JOURNAL OF MATERIALS SCIENCE 28 (1993) 6503–6509

Orthogonal structure in mesophase pitch-based carbon fibres

G. H. TAYLOR
Research School of Earth Sciences, Australian National University, GPO Box 4, Canberra 2601, Australia

L. F. CROSS
CSIRO Division of Coal and Energy Technology, PO Box 136, North Ryde, NSW 2113, Australia

Some carbon fibres showed the presence of an orthogonal structure when cross-sections were viewed with light or transmission electron microscopy. This structure was formed from a re-ordering of layer planes as a result of the interaction of mesophase with a stainless steel, square-mesh filter above the spinnerette, using laboratory-scale equipment. Where the mesophase was comparatively viscous the structure persisted and was present in the undrawn and drawn fibre; with mesophase of higher fluidity the orthogonal structure was preserved only in fragmentary or distorted form, or not at all. The structure inferred from these microscopical studies differs from that of an orthogonal pattern previously reported. Fibres spun with a filter appear to have improved mechanical properties, compared to those where no filter was used.

1. Introduction

In the course of examining carbon fibres produced from mesophase pitch on small-scale laboratory equipment, it was observed that there was a remarkably regular orthogonal pattern in some fibres, when viewed in cross-section in polarized light. These initial observations were followed by detailed studies to establish the reason for the formation of this structure in some fibres and the implications of its formation in relation to mechanical properties.

No explicit mention or description of this structural pattern has been found in the normal scientific literature. However, during this study, a patent claim by Hara *et al.* [1] appeared. In this claim, structural features, apparently similar to those observed by the present authors, were reported. However, the basic structure found by the two groups is fundamentally different, as is discussed in more detail below.

2. Experimental procedure

Material studied included a range of coal tar and petroleum pitches, both as isotropic pitch and after conversion (wholly or partly) to mesophase. The most striking patterns were obtained with some of the mesophase pitches prepared from coal tar, and greatest emphasis has been given to these.

The spinning equipment comprised a cylindrical stainless steel vessel with a removable top flange housing the stirrer mechanism; the spinnerette was bolted to the base of the vessel. A stainless steel mesh filter, with 130 μm square openings, could be mounted in the sealing ring groove between the base of the vessel and the cone-shaped opening above the spinnerette orifice. Several spinnerettes with orifice diameters 150–300 μm and length:diameter ratios of 2:1 were used. The pitch was heated by controlled external heating of the vessel, and pitch and spinnerette temperatures were monitored with thermocouples. Pitch was extruded through the spinnerette by pressurizing the head-space of the vessel with nitrogen. Filament draw-down and collection were effected by means of a revolving drum. The spinning conditions, i.e. pitch temperature, extrusion pressure and take-up speed, depended upon the rheological properties of the mesophase and upon the fibre diameter required. Typically, filaments were spun with the pitch temperature in the range 340–380 °C, with nitrogen pressure in the range 70–2800 kPa, and at an uptake rate of 20–100 $\mathrm{m\,min^{-1}}$.

Samples examined included fibres which had been spun and drawn down in the normal way, both in the as-spun condition, and after stabilization and carbonization to 1200 °C. Samples were also taken of fibres which had been drawn down to only a small extent and had diameters of up to 250 μm.

Most microscope studies were carried out using polished surfaces and reflected light microscopy with glycerine or oil immersion objectives. A sample for transmission electron microscopy (TEM) was prepared by sectioning fibres, mounted in epoxy resin, with a diamond knife mounted in an ultramicrotome.

3. Results

An example of highly regular orthogonal structure is shown in the cross-sections of fibres in Fig. 1. The

0022-2461

pattern in each fibre comprises two intersecting sets of lines made visible as a result of absorption of polarized light. The pattern is regular at the centre of the fibre cross-section, becoming less regular and disappearing altogether about half way between the centre of the fibre and its margin. If the microscope stage carrying the specimen is rotated, the pattern for a single fibre changes progressively to give the appearance in Figs 2 and 3. Fig 2a represents a fibre cross-section where the stage position allows the orthogonal pattern to be seen most clearly. Fig. 2b is the appearance of the same fibre when the stage has been rotated by 90°. The appearance in Fig. 2b is similar to that in Fig. 2a with a similar interval, d_1, between the lines in a set. When the stage is rotated to the 45° positions, a somewhat different regular array appears (Fig. 3a and b). The periodicity in the 45° orientation, d_2, is smaller than in the 90° positions. If these two spacings are compared, it is found that for any particular fibre in which the orthogonal pattern is present

$$d_2 = \frac{d_1}{2^{1/2}} \tag{1}$$

If the microscope stage is set at one of the 90° positions (as in Fig. 2a and b) and a lambda (sensitive tint) plate inserted, the appearance is as in Fig. 4. Because the colours generated with this kind of imaging can be interpreted in terms of layer plane

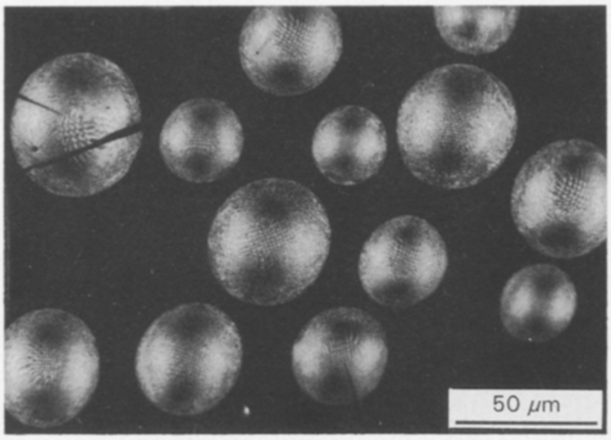

Figure 1 Photomicrograph of polished cross-section of group of fibres spun from coal tar mesophase pitch. The orthogonal pattern is present at the centre of the cross-section of each fibre. Incident polarized light, oil immersion objective.

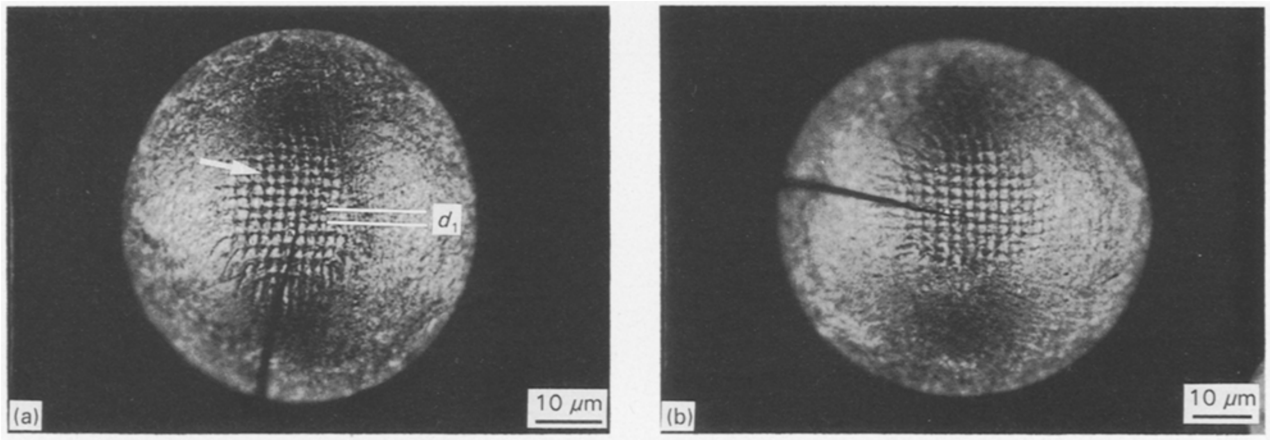

Figure 2 (a) Photomicrograph of fibre section. Two sets of parallel lines occur at right angles to one another; the spacing between lines, d_1, is about 3 μm. Some loop structures are just visible (one arrowed) at intersections. The dark areas above and below the orthogonal pattern result from absorption of polarized light and are indicative of radial structure in this outer section of the fibre. Incident polarized light, oil immersion objective. (b) Same field as in (a), stage rotated 90°.

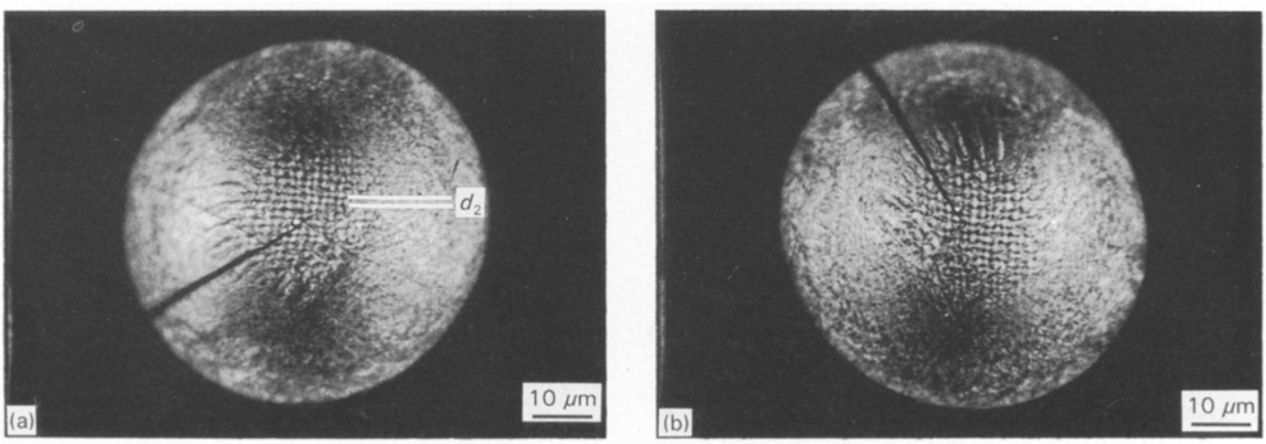

Figure 3 (a) Same field as in Fig. 2a, stage rotated 45°. The spacing between lines, d_2, is about 2.2 μm. (b) Same field as in Fig. 2a, stage rotated 45° from Fig. 2b.

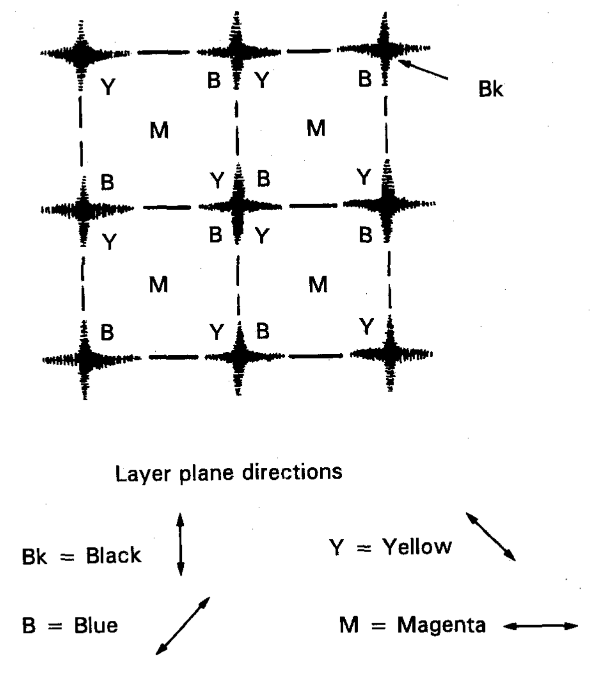

Figure 4 Schematic illustration of the appearance of the field shown in Fig. 2a with crossed polars and lambda plate inserted.

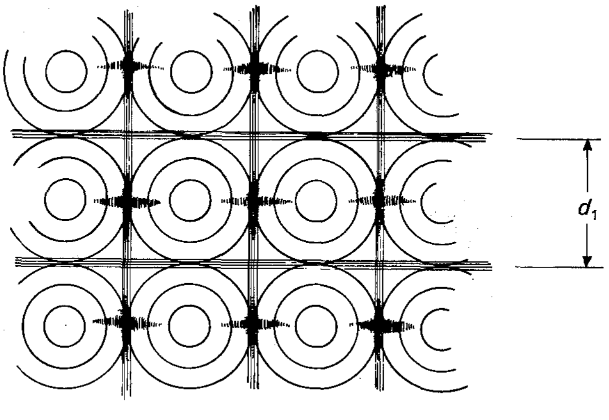

Figure 5 Schematic illustration of the layer plane structure deduced from Fig. 4.

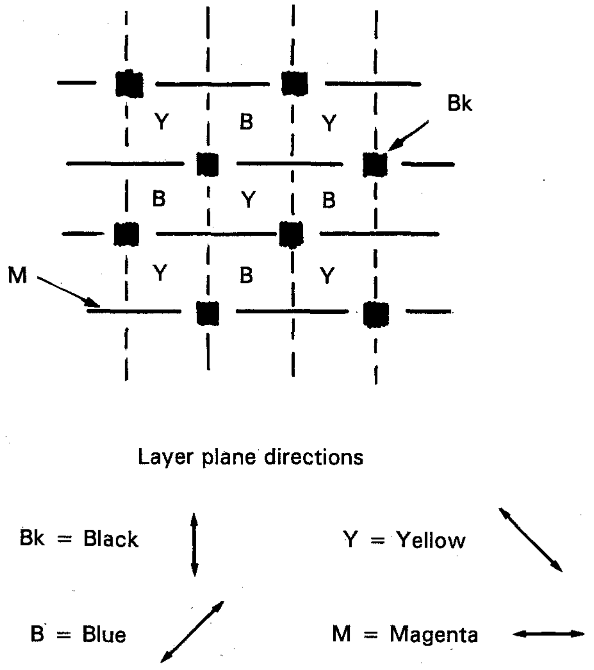

Figure 6 Schematic illustration of the field shown in Fig. 3a with crossed polars and lambda plate inserted.

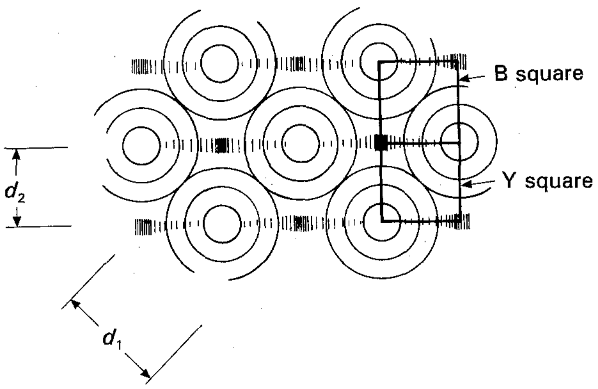

Figure 7 Schematic illustration of the layer plane structure deduced from Fig. 6. Squares B and Y refer to the blue and yellow squares in Fig. 6.

orientations (as indicated in Fig. 4), the averaged layer plane configuration must be as in Fig. 5.

When the stage is set at the 45° position (as in Fig. 3a and b), and the lambda plate inserted, the appearance is as in Fig. 6. This appearance in the 45° position can be understood (Fig. 7) in terms of the structure already deduced in Fig. 5.

When the microscope stage position is such as to show the orthogonal pattern with greatest clarity, the intersections of the perpendicular lines can sometimes be observed to show micrometre-sized loops rather than simple cross-overs (Fig. 2a). Because the light microscope is being used at or near its limit of resolution, the images seen in photomicrographs of fibre cross-sections are not always sharply defined. In general, the scale of the pattern diminishes with the fibre diameter, so that in small (highly drawn-down) fibres, it may not be possible to resolve the detail completely.

Outside the orthogonal pattern the averaged layer plane orientations are approximately radial, as evinced by the absorption of polarized light. Needle-shaped domains parallel to the axis of the fibre form the most prominent structural units [2] (as for other mesophase pitch-based fibres). In fact, the orthogonal and radial patterns seen in microscopical cross-sections represent a lining up of the preferred layer plane orientations of domains. The domains in these samples were mostly of sub-micrometre-size and were difficult or impossible to resolve with light microscopy in cross-section, although more readily visible in longitudinal section (see below).

At the edges of the regular orthogonal pattern described above, the lines tend to become curved and diverge so that they lie in approximately radial orientation; they become less distinct and generally disappear without reaching the fibre margin (Fig. 2a). This more nearly radial arrangement is consistent with the average layer plane orientation in the outer part of the fibre (also radial) where the orthogonal pattern is degraded or absent.

In longitudinal section, these samples showed the usual needle-like domain structures typical of mesophase pitch-based carbon fibres [2] across the full diameter, but a pattern corresponding to the orthogonal structure could not be seen. However, this is not surprising, because the orientations corresponding to the orthogonal structure would be extremely difficult to distinguish amongst the many domain orientations present, even if the pattern was sectioned exactly parallel to one of the orthogonal directions, which would hardly ever be the case.

As noted above, the dimensions of the orthogonal pattern were generally smaller in fibres of smaller diameter, suggesting that the structure of the cross-section is maintained on a progressively smaller scale as the fibre is drawn down. It thus seemed likely that the pattern would be found on a larger scale in fibres which had been drawn down much less than usual, and this proved to be the case. Polished sections of such "fibres", up to 250 μm diameter, were prepared and revealed orthogonal patterns where the interval between lines was as great as 20 μm (Fig. 8). These patterns provided confirmation of the structural features inferred from the drawn fibres of much smaller diameter, including the orientation of layer planes within the orthogonal structure, that is, the structure indicated in Fig. 5.

A drawn fibre was sectioned with an ultramicrotome, and examined with TEM using both bright- and dark-field illumination. Fig. 9 is a typical dark-field image of the cross-section, showing an orthogonal pattern in which the unit is about 0.6 × 0.6 μm. Fig. 9 also shows the loss of regularity of the pattern at its margins. The TEM image shows some irregularities which probably correlate with the "loops" found with light microscopy (cf. Fig. 2a).

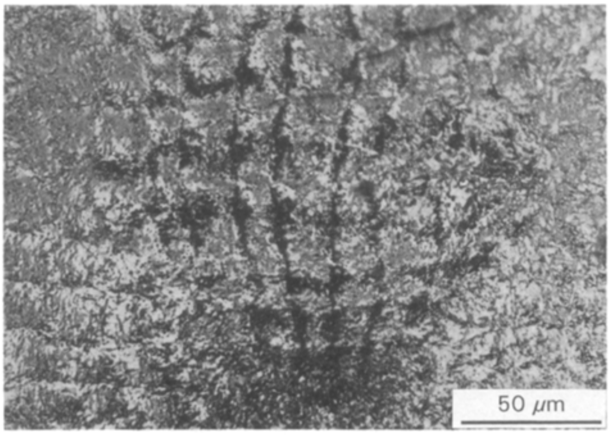

Figure 8 Photomicrograph showing orthogonal pattern in the cross-section of a partly drawn fibre. Incident polarized light, oil immersion objective.

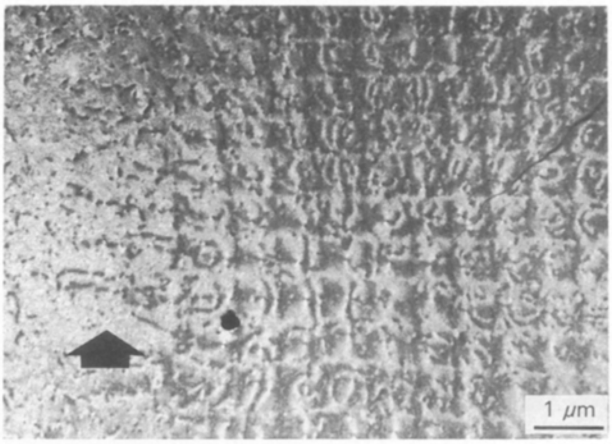

Figure 9 Transmission electron micrograph taken in dark-field mode showing approximately 0.6 μm repetition of pattern and loss of regularity at the margin of orthogonal structure (arrow).

Because it seemed probable that the orthogonal pattern was induced by the stainless steel filter at the top of the spinnerette, test fibres were spun with and without the filter. It was confirmed that, when the filter was not used, the orthogonal pattern was invariably absent. When the filter was used, the pattern was present in fibres spun from some, but not all, mesophase pitches. Also, the pattern was not necessarily present in every fibre of a batch. It was noted that the mesophase pitches which gave rise to fibres with the orthogonal pattern were, in general, of coal tar origin and of comparatively high viscosity. Fibres made from other mesophase pitches, including mesophase from Ashland A240 pitch, either showed a fragmentary or distorted pattern or none at all, with the spinning conditions used.

Nevertheless, in all mesophase pitches tested, the filter did have an effect on the structure. The domain size of the mesophase was significantly smaller and more regular in cross-section when the filter was used. The radial pattern (i.e. in the absence of orthogonal pattern) was also better developed when the filter was used.

The examinations described above were conducted principally on as-spun fibres. Fibres spun from mesophase pitch were also examined after stabilization and heat treatment at 1200 °C. Apart from the increase in

TABLE I Mechanical properties of carbon fibres spun with and without filter.

Fibre without filter				Fibre with filter			
Diameter (μm)	Strength (GPa)	Elongation (%)	Modulus GPa	Diameter (μm)	Strength (GPa)	Elongation (%)	Modulus GPa
12.5	0.87	0.69	120	13.0	1.3	0.96	140
13.5	0.99	0.69	150	13.0	1.3	0.83	170
12.0	1.0	1.0	87	13.0	1.4	0.86	180
14.0	1.3	0.66	210	15.0	2.4	1.3	190
12.0	1.3	1.0	120	12.5	3.7	1.0	270

optical anisotropy and other changes linked with heat treatment, the orthogonal and other structures were the same. The mechanical properties were measured of heat-treated fibres spun from a coal tar mesophase pitch with and without the filter; the results are set out in Table I. The fibres spun with the filter showed somewhat improved strength characteristics. (It should be noted, however, that while the data for fibres made with and without a filter are valid for purposes of comparison, conditions of stabilization and carbonization were not necessarily optimal).

Fibres made from isotropic pitches and pitches partly converted to mesophase were also examined microscopically, but no evidence of orthogonal pattern was found. This was to be expected, because when the orthogonal pattern is observed, it is visible because of systematic arrangements of layer planes in mesophase – something that could not occur in isotropic pitch with its random molecular structure.

4. Discussion

There can be no doubt that the orthogonal pattern is related to the use of a filter; this is borne out by the absence of the pattern in all cases where a filter was not used. There appears to be no other feasible source of such a pattern. Hara *et al.* [1] also traced the occurrence of the pattern to the use of a filter in the upstream part of each spinning nozzle.

While the present authors agree with Hara *et al.* as to the origin of the pattern, they do not find the same appearance in the microscope or infer the same structure. In the Patent claim of Hara *et al.*, the structure shown is as in Fig. 10a, whereas the structure consistently obtained during this study is that shown in Fig. 10b. Although both are orthogonal structures, the difference between them is not trivial. In the structure proposed by Hara *et al.*, the "bars" of the orthogonal pattern occur as two sets in which the layer plane orientations are mutually perpendicular. This is true for our inferred structure but with the very important difference that the layer plane orientations are parallel, not perpendicular, to the long dimensions of the bars.

The layer plane structure in the "squares" formed by the bars; i.e. the regions comprising most of the orthogonal structure, is radial, according to Hara *et al.* However in all our observations, the structure is circumferential or approximately so within each square. The layer plane orientations making up the orthogonal pattern in our samples have been repeatedly checked using the absorption of singly polarized light, as well as the behaviour in doubly polarized light with and without the lambda plate.

It is not hard to understand the way in which the pattern inferred by us is generated. Pitch mesophase comprises layered sheet-like molecules which, except for the layering, are randomly ordered. The liquid crystal properties of mesophase depend upon the ease with which shear occurs in the layer plane direction. Thus, when mesophase is extruded from an opening, the layer planes will reorient to be parallel to the axis of flow through the opening. If the opening is circular the layer planes close to the walls of the opening will be parallel not only to the axis of flow, but also to the adjacent part of the wall. This is because the mesophase, when so arranged, can shear and flow, but in other orientations cannot do so (or not as readily). In this context "close" means probably from a few micrometres to a few tens of micrometres, depending upon the inherent properties of the pitch and the conditions of extrusion. Thus for a small circular opening, an extruded cylinder of mesophase would be expected to have a concentric cross-section as the cylinder emerges from the opening. For a large circular opening, the cylinder would have concentric cross-sectional structure at its margins, becoming less regular in the centre.

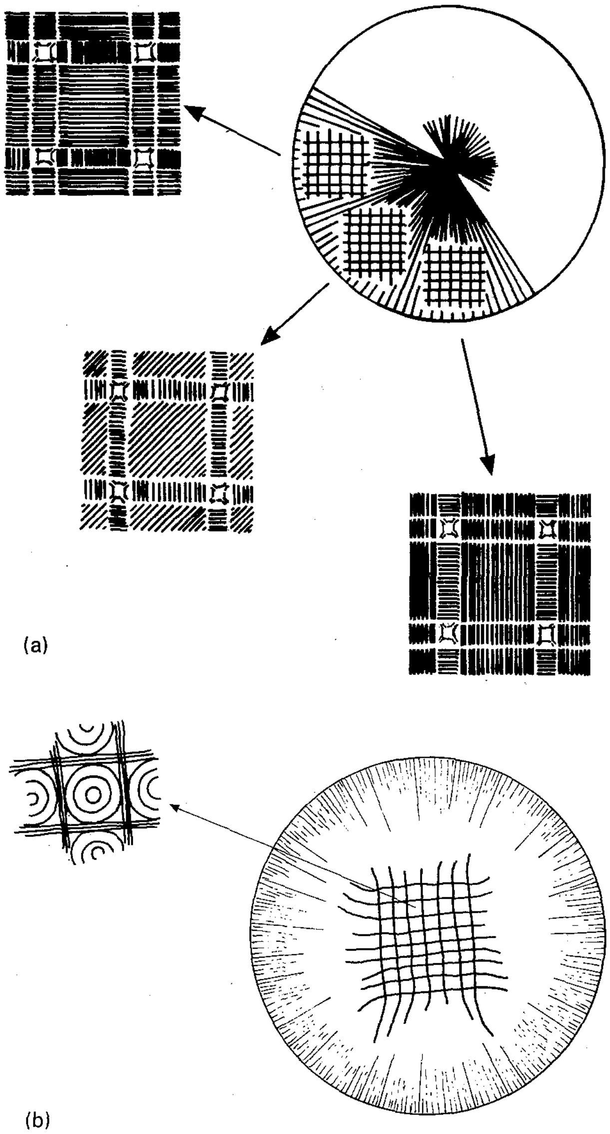

Figure 10 (a) Structure inferred by Hara *et al.* [2] (their Fig. 2). (b) Structure determined as a result of the present study.

As soon as the cylinder emerges from the opening, during spinning, and the constraint of the orifice wall is removed, the mesophase will tend to return to the least-energy structural condition. The latter, as is known from the structure of mesophase spheres in isotropic pitch, is a compromise between (1) maintaining a regular parallel layer-plane structure, and (2) having the layer planes oriented perpendicular to the interface. Providing the mesophase remains liquid long enough and does not freeze, the structure will change to a more nearly radial cross-sectional arrangement, or to the "PanAm" (or "oriented core") configuration, which achieves the compromise referred to.

For a single extrusion opening which is square rather than circular, the same reasoning as above applies, except that the cross-sectional structure is modified, and some disturbed areas occur in the corners where the layer planes encounter a number of different influences. The position with multiple square openings is an extension of that already described. The multiple extruded square "tubes", formed as the mesophase is forced through the filter, rejoin below the filter. Because the surfaces coming together have, at least in part, a common layer plane orientation (Fig. 5), the combined "tubes" form a regular orthogonal pattern. The filter used in our experiments was of stainless steel and its surface was smooth; it seems reasonable to expect that the smoother the surface of the filter bars, the more perfect the orthogonal structures are likely to be, other things being equal.

In a spinnerette, the mesophase leaving the filter passes into the narrowing bore of the spinnerette and the emerging fibre is subsequently drawn down. This reduction of diameter as the fibre is formed occurs with the flow of mesophase, always involving shear in the layer plane direction. If the extent of this shear is constant right across the fibre cross-section, the orthogonal pattern induced by the filter would remain the same except for a progressive reduction in size with diminishing cross-section. However, in the fibres studied, the orthogonal pattern was regular and well-defined in the central part of the fibre cross-section, but was highly distorted or absent in the outer part of the fibre. We attribute this to one or more of (1) a higher degree of shear in the outer part of the fibre (close to the interface with the spinnerette), (2) more rapid cooling, with consequent change in mechanical properties, in the outer part of the emerging fibre, or (3) re-ordering (as described above) having begun in the outer section of the fibre, but not having extended radially into the centre by the time the whole fibre has cooled. Probably (3) is the most important, because the structure in the outer parts of fibres, which showed a central orthogonal structure, was predominantly radial.

Thus, if the mesophase is comparatively viscous or is chilled quickly, the orthogonal pattern will be preserved across the full cross-section, as found by Hara *et al.*; under other circumstances (as in the fibres studied by us) it may survive only in the centre of the fibre. If the mesophase has still more mobility and time, wholesale re-ordering occurs and no trace of orthogonal pattern remains in the finished fibre.

The orthogonal structure appears to persist more or less indefinitely in the direction of the fibre axis. The loop structures observed in light microscopy and with TEM are believed to reflect the particular rheological conditions near the positions of the grid bar intersections.

Our results, like those of Hara *et al.*, indicate that the strength of fibres is enhanced by the presence of the filter. Hara *et al.* attribute the increase in tensile strength to improved flow properties (because of the filter), the suppression of gas bubbles by pressurization and the elimination of wedge-shaped cracks because of a "regular and fine orientation structure with substantially uniform fine domains" resulting from the use of the filter. We judge the latter point to be important, because it was observed during this study that in all cases – whether an orthogonal pattern appeared or not – the domains as viewed in cross-section were finer and more regular than when no filter was used. The effect of this would be to minimize the dimensions of cracks formed during heat treatment as a result of anisotropic shrinkage of domains.

The reported reduction in the number of wedge-shaped cracks [1] is readily understood on the basis of the structure determined by the present authors, which is radial only in the outermost part of the fibre cross-section. (On the other hand, the structure proposed by Hara *et al.* is predominantly radial to the centre of the fibre.)

The observation that some mesophases and not others give rise in our experiments to orthogonal patterns must have a rheological basis. It seems likely that the layer planes of all mesophases would undergo reorientation as the mesophase moves through the filter. (The influence of the filter on the mesophase would diminish with distance from a filter bar, which is a reason for the filter openings to be fairly small.) When the mesophase is sufficiently mobile under the spinning conditions used, the influence of the filter is rapidly lost because the mesophase is able to reorient. Thus, in comparatively fluid mesophases the structure preserved on cooling does not exhibit orthogonal structure, nor shows it only in fragmented or distorted form. The presence or absence of orthogonal structure is thus closely related to both the inherent properties of the mesophase and to the conditions of spinning, especially the detailed geometry of the spinnerette and the temperature profile through all stages of spinning and subsequent cooling.

Commercial mesophase pitch-based fibres have been examined for the possible presence of orthogonal pattern but, with one exception, it seems to be absent. The exception is the P25 fibre of Union Carbide (cf. Fig. 6c of [1]). In this case, a fine orthogonal structure is visible. It appears to be of similar type to that described above, but because of its fineness cannot be fully resolved with the light microscope. The pattern appears to be present over all, or at least the greater part of the cross-section of each fibre. It thus seems doubtful that the claim by Hara *et al.* to have invented a "carbon fibre having a novel cross-sectional structure" can be sustained.

It is possible to think of fibres with the orthogonal structure as "ready-made" composites. This conception could be carried further to envisage extruded shapes other than fibres. Also, because of the layer plane orientations, the cylindrical structures are likely to be excellent conductors of heat and electricity along their length, but poor conductors across their thickness. Because the orthogonal pattern persists parallel to the fibre axis, each unit may be capable of conducting more or less independently of the rest.

5. Conclusions

1. Orthogonal structures occur in carbon fibres made from certain mesophase pitches when an appropriate filter is used above the spinning nozzle.

2. The orthogonal structure is formed as a result of layer plane reordering as mesophase is extruded through the filter.

3. The unit of structure comprises orthogonal bars in which the layer planes are oriented parallel to the long dimensions of the bars; the structure within the bars is modified circumferentially.

4. Fibres spun with a filter have improved strength characteristics (compared to those where no filter is used). This is probably because of the variety of layer plane orientations present and the generally finer and more regular domain structure.

Acknowledgements

Mr Ross Meakins contributed to the design of the spinning equipment used and carried out some spinning trials. Samples were prepared for microscopical examination with great skill by Mr Paul Marvig, Ms Emer O'Gara and Mr Lee Brunckhorst. G.H.T. gratefully acknowledges the help of his colleagues, Dr Gill Pennock and Dr John Fitz Gerald.

References

1. R. HARA, M. KAGIZAKI, T. TAKAKURA and S. TOMONO, US Pat. 4923648, 8 May 1990.
2. J. D. FITZ GERALD, G. M. PENNOCK and G. H. TAYLOR, *Carbon* **29** (1991) 139.

Received 24 September 1992
and accepted 27 April 1993