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Microstructural inhomogeneity in carbon fibres

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Variations in the layer plane configurations of PAN-based carbon fibres have been studied. The predominant configuration in the surface zones of all fibres is a general circumferential alignment. In highly graphitized fibres, the type of internal structure depends sensitively on fibre thickness. A duplex structure, comprising a core of radially oriented graphite layers and an outer circumferentially aligned zone, is only detected in fibres having diameters of approximately 8 μm. Thicker fibres contain more complex configurations, while thin fibres consist entirely of circumferentially aligned layers. Structural parameters associated with each layer alignment are reported.

1. Introduction

The longitudinal microstructure of PAN-based carbon fibres has been extensively examined [1–3] and a number of parameters have been identified which are important in characterizing the microstructural development induced by a range of heat-treatment temperatures. On the basis of these investigations, a structural model has been developed [4] which envisages extended layers of turbostratic graphite having a preferred orientation parallel to the fibre axis. Regions within which parallel layer growth has occurred, termed crystallites, are delineated by low-angle dislocation boundaries spaced along the layers and by sharp-edged microvoids in the transverse direction.

The effect of graphitizing heat-treatments on the Young's moduli of fibres can be adequately explained in terms of variations in the crystallinity parameters implicit in this model. The corresponding variations in fracture strength are attributed to the development of stress-raising flaws during graphitization and to the effect of pre-existing flaws in the precursor fibre [5]. Inhomogeneity in the configurations of layer planes, leading to delamination within the fibre on cooling from the graphitization temperature, has also been held to be responsible for the relatively poor mechanical strength of highly graphitized fibres [6].

The details of the proposed model are believed to correspond accurately to microstructural features over a scale of up to 1000 Å. However, it is now accepted that microstructural inhomogeneity exists on a larger scale, due to the presence of three co-existing phases [7]. The distributions and relative proportions of these phases in fibres of differing degrees of graphitization are unknown, but the structure is generally described as a duplex structure interspersed with three-dimensionally ordered graphite [8].

The purpose of the present study is (1) to investigate the spatial arrangements of layer planes in the core and sheath zones comprising the duplex structure, and (2) to examine the variations in crystallite size and layer alignments between these zones for a range of fibre conditions.

2. Experimental

Fibres, designated here by their heat-treatment temperatures of 1600 and 2500° C, which induce low and high modulus properties respectively, were purchased from Morganite Modmor Ltd; a fibre batch graphitized at 1900° C was manufactured to collaboration with Weapons Research Establishment, South Australia. Diameters of the fibres, measured by a Watson shearing eyepiece, varied between 6 and 10 μm with an average value of approximately 8 μm. Exceptionally large fibres with diameters up to 40 μm were occasionally found in all the tows.

Two crystallinity parameters were used to characterize variations in the development of graphitization from the interior to the surface of these fibres. The first, the average misorientation of graphitic layer planes with respect to the fibre axis (ϕ), is represented by the angular half-width of the X-ray or electron intensity distribution diffracted into the (0 0 2) reflection. The second, the average crystallite dimension in the c direction (L_c) was measured using the breadth of the diffracted intensity profile. Both parameters were recorded at various depths in the fibre using the following procedure. Single fibres were thinned to a "pencil-point" taper for electron microscope examination using a flame-polishing technique in which the fibre temperature rarely exceeded 1000° C for more than a few seconds [3], mounted on a grid (using conductive paint to minimize distortion due to electrostatic charging) and examined in a Philips E.M. 200 electron microscope. Diffraction patterns from electron-transparent sections were then taken at increasing distances along the taper by re-positioning the selected-area diffraction aperture; the corresponding fibre diameter was also recorded at each position.

Comparative crystallite sizes were determined from the corrected peak width of reflections from the two-dimensional turbostratic lattice, using the relationship [8]

$$L_c = \frac{0.92\lambda}{\beta \cos \theta}$$

where λ is the electron wavelength, β is the half-width of the line and θ is the position of the (0 0 2) peak. No correction for instrumental broadening was made in these experiments, but the effect was minimized by maintaining a constant divergence of the electron beam at the sample. Although this method is unlikely to give correct absolute values of L_c, it should indicate relative changes, e.g. over a fibre length or between different fibres of similar diameter.

Differences in the surface and interior microstructures of fibres were studied using the (0 0 2) diffracted X-ray beam from single fibres. Fibres were mounted in a Philips 57 mm camera modified to operate in a helium atmosphere to reduce scatter; exposures were up to 12 h. Diffracted line profiles were obtained from each fibre before and after an oxidizing treatment in a tube furnace at 700° C which thinned fibres to a minimum diameter of 4 μm. Fibre surfaces were examined in a Cambridge Scanning Electron Microscope.

Aggregate configurations of layer planes in fibre cross-sections were determined using polarized light microscopy. Composite specimens in an epoxy resin matrix were ground on 120 to 600 grit silicon carbide paper and subsequently polished for 24 h on a vibratory polisher, using gamma alumina dispersed in distilled water. This method gave uniform flat surfaces, without fibre relief, which were then examined on a Bausch and Lomb Metallograph.

3. Structural studies

3.1. Electron diffraction

Variations in the layer-plane misorientation parameter (ϕ) and crystallite size (L_c), using values obtained from analysis of the diffracted line profiles and averaged over four fibres from batches heat-treated at 1600, 1900 and 2500° C, are shown in Fig. 1. These fibres were all selected with initial diameters of approximately 8 μm. Attempts to correlate these measurements of crystallite dimensions with those obtained from dark-field transmission micrographs, using the (0 0 2) reflection, were unsuccsssful because of variability in the intensities of the diffracted beams from individual crystallites.

Fig. 1 shows a trend of decreasing values for the layer misorientation parameter, corresponding to increasing alignment with respect to the fibre axis, from the centre to the surface for all fibre types. Crystallite sizes show a trend of decreasing values over the same range whilst both trends are continuous for fibres heat-treated at low graphitization temperatures, a duplex structure becomes more prominent in higher modulus fibres and, in fibres heat-treated at 2500° C, two distinct regions can be distinguished, namely (1) an inner region, or "core", characterized by relatively low axial alignment and large crystallite size, and (2) an outer sleeve, or "sheath", of material of high axial preferred orientation and low average crystallite size. In high modulus fibres, the transition annulus between the two regions is distinct, with a thickness of approximately 1 μm; this annulus separates a core approximately 3 μm in diameter from a sheath approximately 1.5 μm in thickness. For fibres graphitized at lower temperatures, the transition region is wider and less distinct, having a thickness of 2 to 3 μm.

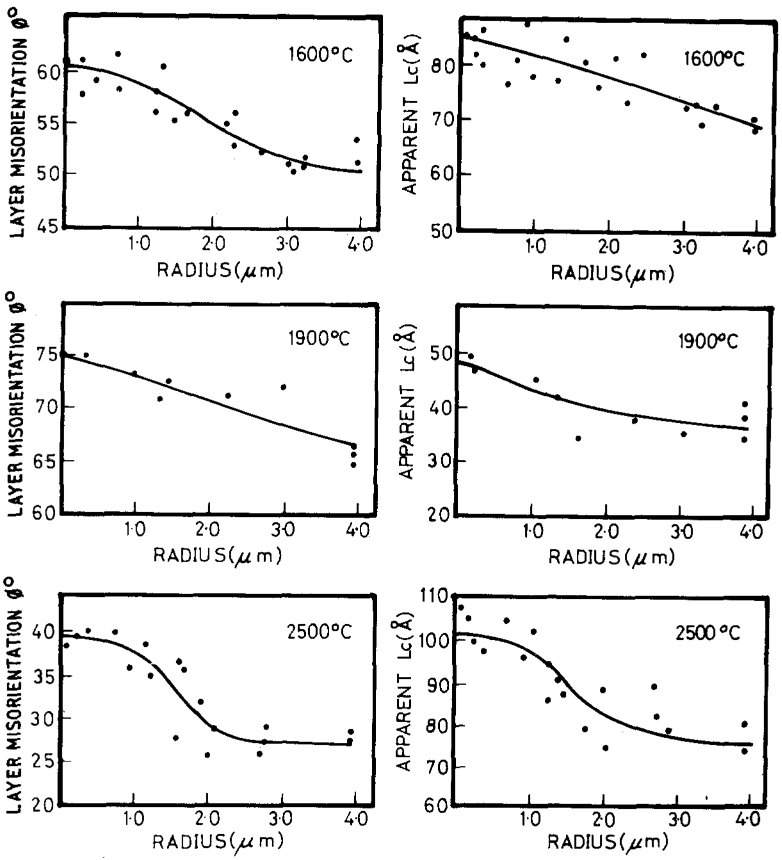

Figure 1 Variations in the misorientation of graphitic layer planes with respect to fibre axis (ϕ) and crystallite size (L_c), as measured by electron diffraction, across fibres heat-treated to different stages of graphitization; the fibres were thinned to taper sections to produce different cross-sections.

The near-surface layers of high-modulus fibres frequently exhibited locally enhanced graphitization, with platelets which appeared to be single crystals of graphite. Platelets of three-dimensionally ordered graphite were also observed in the body of the fibres.

3.2. X-ray diffraction

The penetration of X-rays is such that the diffracted beam from an oriented carbon fibre provides averaged information of crystallinity parameters from the whole volume irradiated. For this reason, diffraction patterns were obtained from single carbon fibres before and after the removal of surface material by oxidation. On the basis of the observed differences in these X-ray patterns and knowledge of the radial variation in substructure, differences in crystallinity between the core and sheath could be determined.

The experimental difficulties inherent in handling and irradiating single carbon fibres, either as-received or thinned, precluded a study of sufficient fibres to provide a statistically representative sample. However, the results do indicate a consistent variation in both orientation of graphite layers and crystallite size with depth in the fibre.

TABLE I The effects of surface removal on measured crystallinity parameters of high modulus fibres. An oxidizing treatment was used to remove the outer layers of each fibre.

	Fibre 1		Fibre 2		Fibre 3	
	As-received	Oxidized	As-received	Oxidized	As-received	Oxidized
Diameter (μm)	7.8	5.3	8.1	7.5	9.4	7.9
Layer misorientation (ϕ)	17	19	20	22	21	22
Crystallite size (L_c)	130	145	100	120	105	115

The results of the diffraction experiments are presented in Table I for three separate high modulus fibres. In each case, the average misalignment of layers along the fibre axis is increased after thinning the fibres, showing that the surface layer is more highly aligned than the remainder of the fibre. Similarly, the averaged crystallite size parameter (L_c) is significantly increased by thinning the fibres (confirming the evidence presented earlier from electron diffraction) which indicates a lower crystallite size in the outer sheath.

Results from X-ray diffraction on as-received single carbon fibres of various diameters heat-treated at 2500° C (Fig. 2) show that the average misalignment of layers (ϕ) is less in thinner fibres. In terms of the core-and-sheath structure, this observation suggests that the sheath constitutes proportionately less of the total fibre volume in larger fibres. This interpretation is consistent with the model derived from the electron diffraction results, which suggests an approximate thickness of 1 to 2 μm for the sheath, independent of graphitization temperature.

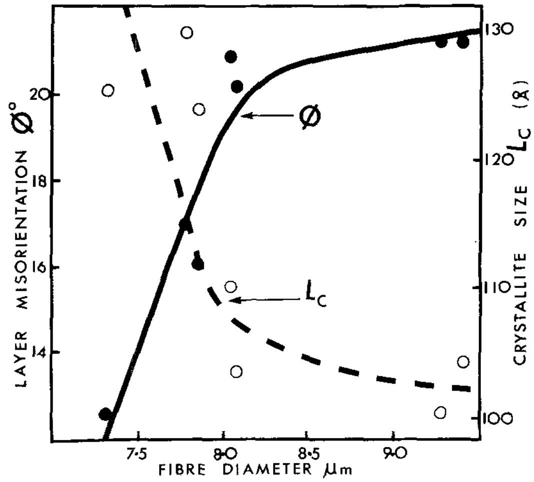

Figure 2 Misorientations of graphitic layer planes with respect to fibre axis (ϕ) and crystallite size (L_c), as measured by X-ray diffraction, averaged over as-received single high modulus fibres of different radii.

The observation of a lower average crystallite size in larger fibres appears inconsistent with the observations (on single fibres) of a larger crystallite size in the core than in the sheath. However, the former observation is believed to be unrepresentative of the gradation in crystallite sizes within a single fibre, since the microstructural conditions which determine crystallite sizes in the cores would probably differ with fibre diameter after the diffusion-controlled oxidation stage of fibre processing.

For fibres graphitized at 1600° C, no significant variation in structure was discernible between thinned and as-received fibres. Average values of layer misorientation and crystallite size, measured in fibres with diameters between 7 and 9 μm, varied by less than 5%, which is within experimental error. It is therefore concluded that microstructural variations within these fibres are relatively minor, with no distinct transition zone as is developed at high graphitizing temperatures.

3.3. Optical microscopy

Because the layer planes of graphite are optically anisotropic, the orientations of aggregates of basal layers within carbon fibres can be determined using polarized light microscopy. Thus, plane-polarized light incident on a fibre cross-section normal to the c direction is reflected as an elliptically polarized beam. When this beam is viewed through crossed nicols, intensity modulations are revealed which are related to large-scale aggregations of basal layers with common orientations. Since extinction occurs when the layer planes are either perpendicular or parallel to the direction of polarization of the incident beam, a tint plate is used to determine the orientation of layers in any particular section.

Three separate spatial configurations of graphitic layer planes were distinguished using this technique: (a) circumferential alignment, in which the c-axes were radially oriented, (b) radial alignment, in which the c-axes were circumferentially oriented, and (c) random alignment, in which no specific c direction was favoured. This last configuration results in macroscopically isotropic optical properties.

Typical micrographs of fibres heat-treated to 2500° C are shown in Fig. 3a. Examination of the symmetrical extinction crosses shows that, for all fibre diameters present in the sample, the predominant structure has circular symmetry. A radial arrangement is, however, discernible in the interior of larger fibres. A diagrammatic representation of layer alignments in designated fibres of different radii is shown in Fig. 3b; the clear areas separating regions of different alignment represent poorly aligned or randomly oriented material. Fibre A (6 μm diameter) consists predominantly of material having a circumferential texture, which

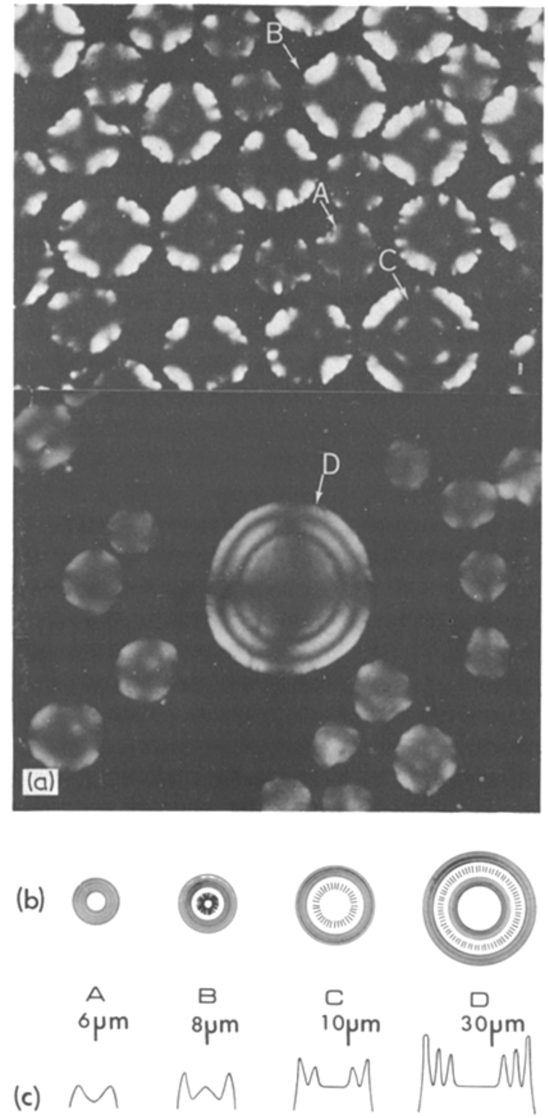

Figure 3 Cross-sections of high modulus fibres: (a) polarized light micrographs showing the effect of fibre diameter on extinction patterns; (b) representations of the layer configuration in the fibres designated in (a); and (c) microdensitometer traces for diametral traverses across the designated fibres in (a).

surrounds a narrow core of relatively poorly aligned layer planes. An outer sleeve of circumferentially aligned layers was common to all fibres, irrespective of thickness. Fibre B (8 μm) contains an interior core of radially textured crystallites separated from the outer sheath by a poorly aligned transition region. In fibre C (10 μm), a large inner annulus of predominantly radial texture surrounds a core of randomly oriented layer planes. Fibre D is an exceptionally large fibre (30 μm) in which three annular zones of texture co-exist, alternately circumferential and radial, with a large inner core in which layer plane alignment is undetectable.

Radial variations in the intensity of optical reflections under crossed polarizers were measured quantitatively using micro-densitometer traces (Fig. 3c). These traces show that the thickness of the outer sheath of circumferentially aligned layers is virtually independent of fibre diameter and hence confirm the existence of the duplex structure suggested by electron and X-ray diffraction. These observations extend the applicability of the proposed duplex structure to the wider range of fibre diameters studied by optical microscopy.

Fibres heat-treated to lower graphitization temperatures show a similar, but less pronounced, texture to high modulus fibres. Extinction patterns from fibres heat-treated at 1600° C are interpreted in terms of a very thin sheath of circumferentially aligned layer planes surrounding a weakly reflecting core which is characterised by a low degree of radial alignment.

Detailed examination of high modulus fibres under crossed polarizers (e.g. Fig. 4) shows that the outer zone is segmented into a number of narrow radial bands. Rotation of the specimen alters the reflected light intensity from the peripheral areas, showing that the visibility of each area depends on the orientation of the specimen with respect to the polarizers. From the manner in which the visibility

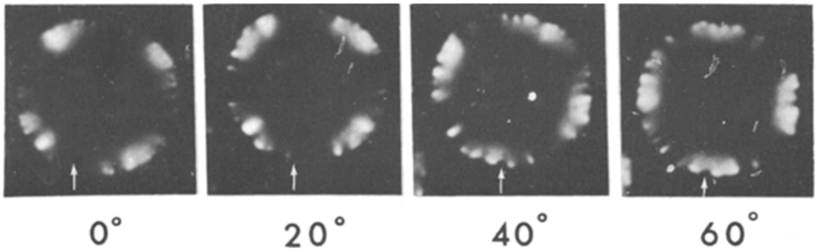

Figure 4 Polarized light micrographs of the cross-section of an 8 μm diameter, high-modulus fibre at different orientations; the angles of rotation about the fibre axis are shown.

of each peripheral area varies with orientation, it is concluded that the outer layers of carbon fibres consist of segmented blocks of layer planes which follow a generally circumferential arrangement. Many of the blocks have dimensions less than 5000 Å. Within this general texture, particular blocks are misaligned with respect to the surrounding structure by as much as 40° (e.g. the arrowed region in Fig. 4).

3.4. Fractography

Fracture surfaces of fibres in composite specimens which have been broken in tension should exhibit topographical features related to variations in the physical properties of the material traversed by the crack front. Thus, fractography should reveal some delineation between zones of different structures, if not the actual configuration of texture of the structures themselves.

Tensile fracture surfaces of low-modulus fibres are essentially featureless (Fig. 5a), indicative of relatively small crystallographic changes along the crack path. However, the morphology of the fracture surface is more complex in fibres heat-treated to higher temperatures (Fig. 5b), in which distinct boundaries separate two areas, of circumferential and radial markings respectively. Presumably, these markings have their origin in the configuration of layer planes in the fibre.

4. Discussion

The existence of a duplex structure in carbon fibres is now generally accepted [8, 9]. The evidence presented here, however, shows that this model is applicable only to highly graphitized fibres with diameters of approximately 8 μm. The structure of these fibres is shown to comprise a sheath of concentrically aligned layers with higher axial alignment and lower crystallite size than the fibre average and a core of layers in a radial configuration with lower axial alignment and larger crystallite size than the fibre average.

The thickness of the outer sheath is apparently constant and independent of fibre thickness, and is separated from the core by a sharp boundary region. The transition between the two structures is less distinct at lower graphitization temperatures where the transition zone occupies a greater proportion of the fibre volume. Fibres heat-treated at 1600° C are essentially homogeneous; only the surface skin shows preference for any particular configuration and only small variations in crystallinity parameters occur across the fibre cross-section. Marked discontinuities in the radial variation of crystallinity parameters, indicative of the development of a duplex structure, appear only in fibres graphitized at temperatures above 1900° C.

The insensitivity of sheath thickness to initial fibre diameter and to high temperature processing

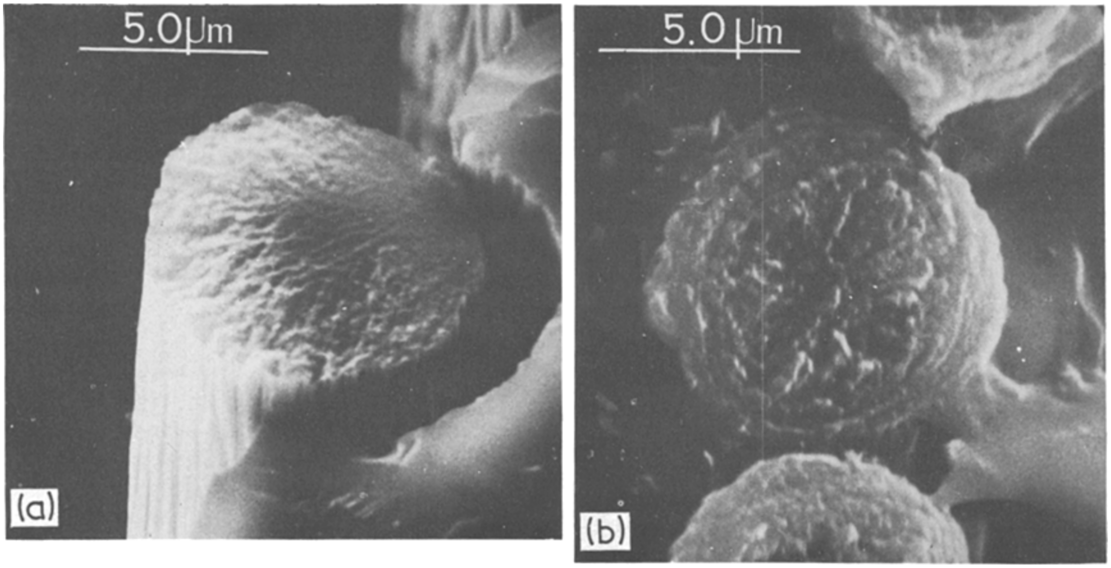

Figure 5 Scanning electron micrographs of fibres in composite specimens which were fractured in tension; (a) a low modulus fibre (b) a high modulus fibre.

suggests that the basis for this microstructural inhomogeneity in carbon fibres is present, in latent form, in low modulus fibres and is pre-determined by the early processing stages. For example, the electron-diffraction measurements (Fig. 1) are consistent with a boundary region between the two micro-structures which, although more diffuse in low modulus fibres, has a depth from the surface of approximately 1.5 μm. This observation is in close agreement with the value of 1.0 μm previously estimated from the diameter-modulus relationship of carbon fibres [9]. Previous studies have shown that the basic development of the sheath-and-core structure in PAN-based fibres occurs during the initial oxidation treatment. The duplex structure observed is thus attributed to the formation of a partially stabilized core and a fully stabilized sheath. The thickness of the sheath is found to be independent of the fibre diameter and unaffected by further graphitizing heat-treatments.

The lower crystallite size in the outer microstructural zone is particularly surprising, in view of the known enhanced growth of crystallites at free surfaces [3]. However, complete graphitization has been observed in the interior of fibres submitted to short periods of oxidation which leave the central zone unoxidized [10]; during subsequent high temperature treatment the core material fuses and a lamellar graphite structure eventually develops. The radial gradation in crystallinity parameters observed here could thus be intermediate between the structure resulting from graphitization of fully stabilized fibres and the formation of three-dimensionally ordered graphite within the core of the fibre. It is possible that the average crystallite size near the surface is reduced because development of circumferentially aligned layer planes in the sheath necessitates severe distortion of the extended layer sheets which comprise the internal structure of the fibres. The driving force for these layer re-alignments is presumably the reduction in surface free energy. During this re-arrangement of layer planes, isolated segments would be expected to retain varying degrees of misalignment, even though a large-scale circumferential configuration is adopted. Such misoriented segments were detected as surface striations by polarized light microscopy; their presence could account for the frequent electron microscope observations of single crystal graphite platelets at the surface of fibres.

The layer plane configurations found in fibres of larger diameter are more difficult to explain. It is suggested that the structure is related both to variations in oxygen concentration with depth during early processing treatments, and to the adoption of minimum free-energy configurations within the fibre. On the basis of the known effect of oxidation on the structure of graphitized fibres, it is reasonable to propose that the thin fibres and the outer layers of thick fibres in the present study represent completely stabilized zones, whereas the interior zones of thick fibres had been effectively exposed to short oxidation treatments. Intermediate depths in the thick fibres and the cores of fibres of average diameter represent zones of partial stabilization.

The tensile properties of fibres heat-treated to different graphitizing temperatures can be related to the different physical characteristics of the core and sheath, due to their different microstructures. For instance, compatibility of strain throughout a fibres is known to be limited by the presence of highly stressed under an applied tensile load than the interior of the fibre. The tensile strength of fibres is known to be limited by the presence of stress-raising flaws, either as pre-existing voids or as randomly oriented platelets of three-dimensionally ordered graphite [5]. Such stress-concentrators should be more effective on the more highly graphitized sheath, since its stored elastic strain energy would be greater than that in the core, assuming that the flaws are distributed between core and sheath. The proposed duplex structure should thus result in a greater reduction in ultimate tensile strength due to stress concentrators than would be the case in a homogeneous fibre. In view of this suggestion, it appears significant that, in this present study, the duplex structure is considerably enhanced by graphitizing temperatures beyond 1600° C – the graphitizing temperature which imparts maximum tensile strength to the fibre.

5. Conclusions

(1) Variations in crystallinity parameters have been recorded across carbon fibre cross-sections. For low modulus fibres, these changes may be summarized as an increase in the axial alignment of layer planes from the fibre centre to the surface, and a corresponding decrease in average crystallite size. In high modulus fibres these variations are more pronounced and, in addition, are separated into two discrete microstructures comprising a sheath and a core.

(2) In thin fibres (8 μm), the spatial orientation of aggregated layer planes is found to be circum-

ferential in the fibre surface structure, but radial in the interior. In larger fibres, the structural morphology is more complex, with the development of a core of isotropic, or randomly aligned, material within the two zones, although the general axial alignment is maintained.

(3) The depth of sheath microstructure in the fibres studied was independent of fibre diameter. It is believed that the basis for microstructural inhomogeneity in carbon fibres originates during the oxidation treatment stage, and is present in latent form in low modulus fibres.

(4) The tensile mechanical properties of carbon fibres are expected to be deleteriously affected by the formation of the duplex, or more complex, structures investigated. Optimum fibre properties could be approached by reducing microstructural inhomogeneity. This can best be achieved in practice by using fibres smaller than 8 μm, or at least by reducing the average fibre diameter within a fibre batch.

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