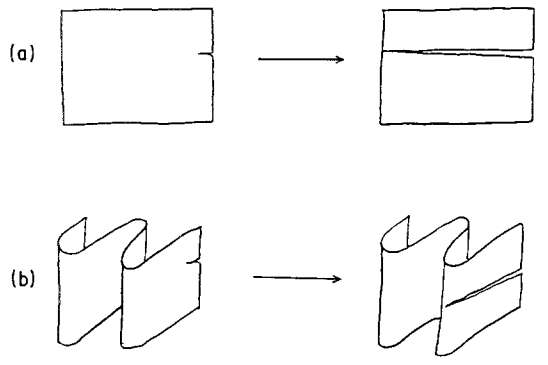

Figure 11 Profile of fracture model for mesophase pitch-based carbon fibre with (a) flat structure unit, and (b) folded structure unit.

Guigon *et al.* [7] for the correlation between strength and the radius of the folds in the case of PAN-based high-modulus CF. On the other hand, because of the high degree of crystallinity of Thornel, they can have a high performance in electron transport properties such as electrical and thermal conductivity of the fibres.

4. Conclusions

The microstructure of carbon fibre produced from mesophase pitch was investigated, and new types of structure were found to contribute to high strength and large elongation, in addition to the high modulus of elasticity. It was suggested that it was effective to produce a controlled folded structure of carbon layers in the cross-section of the fibre to improve the strength and elongation, which is similar to that of high-modulus carbon fibres from PAN. These controlled microtextures restrict the graphitizability of the fibres, and are maintained even in turbostratic structure after high-temperature treatment, though the high degree of graphitizability of mesophase pitch. A highly orientated layer structure in the direction of the fibre axis also contributes to the ultra-high modulus.

However, because the strength of the fibre from mesophase pitch is not high enough (though the structure of the fibre is identified as being improved as demonstrated) in comparison to that of high-strength carbon fibres from PAN, it is expected that future research should be directed towards the highly controlled microtexture to achieve a higher strength comparable to the ultra-high strength PAN-based carbon fibres.

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